MITNE-20

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SUMMARY REPORT FOR THE PERIOD
JULY 1, 1960 TO MARCH 31, 1962

By

Richard E. Skavdahl
Edward A. Mason

June 1, 1962

DEPARTMENT OF NUCLEAR ENGINEERING
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE 39, MASSACHUSETTS

Work Performed Under Subcontract No. 1327
Under Contract No. W-7405-ENG-26 with
Union Carbide Nuclear Corporation
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ABSTRACT

An investigation of the solvent extraction characteristics of the nitro and nitrato complexes of nitrosylruthenium in nitric acid-sodium nitrate aqueous media was conducted. As the organic extractant phase, a solution of trilaurylamine (TLA) in toluene was utilized.

In addition to the usual process parameter variation type of experiment, a rapid dilution type of experiment was used extensively to determine qualitative and semi-quantitative results regarding the degree of extractability and concentration of the more extractable species of the nitrato complexes of nitrosylruthenium. It was found that the acids of the tetra-nitrato and penta-nitrato complexes were the more extractable species for that set of complexes and that the acid of the penta-nitrato complex was the more extractable of the two.

It was observed that for freshly prepared solutions, the dinitro complex of nitrosylruthenium was much more extractable than the gross nitrato complexes solutions. Nitro complexes in general, and the dinitro complex in particular, may be the controlling agent in ruthenium decontamination of spent nuclear fuel processed by solvent extraction methods.

The experimental results from both sets of complexes could be more meaningfully correlated on the basis of unbound nitric acid concentration in the organic phase than on the basis of nitric acid concentration in the aqueous phase. The extraction of nitric acid by TLA from nitric acid-sodium nitrate aqueous solutions was investigated and the results correlated on the basis of activity of the undissociated nitric acid in the aqueous phase.

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I. SUMMARY

1.0 General Discussion

The difficulty of the separation of ruthenium from uranium and/or plutonium in the solvent extraction reprocessing of spent nuclear fuels is well established. It is generally agreed that the major factor influencing the extractability, or non-extractability, of ruthenium is, respectively, the presence, or lack, of the nitrosyl form of ruthenium (RuNO). (3, 4, 8, 28). There is, however, widespread disagreement (1, 7, 11, 12, 26, 27) with regard to which of the nitrosylruthenium species are the more extractable and under what conditions the extractability and/or concentration of the more extractable species are either enhanced or reduced. It was the principal objective of this study to investigate the solvent extraction characteristics of the nitrosylruthenium species thought most likely to be found in nitrate dissolver solutions of spent nuclear fuels.

1.1 Experimental Procedure

1.1.0 General Considerations

The experiments were performed on the two sets of nitrosylruthenium complexes that are generally agreed to be of importance in nitrate solutions. The complexes investigated were:

(1) The RuNO-Nitrato complexes, $\left[Ru(NO)(NO_3)_x(H_2O)_{5-x}\right]^{+3-x}$, where x equals from one to five, and

(2) The RuNO-Nitro complexes, as represented by the dinitro complex, $RuNO(NO_2)_2(OH)(H_2O)_2$.

The mole fraction of each of the five nitrato complexes existing in aqueous nitric acid solutions is a function of acid concentration and solution age. There is, however, an "equilibrium" aging time, after which the relative proportions no longer depend upon solution age but are functions only of acid concentration (and, presumably, temperature).

The experiments were made separately upon each of the two sets of complexes in aqueous nitric acid-sodium nitrate solutions. The organic phase was a solution of trilaurylamine (TLA) in toluene. The TLA was purchased from Distillation Products Industries, Rochester, New York and was used in the "as received" condition. Analysis of

the TLA, performed at MIT by the differential titration method, showed the reagent to contain 97.3% tertiary amine, 2.7% secondary amine, and less than 0.1% primary amine.

The experiments were of two general types, the parameter variation type and the rapid dilution type.

1.1.1 The Parameter Variation Experiments

The parameter variation experiments were designed so as to determine the effect of certain process variables upon the extraction characteristics of the gross complexes solutions. The variables studied were solution age of the complexes, aqueous nitric acid concentration, aqueous total nitrate concentration, contacting time of the two phases, aqueous ruthenium concentration, and organic TLA concentration. The parameter variation experiments were performed on both sets of complexes.

Contacting of the phases, for the parameter variation experiments, was accomplished by submerging 50 ml round bottom centrifuge tubes in a horizontal position in a constant temperature bath equipped with a shaker rack. The tubes were clamped to the rack and the rack oscillated at 89 cycles per minute with about a 2" excursion. After the requisite contacting time was completed, the tubes were removed from the bath and put

into a centrifuge for phase disengagement. The phases were then separated by use of a vacuum operated phase separator.

1.1.2 The Rapid Dilution Experiments

The rapid dilution experiments were designed to investigate the complexes in more detail and to determine particular quantitative and qualitative information regarding the extractability and concentration of the more extractable of the complexes. The rapid dilution experiments were performed on the RuNO-Nitrato complexes only.

In this method, an aged (to equilibrium), non-salted (no sodium nitrate), nitric acid stock solution of the RuNO-Nitrato complexes of relatively high acid concentration was diluted rapidly to a lower acid concentration, immediately contacted with TLA for 30 seconds, and then the phases quickly separated.

The advantage of this type of experiment was that it was possible to accomplish the dilution with several different initial (before dilution) acid concentrations and with a single final (after dilution) acid concentration and thereby obtain a semi-quantitative idea of the effect of the initial acid concentration upon the relative amount of extractable species at equilibrium in the aqueous solutions.

Since it is believed that the degree of extractability of the complexes depends on the final conditions, it was also possible to obtain an idea of the effect of acid concentration on the degree of extractability by diluting a single, similar initial acid concentration to a series of different final acid concentrations.

The variables investigated for the rapid dilution experiments were the initial acid concentration, final acid concentration, phase volume ratio, and delay time.

The method can be more clearly explained by the use of an example. The following is a summary of sample 165:

The desired final aqueous nitric acid concentration was 1.0N. The initial acid concentration was 4.9N. HNO_3. The desired total volume of each phase was approximately 20 ml. (Phase volume ratio = 1). When a stock solution volume of 4 ml was used, then 15.6 ml of distilled deionized water (DDW) was mixed with it to reduce the HNO_3 concentration from the initial 4.9N. to the final 1.0N. The total volume of each phase was then 4+15.6 = 19.6 ml. Therefore, 15.6 ml of DDW and 19.6 ml of 0.26M TLA in toluene were pipetted into the centrifuge tube in that order, care being taken not to pre-mix the phases. The stock solution was taken up in a 4 ml pipette and the pipette placed in position for delivery

to the centrifuge tube. The stock solution was run into the centrifuge tube down the wall of the tube and not directly through the organic phase so as to reduce the precontact time to a minimum. At the same time that the stock solution started down the wall of the centrifuge tube, an electric timer was started. As soon as the stock solution had all been added, the tube was capped, shaken by hand for 30 seconds, and then placed in a centrifuge for rapid phase separation. The length of time elapsed between the start of addition of stock solution and the start of shaking is defined as the "delay time" and for all samples was on the order of 20-30 seconds, unless otherwise specified.

1.1.3 Spectrophotometric Studies

The optical density, or absorbance, of various aqueous phase and organic phase solutions was measured as a function of various parameters and was useful in determining redistribution rates and qualitative identification of the complexes. The measurements were made on a Beckman Model DU Spectrophotometer using 1 cm absorption cells.

1.1.4 Ruthenium Analysis

The quantitative analysis for ruthenium employed was the $KOH-KNO_3$ fusion method as described by Marshall and Rickard (13).

1.2 Results

1.2.1 Nitrosylruthenium Chemistry

The equilibrium aging time of the nitrato complexes at room temperature was determined by observing the spectra of aqueous solutions of the complexes as a function of solution age. The equilibrium aging time was observed to be between 16 and 22 days (see Fig. 3.7). The spectra of equilibrium nitric acid solutions of the complexes are to be seen in Figure 3.6.

The nitrato complexes were prepared by dissolution of the compound $RuNO(NO_3)_3 \cdot 2H_2O$ in various nitric acid-sodium nitrate solutions. The solution age was measured beginning with the time at which the compound was first put into solution. The compound was prepared from either $RuCl_3$ or $RuNO(OH)_3 \cdot 2H_2O$ and the method of preparation was essentially that outlined by Fletcher, et al (9), with some slight modification.

Spectra studies on the nitro complexes, similar to the nitrato complexes, were performed in order to determine their equilibrium aging time. As can be seen

from Figure 3.12, no equilibrium aging time appears probable even after from 4 to 5 1/2 months of aging. From the manner of the change in the spectra with solution aging, it appears that the RuNO-Nitro complexes are slowly being transformed, either wholly or in part, to the RuNO-Nitrato complexes and/or mixed RuNO-Nitro-Nitrato complexes. The observed qualitative trend of change and rate of change are consistent with the observations of Brown (1).

The complexes were prepared by dissolution of the dinitro complex, $RuNO(NO_2)_2(OH)(H_2O)_2$, in various nitric acid-sodium nitrate solutions. The solution age was measured beginning with the time at which the compound was first put into solution. The dinitro complex was prepared from $RuCl_3$ according to the method of Brown (1).

1.2.2 TLA Extraction of RuNO-Nitrato Complexes-Parameter Variation Experiments

The effect of solution age on the solvent extraction of the RuNO-Nitrato complexes can be seen in Figure 4.4. The manner in which the distribution ratios (E_A^o) varied is consistent with the observation of Fletcher, et al (7) that nitrate complexing decreases with aging at the low acid concentrations and increases with aging at

the higher acid concentrations. The distribution ratio, E_A^o, is defined as the concentration of total ruthenium in the organic phase divided by the concentration of total ruthenium in the aqueous phase.

From Figure 4.2 it can be seen that the effect of acid concentration is generally to increase the extraction at low acid concentrations, and then after passing through a maximum, decrease the extraction at high acid concentrations. This type of behavior is a result of two opposing effects. As nitric acid concentration of the stock solution is increased, the relative amount of the more extractable species is also increased. But as nitric acid concentration is increased, the extractability of the complexes is decreased. The shape of the E_A^o versus nitric acid concentration curve is a reflection of the product of those two effects.

The values of E_A^o are seen to increase with increasing contact time. As the more extractable nitrato species are removed from the aqueous phase by the extraction process, redistribution of the complexes in the aqueous phase would take place to satisfy the aqueous equilibrium conditions among the complexes. However, as the extractable complexes are formed in the aqueous phase, a portion of them is extracted into the organic phase in order to satisfy that equilibrium, the net result being an

increase of E_A^o with increasing contact time. As can be seen from the rate of increase of E_A^o with respect to nitric acid concentration, the redistribution rates of the complexes decrease with increasing acid concentration.

Extraction of nitric acid into the organic phase has been well established. In the present work, it was found that the amount of acid extracted into the organic phase was affected by the concentrations in the aqueous phase of both HNO_3 and $NaNO_3$. The results of the investigation are given in Figure 4.8 and show a large effect of sodium nitrate salting on nitric acid extraction when the unbound nitric acid concentration in the organic phase is plotted against the aqueous phase nitric acid concentration. At the suggestion of Dr. C. F. Coleman of Oak Ridge National Laboratory (19), an attempt was made to correlate the date on the basis of aqueous phase undissociated nitric acid activity. The result is shown in Figure 4.29. Due to the lack of accurate dissociation data below 2N HNO_3, only five non-salted solution points could be calculated. As can be seen from Figure 4.29, this type of correlation looks very promising.

Since there appeared to be no data available on the activity of undissociated nitric acid in mixed nitric acid-sodium nitrate solutions, it was necessary to make

an assumption regarding the activity coefficient of the undissociated nitric acid in salted solutions. Upon the suggestion of Prof. G. Scatchard of the Chemistry Department at MIT (21), the values of the activity coefficient of undissociated nitric acid were assumed to be dependent upon the total stoichiometric nitrate concentration of the aqueous phase rather than upon the stoichiometric concentration of only the nitric acid in solution. Proceeding on that basis, the results of Figure 4.29 were obtained.

From the present investigation, it has been discovered that presentation of the distribution ratios (E_A^o) as a function of organic phase nitric acid concentration rather than as the usually employed aqueous phase nitric acid concentration gave more meaningful results. The distribution ratio (E_A^o) for the nitrato complexes was observed (Fig. 4.10) to be dependent upon approximately the 1.3 to 1.7 power of the nitrate concentration when presented in the above manner.

Investigation showed that the value of the distribution ratio was independent of the value of the aqueous ruthenium concentration in the range of aqueous concentrations of from 0.3 gm/l to 8 gm/l of ruthenium.

Over the range of TLA concentrations from about 0.05M to about 0.13M, the value of E_A^o was observed to be dependent upon the 1.5 power of the TLA concentration.

Between 0.13M and 0.26M TLA, the power dependence decreased to about 1.0.

1.2.3 TLA Extraction of RuNO-Nitrato Complexes—Rapid Dilution Experiments

In the rapid dilution experiments, the values of E_A^o were observed (See Fig. 4.16) to increase as the nitric acid concentration of the stock solution was increased, indicating that the relative proportions of the extractable species increase as the acid concentration increases. The values of E_A^o were also observed to decrease as the final nitric acid concentration was increased, indicating that the partition coefficients of the extractable species decrease as the acid concentration increases.

The partition coefficient (P_x) of a complex is defined as the concentration of that complex in the organic phase divided by the concentration of that complex in the aqueous phase. In the limiting case, when there is only one species in solution, the distribution ratio, E_A^o, and the partition coefficient, P_x, are identical. In solutions that contain more than one species, E_A^o then becomes a function of the partition coefficient (P_x) of each complex, the aqueous-phase mole fraction (M_x) of

each complex before contacting, and the phase volume ratio ($T = \frac{\text{aqueous volume}}{\text{organic volume}}$). For the rapid dilution experiments, the relationship can be shown to be

$$E_A^o = T\left[\frac{\sum_x \left(\frac{M_x P_x}{T+P_x}\right)}{1-\sum_x \left(\frac{M_x P_x}{T+P_x}\right)}\right] \qquad (1\text{-}1)$$

The effect of variation of the phase-volume ratio can be seen in Figure 4.17. The largest value of E_A^o observed is seen in Figure 4.17 and is for an initial acid concentration of 8.7N HNO_3, a final acid concentration of 1.0N HNO_3, and a phase volume ratio of 79. The value observed is 5.2, and therefore the partition coefficient, at this final acid concentration, of the most extractable species must be at least equal to, or greater than, 5.2. Since the rate of increase of E_A^o with increasing values of T is rather large and shows no indication of approaching asymptotic value at the values of T investigated, it can be concluded that at least one extractable species has a large partition coefficient.

It had been assumed that a delay time of 20-30 seconds did not allow sufficient time for any appreciable redistribution of the complexes. In order to determine the validity of that assumption, a series of experiments was conducted using the delay time as a variable. The

experimental procedure was identical to that of the previously described dilution experiments except that the period of time between the end of addition of stock solution and start of shaking was varied in a controlled manner. The experiments were performed for several different values of initial and final acid concentrations. In each case, extrapolation back to zero delay time resulted in an increase in the value of E_A^o by about 10% over the 30-second value.

It was possible to titrate the ruthenium extracted into the organic phase. Figure 4.25 shows the titration of the organic phase of sample 178. By quantitative analysis, the total ruthenium concentration was determined to be 3.58 gm/l, or 0.036M. The first inflection point of Fig. 4.25, at 0.75 ml, is the result of the neutralization of the unbound nitric acid and is equivalent to an unbound nitric acid concentration of 0.033N, which would be expected from Figure 4.8. The second inflection point, at 2.4 ml, is equivalent to a concentration of 0.073N between the first and second inflection points. In this titration, as well as several others, the second neutralization corresponds to approximately twice the molarity of the extracted ruthenium. As a result, it is suggested that the extractable forms of nitrosylruthenium are the acids of the tetra- and

penta-nitrato complexes ($HRuNO(NO_3)_4(H_2O)$ and $H_2RuNO(NO_3)_5$), the latter being the more extractable of the two. The data from the extraction studies and organic phase titrations could not be correlated well assuming only one extractable species but could be correlated very well assuming two extractable species, suggesting the presence of a small amount of extractable tetra-nitrato complex.

From the position of neutralization of the titratable ruthenium, it can be seen that the species are not as available for neutralization as the unbound nitric acid but are more available than the chemically bound nitric acid associated with the amine nitrate.

1.2.4 Correlation of Results

The number of possible species in the RuNO-Nitrato complexes system appears to be limited to five (mono-nitrato through penta-nitrato complexes). The results of the organic-phase titrations indicated that there may be only two. The correlations were carried out assuming first only one extractable species and then two extractable species. The correlation assuming two extractable species was in much better agreement with the observed results than was the correlation for only one species.

The method of correlation employed the use of Equation (1-1), for x=1 and 2, and the data from the rapid dilution experiments. Expansion of Equation (1-1) for x=2 yields Equation (1-2).

$$E_A^o = T \left[\frac{\left(\frac{M_1 P_1}{T+P_1}\right) + \left(\frac{M_2 P_2}{T+P_2}\right)}{1 - \left(\frac{M_1 P_1}{T+P_1}\right) - \left(\frac{M_2 P_2}{T+P_2}\right)} \right] \qquad (1\text{-}2)$$

By the use of a reiterative "best fit" method, the values of the mole fractions (M_1 and M_2) and the partition coefficients (P_1 and P_2) were derived as a function of acid concentration. The results of the correlation are shown in Figures 3.4 and 4.23. Species "1" and species "2" were identified by organic phase titrations to be the acids of the penta-nitrato and tetra-nitrato complexes, respectively.

In Figure 3.4, the values of the "Group D" mole fractions of Fletcher, et al (7) are also plotted for comparison. Fletcher assumed that the Group D complexes were the sum of the tetra-plus penta-nitrato complexes and the values of the mole fractions were determined by paper chromatography. Fletcher's Group D values and the MIT values of the mole fractions of the sum of the two species are seen to differ by about a factor of two.

From the data of the rapid dilution experiments involving the variation of delay time, it was possible to calculate a set of values for the rate constants for the disappearance of the two extractable species during complex redistribution.

By rearranging Equation (1-2), it is possible to obtain Equation (1-3)

$$\left(\frac{E_A^o}{T+E_A^o}\right) = \left(\frac{P_1}{T+P_1}\right)M_1 + \left(\frac{P_2}{T+P_2}\right)M_2 \qquad (1\text{-}3)$$

Assuming that the following denitration reactions are the cause of the disappearance of the respective species upon dilution, and that they proceed with the indicated reaction rate constants (which are first order with respect to ruthenium), it is possible to derive Equations (1-6) and (1-7) for the value of the mole fractions as a function of time after dilution.

$$H_2RUNO\ (NO_3)_5 + H_2O \xrightarrow{k_1} HRuNO\ (NO_3)_4(H_2O) + HNO_3 \qquad (1\text{-}4)$$

$$HRuNO\ (NO_3)_4(H_2O) + H_2O \xrightarrow{k_2} RuNO\ (NO_3)_3(H_2O)_2 + HNO_3 \qquad (1\text{-}5)$$

$$M_1 = M_1^* + (M_1^o - M_1^*)\ e^{-k_1 t} \qquad (1\text{-}6)$$

$$M_2 = M_2^* + (M_2^o - M_2^*)\ e^{-k_2 t} + \frac{k_1(M_1^o - M_1^*)}{(k_1 - k_2)}\left[e^{-k_2 t} - e^{-k_1 t}\right] \qquad (1\text{-}7)$$

Where M_1^o and M_2^o are the equilibrium stock solution mole fractions at the initial acid concentration, M_1^* and M_2^* are the equilibrium stock solution mole fractions at the final acid concentration, k_1 and k_2 are the reaction rate constants (min^{-1}), and t is the dilution delay time (minutes).

With the use of Equations (1-3), (1-6), and (1-7) and the data from the rapid dilution experiments regarding the variation of delay time, a set of values for k_1 and k_2 was derived by the same reiterative best fit method previously employed. The results are shown in Table 1.1.

TABLE 1.1

Disappearance Rate Constants of Tetra-and Penta-Nitrato Complexes at Room Temperature

Initial HNO_3 Conc.,N	Final HNO_3 Conc.,N	Rate Constants (min^{-1}) Tetra	Penta	Reaction Half Times (minutes) Tetra	Penta
9.7	1.0	0.065	1.0	11	0.7
6.8	1.0	0.065	1.0	11	0.7
9.7	3.0	0.055	0.50	13	1.4
9.7	4.9	0.045	0.25	15	2.8

These are to be compared with the values of k=0.024 min^{-1} and $T_{1/2}$ = 30 minutes for the disappearance of the Group D complexes in 3M HNO_3 at 25°C observed by Fletcher, et al (7) by paper chromatography.

The delay time in the MIT experiments was only varied between 30 seconds and 5 1/2.minutes. Since the values of the delay times were not large compared to the disappearance half-times, their quantitative accuracy is questionable. A second possible source of error exists in the form of temperature during extraction. The heat due to the extraction reaction and physical shaking could raise the temperature of the system a few degrees and consequently raise the values of the rate constants, which have been shown by Fletcher (7) to be very temperature dependent. The control of temperature was not possible due to the short times involved in the rapid dilution experiments.

Of considerable interest, however, is the indication of two values of the rate constants, one for each complex, and of the relative magnitude of each.

When the above rate constants are compared with the data of Fletcher, it is interesting to speculate that his value is possibly the disappearance rate of only the tetra-nitrato complex. Since his measurements were made over the space of several hours, during which the penta-nitrato complex could have rapidly denitrated

to the tetra-nitrato complex, the long-time disappearance rate measured could have been that of only the tetra-nitrato complex.

1.2.5 TLA Extraction of RuNO-Nitro Complexes

In Figure 5.1 are shown the results of two-minute contacting of freshly prepared (age after dissolution of the dinitro compound in DDW approximately 1-2 hours) solutions of the nitro complexes. Of interest are several points:

(1) The curve shows no maximum but decreases steadily with increasing aqueous nitric acid concentration.

(2) From Figure 5.1, it appears that sodium nitrate salting decreases the extractability of the freshly prepared nitro complexes. However, by plotting the values of E_A^o against the final organic phase unbound nitric acid concentration rather than the final aqueous phase nitric acid concentration, it can be seen (Figure 5.2) that actually the salting has no observable effect.

(3) The freshly prepared RuNO-Nitro complexes are more highly extractable as a whole than the freshly prepared RuNO-Nitrato complexes, particularly at low acid concentration. Figure 5.4 shows the two systems plotted so as to enable comparison.

After aging at room temperature for one month, the solutions decreased in extractability, but the salted nitro-complexes solutions were more extractable than the non-salted solutions. (See Figs. 5.2 and 5.6)

For solutions aged one month, the values of E_A^o were observed to be dependent upon the 0.4 to 0.8 power of the total aqueous nitrate concentration for constant unbound nitric acid concentration in the organic phase.

For solutions aged two months, the final organic phase ruthenium concentration was observed to be dependent upon the 1.2 power of the final aqueous phase ruthenium concentration in the range of final aqueous ruthenium concentrations of from about 0.2 gm/liter to 5 gm/liter of ruthenium.

In a similar fashion to the aged RuNO-Nitrato complexes, the distribution ratio of aged (two-months) RuNO-Nitro complexes increases initially with the 1.2 power of the amine concentration and then tapers off to a lower power dependence above an amine concentration of about 0.13M.

1.3 Significance of Results

1.3.1 RuNO-Nitrato Complexes

As mentioned previously, the possible number of species appears to be limited to five. Of the five nitrato complexes, the lower two (mono-and di-) do not seem to be likely prospects as extractable species for several reasons. First, it was shown that the more extractable species increase in proportion as the stock solution nitric acid concentration is increased, which is quite the opposite of the mono-and di-nitrato complexes. Second, the possible forms of those species during extraction would necessarily have to be either cationic, which does not seem compatible with amine extraction, or else neutral with the possible ligands being either OH^- or NO_3^-. Ligand substitution by OH^- seems very unlikely due to hydrolysis and ligand substitution by NO_3^- would then change the complexes to higher nitrato complexes. Therefore, the possible extractable species seem to be limited to the tri-, tetra-, and penta-nitrato complexes. The correlation of the rapid dilution experiments, in conjunction with the organic phase titrations, appears to limit the extractable species to the tetra-and penta-nitrato complexes. However, the correlation was not performed for the case of three

extractable species and so the extraction of a certain amount of the tri-nitrato complex cannot be completely ruled out.

The qualitative establishment of the more extractable species and the semi-quantitative estimations of their relative proportions and extractability seem to be fairly reliable.

The disagreement between the MIT values of the mole fractions and those of Fletcher (7), deserves an explanation. However, since neither of the investigations involved an actual separation and positive identification of each, or either, species, such an explanation is difficult to develop. Some possible reasons for the discrepancy are listed as follows and are meant only to be suggestions possibly worthy of investigation and are not intended to "resolve" the issue.

(1) The possibility that Fletcher's "Group D" is actually the sum of three complexes, the tri-, tetra-, and penta-nitrato complexes.

(2) The possibility that the tetra-and penta-nitrato acid complexes exist in equilibrium as both undissociated and dissociated acids, i.e.

$$H_2RuNO\ (NO_3)_5 \rightleftarrows HRuNO\ (NO_3)_5^- + H^+ \qquad (1\text{-}8)$$

$$HRuNO\ (NO_3)_4(H_2O) \rightleftarrows RuNO\ (NO_3)_4(H_2O)^- + H^+ \qquad (1\text{-}9)$$

and that the MIT mole fractions are for only the extractable undissociated forms while the Fletcher Group D mole fractions are for the total sum of the two complexes.

(3) The possibility that the correction of unknown experimental and/or correlation error in either one or both of the studies could bring the two sets of data into closer agreement.

The correlation performed utilizing nitric acid activity appears very promising. The finding that the extraction mechanism may be more dependent upon organic phase unbound nitric acid concentration than upon aqueous phase nitric acid <u>concentration</u> seems firmly established. However, the effect of organic-phase unbound nitric acid concentration (or activity, since the concentrations in the organic phase were relatively small) and/or aqueous phase nitric acid <u>activity</u> upon the extraction mechanism appears to be inseparable. These two effects are probably one.

In any case, where activity data are available, the effect of activity (aqueous and/or organic phase) on solvent extraction processes in general should be considered.

1.3.2 RuNO-Nitro Complexes

The result of primary importance is the establishment of the stability and relatively high extractability of the dinitro complex. ($RuNO(NO_2)_2(OH)(H_2O)_2$). These two properties suggest that under actual process conditions, the nitro complexes in general, and perhaps the dinitro complex in particular, are the cause of the poor ruthenium decontamination. Reduction, or elimination, of process conditions leading to formation and/or stabilization of ruthenium nitrosyl nitro species should therefore result in significant improvement in ruthenium decontamination of spent nuclear fuels. Adjustment of dissolver conditions to reduce formation of $NO-NO_2$ gases as well as reduction, or elimination, of the addition of sodium nitrite should be considered.

The results of both the spectra studies and the extraction studies indicate that the nitro complexes slowly transform into the nitrato complexes. It was not determined, however, through what intermediate compounds and/or complexes the process proceeds.

II. INTRODUCTION

2.0 General Discussion

Under a subcontract with the Oak Ridge National Laboratory (ORNL), a program of study was initiated in 1958 in the Nuclear Engineering Department at the Massachusetts Institute of Technology (MIT) on the use of alkyl organonitrogen compounds as solvent extraction agents for materials important in the reprocessing of nuclear reactor fuels in nitrate systems. The initial phase of the program at MIT was a broad study of the extraction of non-radioactive isotopes of typical fission-product elements and cladding or alloying materials. The results of that phase of the study are to be found in the Summary Report by Vaughen and Mason (24).

The conclusions obtained as a result of that study cover a range of elements and extractants. However, in general, it was found that the two elements most likely to cause problems in decontamination of uranium are zirconium and ruthenium.

The work of Vaughen and Mason (24), although mainly of a survey nature, did include a somewhat

detailed study of the extraction characteristics of zirconium.

With respect to ruthenium, however, it was observed that a tertiary amine (trilaurylamine, TLA) gave separation factors between uranium and ruthenium approximately the same as those obtained with tributylphosphate (TBP), but gave separation factors higher than TBP for the other fission products studied. Because of the difficulty encountered in ruthenium decontamination and because of the anomalous results of other investigations of ruthenium chemistry and extraction, the present study was initiated in the hope of shedding light on the solvent extraction characteristics and solution chemistry of ruthenium.

2.1 Objectives of the Present Investigation

The broad objective of the investigation was to conduct a systematic study of the ruthenium complexes believed to be important in the solvent extraction reprocessing of spent nuclear fuels and thereby add materially to the understanding of the solution chemistry and solvent extraction characteristics of these complexes.

In particular, for the TLA-nitrate system, a few of the desired results were:

(1) The qualitative determination of the more

extractable species of ruthenium in nitrate systems.

(2) A quantitative measure of their extractability.

(3) A quantitative measure of their concentration in various aqueous nitrate solutions.

(4) The effect of various process variables, such as extractant concentration, acid concentration, etc., on the extractability and/or concentration of the extractable species in nitrate systems.

2.2 Previous Investigations

Probably the major difficulty encountered in the early work on ruthenium solvent extraction was the existence of the many oxidation states and possible complex forms of ruthenium. A summary of these can be seen in Table 2.1, which is taken from Reference (25).

The first step in the solution of ruthenium solvent extraction difficulties must be the determination of the general class of extractable ruthenium oxidation states and/or complexes. Fortunately, in this regard, there is widespread agreement that the controlling factor is the presence, or lack, of the nitrosyl form of ruthenium (RuNO).

TABLE 2.1

OXIDATION STATES OF RUTHENIUM

OXIDATION STATE	REPRESENTATIVE COMPOUNDS
0	Ru, $Ru(CO)_4$, $Ru(NO)_5$
1	RuCOI, RuCOBr, RuCl
2	Ru^{+2}, $RuCl_2$
?	$RuNO^{+3}$
3	Ru^{+3}, $RuCl^{+2}$, $RuCl_2^{+}$, $RuCl_5^{=}$
3.5	?
4	$K_4[Ru_2Cl_{10}O]$, RuO_2, Brown Ru
4.2	?
5	RuF_5
6	Na_2RuO_4
7	$KRuO_4$
8	RuO_4

For example:

(1) Bruce (4) says "Since addition of nitrite ion results in a marked increase in ruthenium extraction under certain conditions, it is evident that the nitroso complex plays an important part in the ruthenium extraction mechanism."

(2) Zvyagintsev (28), in speaking of studies performed with the organic solvents most widely described in the literature, (TBP, dibutyl ether, etc.), says "The experiments showed that these solvents extract nitrosyl compounds of ruthenium almost exclusively."

(3) Fletcher and Martin (8), report that, "As a result of work undertaken at A.E.R.E. or sponsored by this establishment, it has become clear that the ruthenium compounds arising from the dissolution of irradiated fuel in nitric acid, are mainly trivalent nitrosylruthenium, (RuNO) (III),..."

(4) Brown, et al (3) have stated, "It has often been postulated that complexities in ruthenium behavior in process chemistry arise from the large number of oxidation states that are possible for this element. Our conclusions indicate that the diversity of compounds containing ruthenium in a common valency state, as RuNO, are of greatest significance and that

ruthenium valency changes have little importance."

The agreement also extends as to which general classes of RuNO complexes are the most important complexes to be considered. The two classes are:

(1) The RuNO-nitrato complexes

(2) The RuNO-nitro complexes

A discussion of the forms and the solution chemistry of the two classes of complexes is presented in Chapter III. A discussion of the conclusions of this study and of previous investigators regarding the relative extractabilities of the two classes and of the extractability of particular species in each class is presented in Chapters IV and V. At this point, it needs only to be said that there are rather divergent conclusions in the present literature regarding the solvent extraction characteristics of these complexes.

2.3 General Approach

The method of investigation employed in this study was first to examine each of the two classes of complexes separately in order to determine the detailed nature of the solution chemistry and solvent extraction characteristics of each, and then to compare the results of the two classes of complexes in order to obtain some conclusions of a general nature with

respect to ruthenium solvent extraction, nitrosyl-ruthenium solvent extraction, and/or solvent extraction in general.

In Chapter III is presented a discussion of the solution chemistry of the two sets of complexes including the results pertinent to that subject obtained at MIT.

In Chapter IV are presented the results of the experimental studies performed at MIT on the RuNO-nitrato complexes along with a rather extensive correlation of the results. Also presented is a discussion of the extraction of nitric acid by TLA and its possible significance in the general solvent extraction process.

In Chapter V are presented the results of the experimental studies performed at MIT on the RuNO-nitro complexes along with a discussion on the comparison of the two classes of complexes. The RuNO-nitro complexes were not investigated in as much depth as were the RuNO-nitrato complexes.

In Chapter VI are summarized the conclusions reached as a result of the experimental work and the recommendations suggested for future work.

III. NITROSYL RUTHENIUM CHEMISTRY

3.0 General Characteristics of Nitrosyl Ruthenium Complexes

Although the present study is restricted to nitrate systems, there are some properties of nitrosyl ruthenium that are reported to be independent of its environment. A summary of these properties is listed as follows and is essentially the same summary as presented by Wallace (25).

(a) Only one NO group is associated with each ruthenium atom in all of its complexes.

(b) All nitrosyl ruthenium compounds that have been examined are diamagnetic.

(c) Ruthenium in RuNO complexes appears always to have a coordination number of 6. (See Figure 3.1) It is generally believed that all RuNO complexes have the structure shown in Figure 3.1. Positions 1 through 5 of the octahedron will always be occupied by some complexing ligand such as H_2O, OH^-, Cl^-, NO_3^-, and NO_2^-. Polymerization is also possible since two such octahedra can form an oxygen bridge between them. Ligands of one type can be substituted for those of another, but the reactions between them are frequently

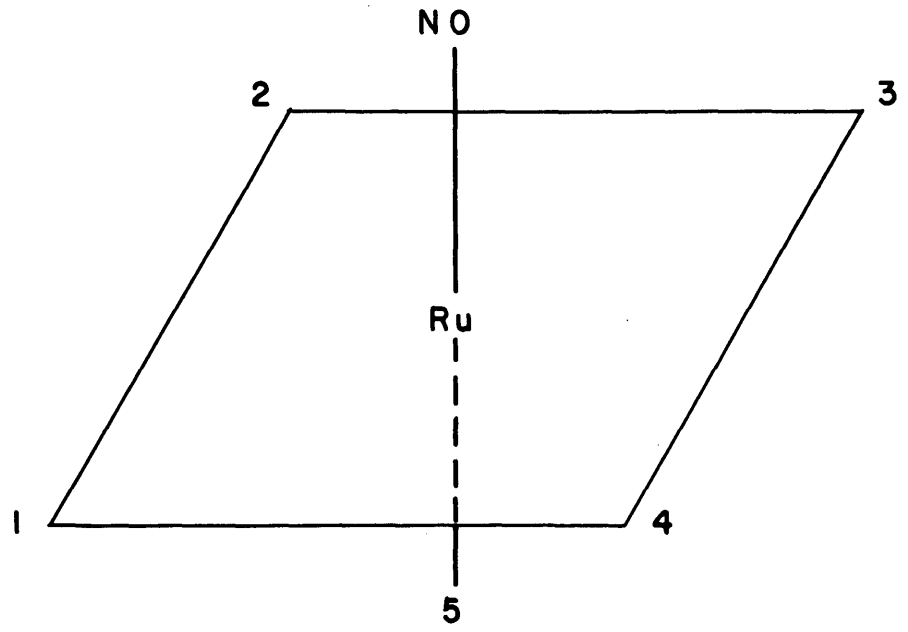

FIG. 3.1 RUTHENIUM COORDINATION OCTAHEDRON

quite slow. Many of the complexes are soluble in polar organic solvents.

(d) The RuNO group is very stable. Oxidation of RuNO complexes to RuO_4 with strong oxidizing agents is much slower than the oxidation of other compounds of ruthenium. Some of the complexes are much more difficult to oxidize than others, i.e., the nitro complexes are much more difficult to oxidize than are the nitrato complexes. Mild reducing agents do not affect the RuNO group; however, ruthenium in these compounds can be reduced to the metal with hydrogen at high temperatures.

(e) Although treatment with strong acids and strong bases will remove other ligand groups from RuNO complexes, the Ru-NO bond is not broken.

(f) The RuNO group has a net charge of +3. All of the RuNO complexes exhibit a very strong absorption band between 1840 and 1950 cm^{-1} in the infrared, which is similar to that found for the nitrosonium ion NO^+ in nitrosyl chloride and perchlorate as well as other nitrosyl metal complexes in which NO is present as NO^+. The infrared spectra and the fact that the complexes are all diamagnetic indicate that Ru is in the +2 state while NO is present as NO^+; however, it is possible that the Ru is in the +3 state and the NO uncharged.

3.1 Ruthenium Analysis

The method of quantitative analysis for ruthenium that was employed in all experiments was the spectrophotometric determination of potassium ruthenate in 2N potassium hydroxide. The procedure is given by Marshall and Rickard (13) and involves the fusion of the ruthenium sample with a mixture of potassium hydroxide and potassium nitrate. The sample to be analyzed was added to a 50 ml nickel crucible with approximately 0.3 grams of potassium hydroxide pellets and 1.0 gram of potassium nitrate powder. The mixture was then slowly fused, allowed to cool, dissolved, and diluted to a known volume with 2N KOH, centrifuged, and read on a Beckman Model DU Spectrophotometer at 464 mμ and 0.30 mm slit width against a distilled water standard.

In order to determine a standard curve (Figure 3.2), weighed amounts of ruthenium metal powder were used as the sample. The metal powder was purchased from Metals and Controls Division, Texas Instruments, Inc., Attleboro, Massachusetts.

The analysis of the organic phase samples was complicated by the presence of the toluene and the TLA. It was necessary to first place the samples, pipetted into the nickel crucible, on a hot plate in order to slowly evaporate the toluene and leave the

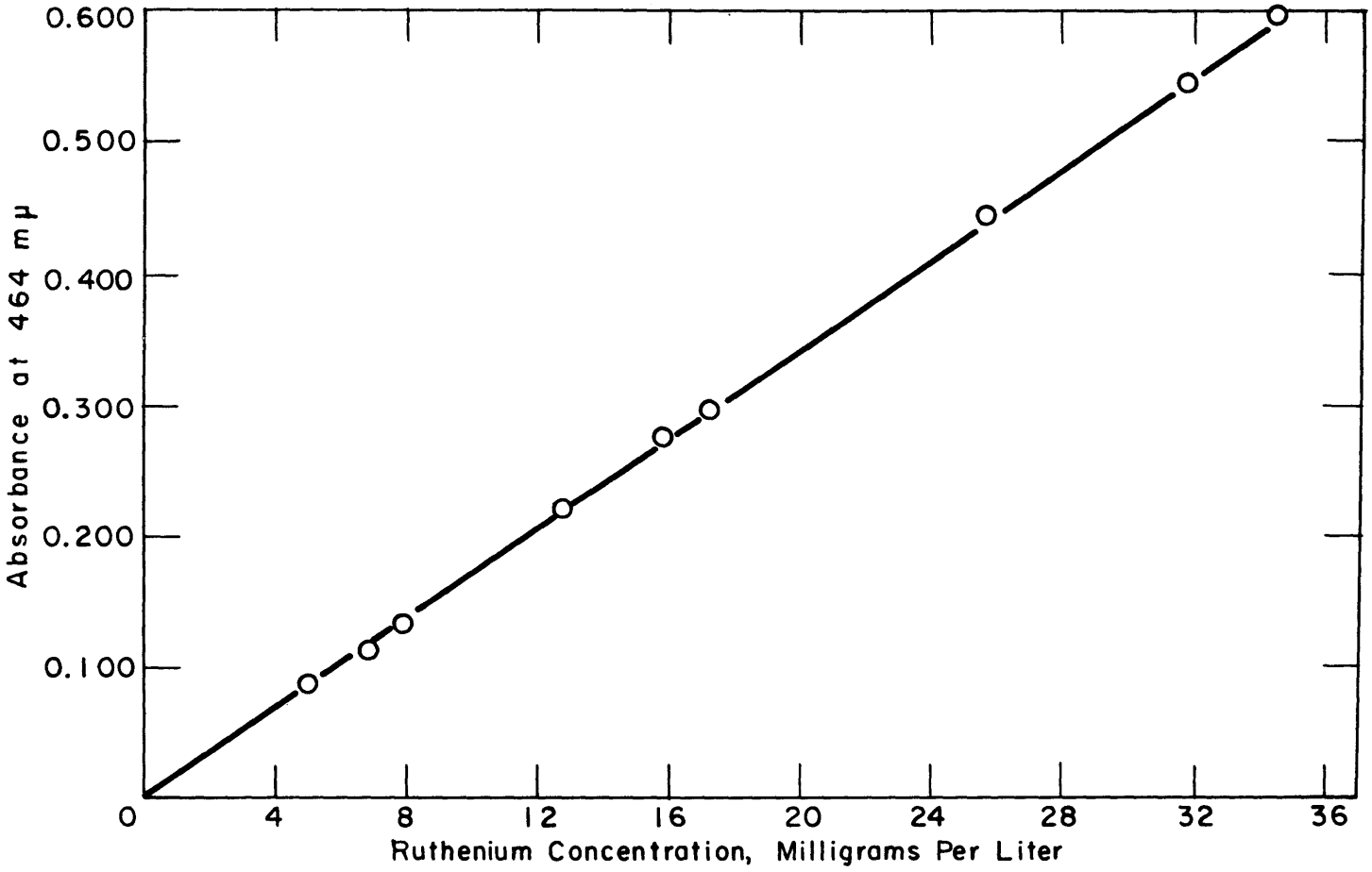

FIG. 3.2 RUTHENIUM STANDARD CURVE KOH-KNO_3 FUSION OF Ru METAL POWDER IN NICKEL CRUCIBLE READ AT 464 mμ ON BECKMAN MODEL DU SPECTROPHOTOMETER AGAINST DISTILLED WATER STANDARD

sample as dry as possible. Any toluene remaining in the sample might catch on fire during the fusion process and deposit soot in the crucible which caused precipitation of RuO_2 during the dissolution in 2N KOH, thus ruining the analysis. It was also necessary to accomplish the fusion slowly in order to prevent the TLA from flashing and also subsequently causing RuO_2 precipitation.

3.2 Nitrato Complexes of Nitrosyl Ruthenium

3.2.1 Solution Chemistry of the Complexes

The solution chemistry of this class of compounds, as well as the class of nitrosyl ruthenium nitro complexes, has been most thoroughly studied by Fletcher and his group at Harwell, England. (1, 3, 5, 6, 7, 9). The general class of nitrato nitrosyl ruthenium complexes existing in aqueous nitric acid solutions can be expressed as

$$[RuNO(NO_3)_x(OH)_y(H_2O)_z]^{+3-(x+y)}$$

where $x+y+z = 5$. In acid solutions above about 0.1N HNO_3, it is doubtful that the hydroxyl group is included in the octahedron, but is probably replaced by H_2O or NO_3^-. Hence, for the conditions under which

this study was conducted, the nitrosyl ruthenium nitrato complexes can be expressed as

$$\left[RuNO(NO_3)_x(H_2O)_{5-x}\right]^{+3-x}$$

It is therefore possible to form anionic species (tetra- and penta- nitrato complexes) as well as neutral (tri-nitrato complex) and cationic (mono- and di-nitrato complexes). It was believed originally (9) that the highest number of nitrato ligands that could exist was three, and hence there could be no anionic species formed. However, a more recent study involving paper chromotography and ion exchange resins (7) has shown that a portion of the complexes are preferentially adsorbed by anion exchange resins and a portion of the complexes are preferentially adsorbed by cation exchange resins. The use of paper chromotographic methods has resulted in the determination of the relative amounts of these cationic and anionic species, as well as the neutral tri-nitrato complex. The relative amounts of each species found in nitric acid solution at equilibrium are dependent upon the nitric acid concentration.

Figure 3.3 shows the distribution of the various complexes (as determined by Fletcher) as a function of aqueous nitric acid concentration at equilibrium conditions. The complexes have been split into four

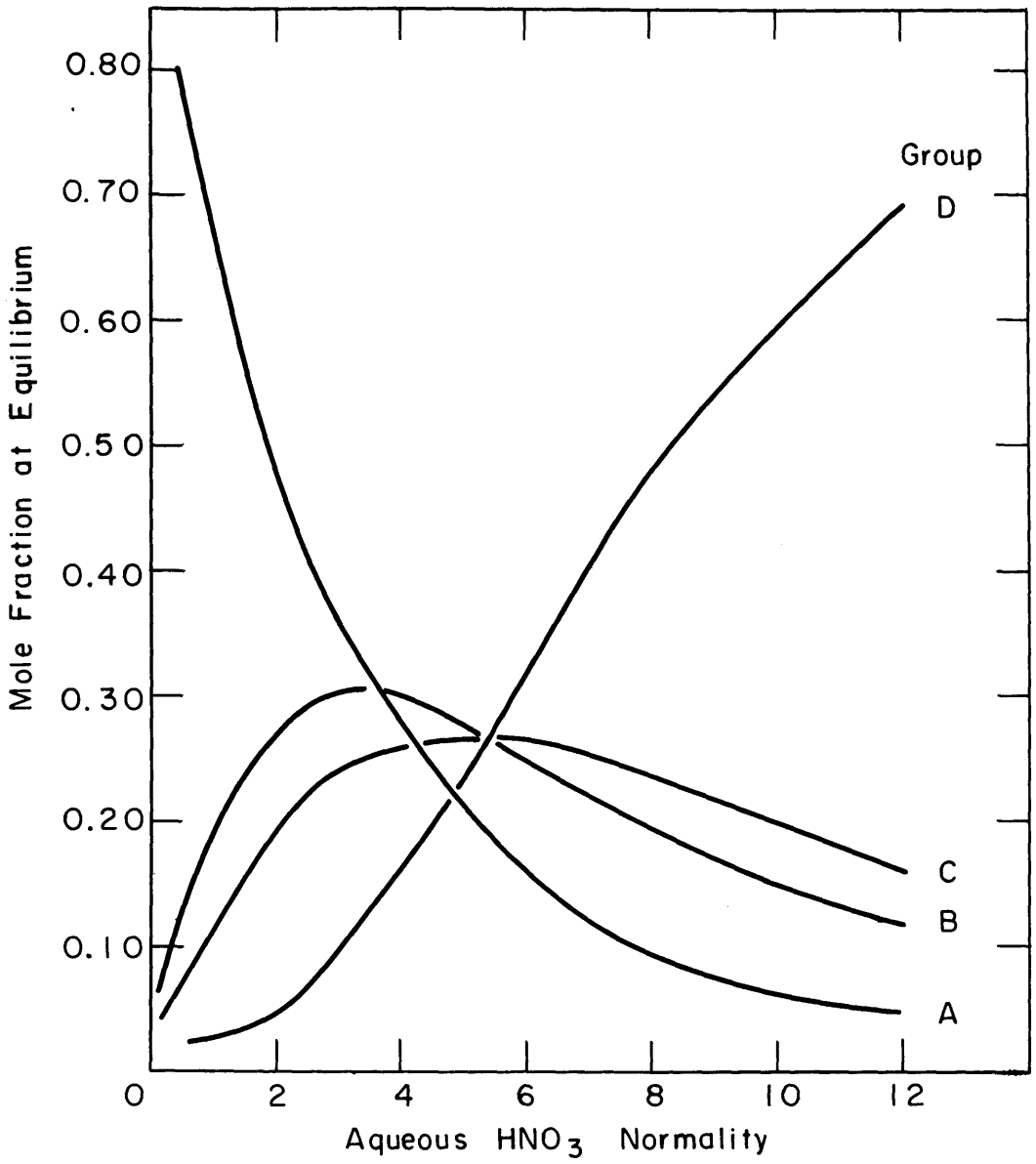

FIG. 3.3 EQUILIBRIUM DISTRIBUTION OF RuNO-NITRATO COMPLEXES IN AQUEOUS NITRIC ACID SOLUTIONS (DATA OF FLETCHER, et al.)

groups, each according to the type of complex. Table 3.1 shows the groups.

TABLE 3.1

NITROSYL RUTHENIUM NITRATO COMPLEXES

GROUP	COMPLEX
A	Mono-nitrato
B	Di-nitrato
C	Tri-nitrato
D	Tetra-plus penta-nitrato

As a result of the interpretation of the solvent extraction studies performed at MIT, the determination of the relative distributions of the extractable species of nitrosyl ruthenium nitrato complexes was accomplished. Figure 3.4 shows the mole fraction distributions at equilibrium conditions for the tetra- and penta-nitrato complexes of nitrosyl ruthenium as a function of nitric acid concentration. The values of Fletcher's Group D mole fractions are also shown in order to enable comparison. It is seen that the MIT values of the sum of the tetra- plus penta-complexes differ from the values of Fletchers Group D complexes by about a factor of two. The reasons for the

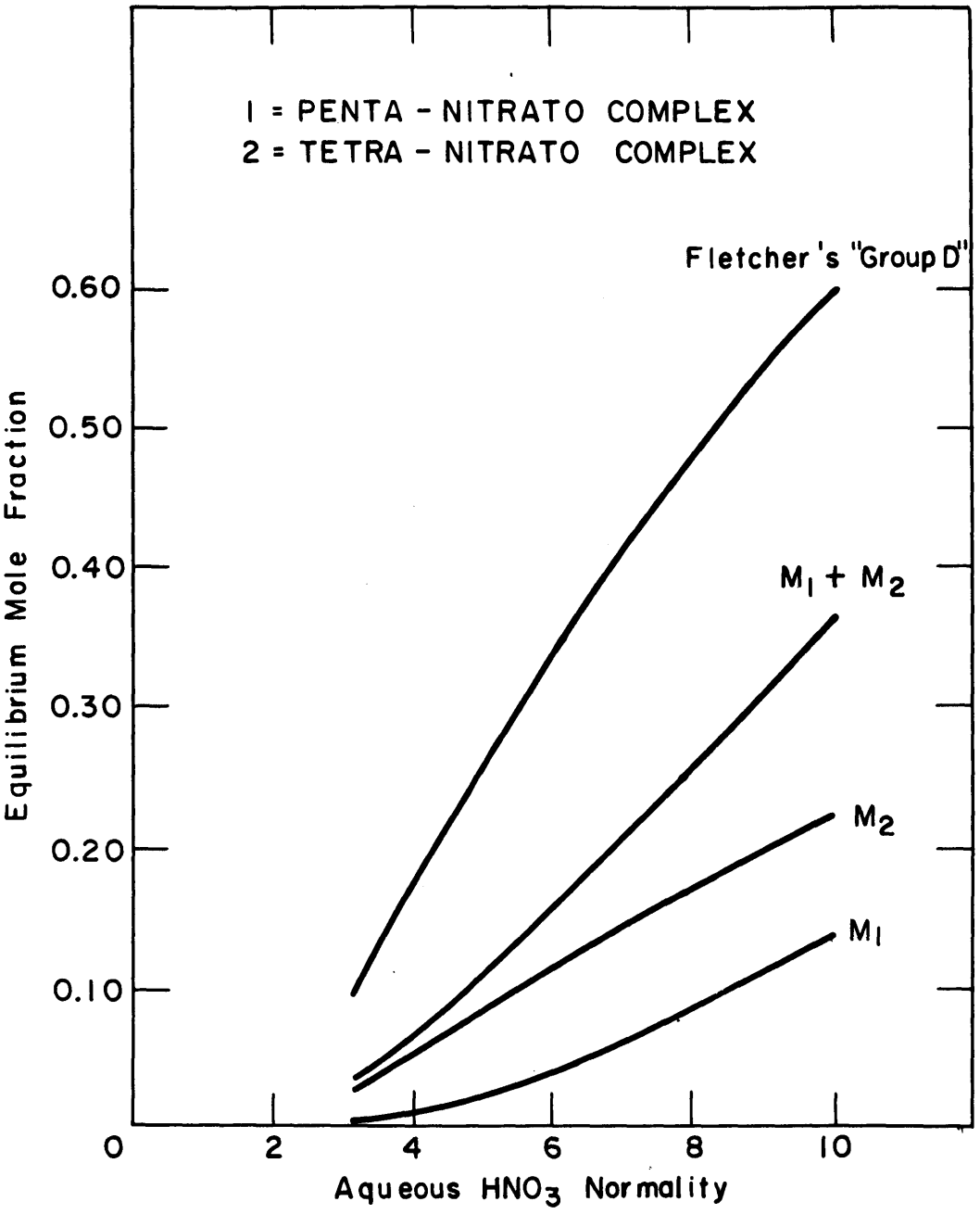

FIG. 3.4 EQUILIBRIUM DISTRIBUTION OF RuNO-NITRATO COMPLEXES IN AQUEOUS NITRIC ACID SOLUTIONS

differences and the methods employed for the determination of the values are discussed in Chapter IV.

It was thought (7) that the equilibrium distributions may be dependent only on total nitrate concentration; however, work at MIT utilizing solvent extraction and absorption spectra methods on nitric acid-sodium nitrate systems indicates otherwise. In an attempt to determine if the distribution of the RuNO-nitrato complexes in aqueous solutions is dependent only on the total nitrate concentration or only on the nitric acid concentration or on a combination of both, spectra were taken of three solutions (Batch B) at aged conditions.

Figure 3.5 shows that the $NaNO_3$ salted solution spectrum is intermediate between the solution having a nitric acid concentration equal to the nitric acid concentration of the salted solution and the solution having a nitric acid concentration equal to approximately the total nitrate concentration of the salted solution. Interpolation by the use of Figure 3.6 shows the salted solution spectrum to be equivalent to that of a non-salted solution of 3.6N HNO_3. From these spectra and from the results of the solvent extraction studies to be discussed in Chapter IV, it appears that sodium nitrate is not as effective a complexing agent as nitric acid.

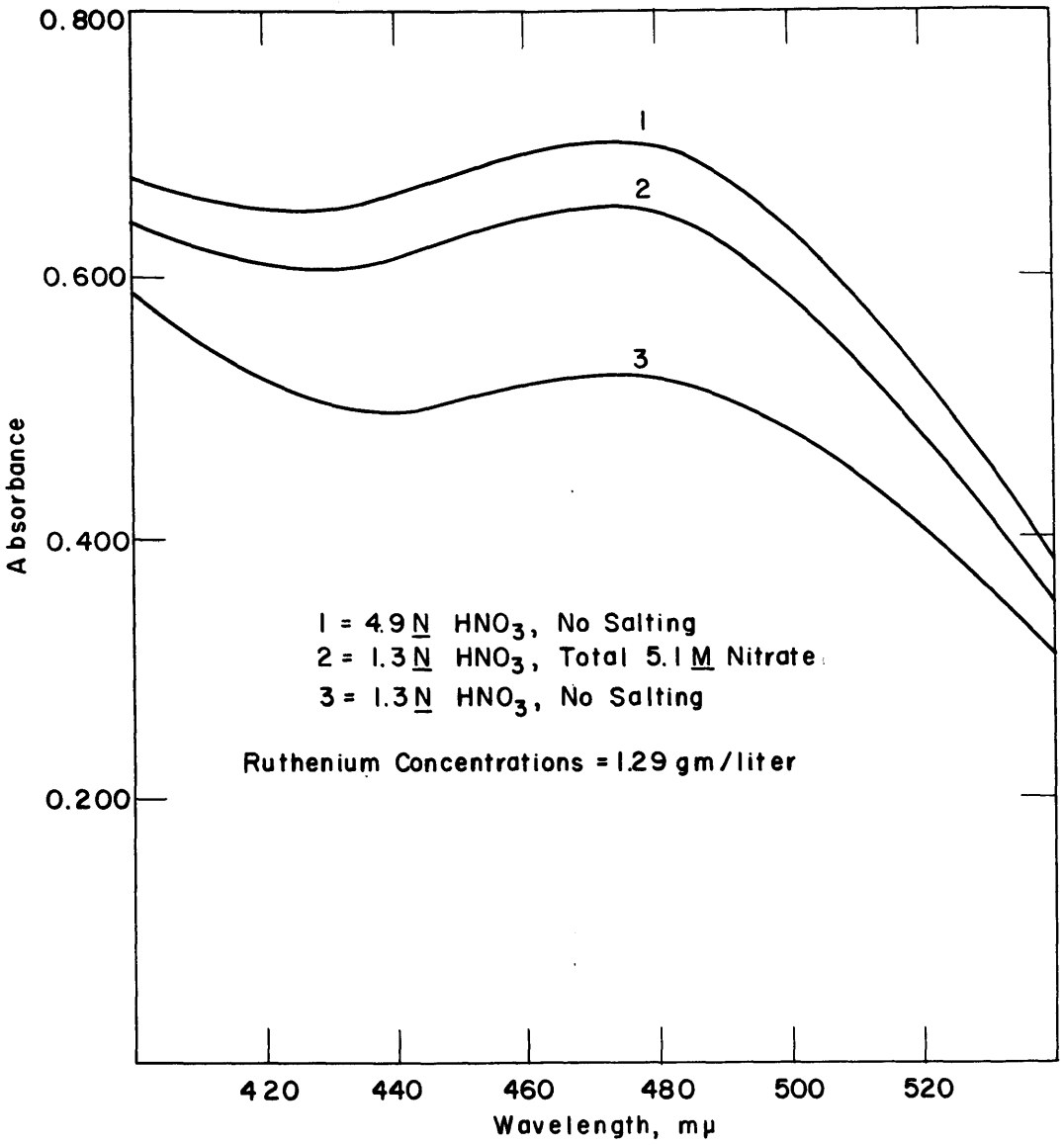

FIG. 3.5 THE EFFECT OF NITRATE SALTING ON THE ABSORPTION SPECTRA OF RuNO-NITRATO COMPLEXES SOLUTIONS (BATCH B)

As a consequence of the less effective complexing of sodium nitrate, and as a result of the interpretation of the solvent extraction studies to be discussed in Chapter IV, there are indications that the tetra-nitrato and penta-nitrato complexes are extracted into the organic phase as the acids of those complexes rather than as the anions. It is suggested that the species in the aqueous solutions are probably the acids $HRuNO(NO_3)_4(H_2O)$ and $H_2RuNO(NO_3)_5$ rather than the anions $RuNO(NO_3)_4(H_2O)^-$ and $RuNO(NO_3)_5^=$.

As mentioned in the previous section, ligand substitution is a slow process. The complexes are formed by dissolution of the tri-nitrato compound, $RuNO(NO_3)_3 \cdot 2H_2O$, in aqueous nitric acid solutions. Upon dissolution of this compound in nitric acid solutions, the length of aging time required for the solutions to reach equilibrium with regard to the relative distribution of the complexes is on the order of a month (9), at room temperature. The work performed at MIT (17) has indicated that the aging time at room temperature is between 16 and 22 days.

Spectra of the aged (equilibrium) solutions of the RuNO-nitrato complexes prepared at MIT (Batch A) are shown in Figure 3.6. The spectra agree well with those of Fletcher (7), exhibiting a maximum in the

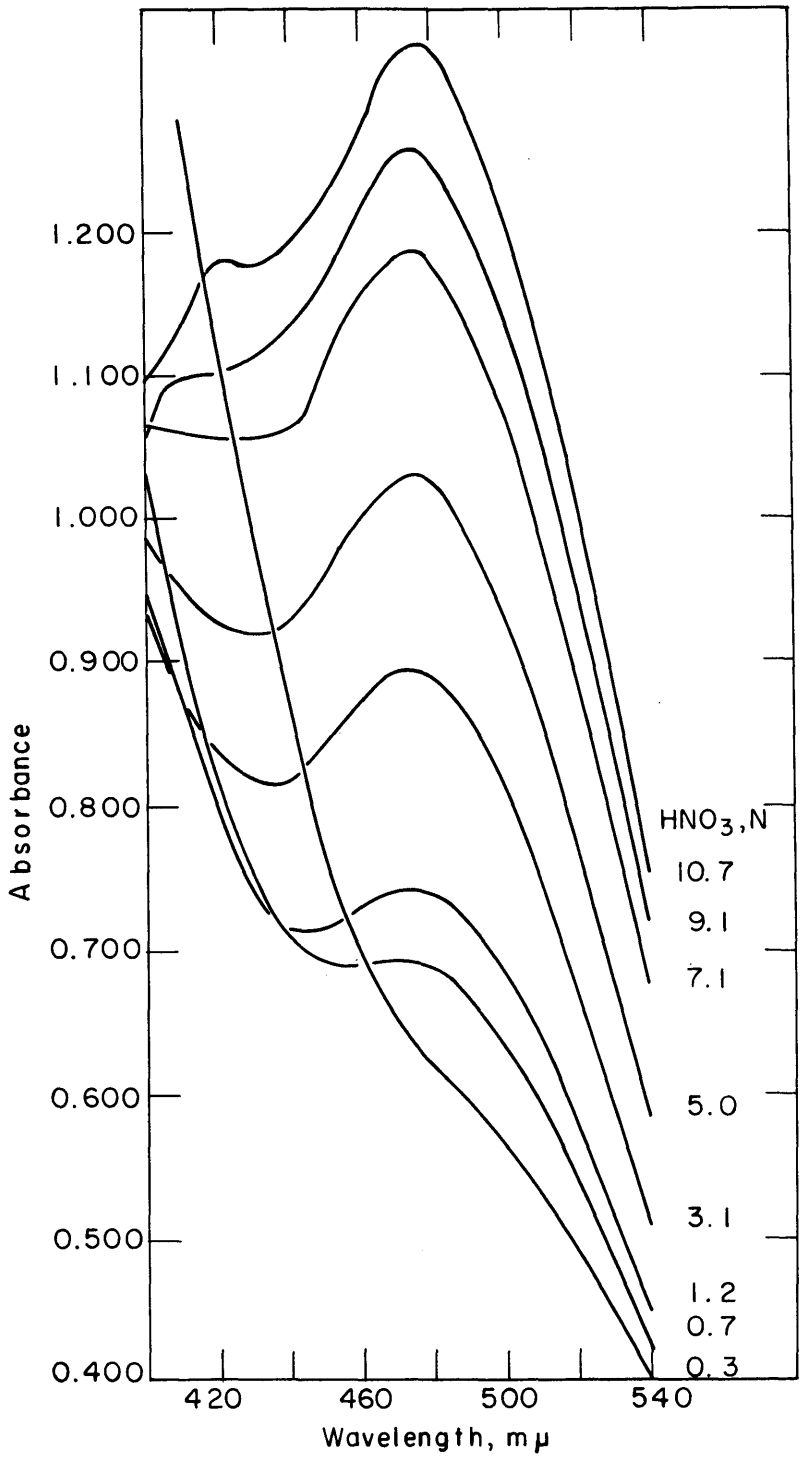

FIG. 3.6 SPECTRA OF AGED RuNO-NITRATO COMPLEXES IN NITRIC ACID SOLUTIONS (BATCH A)
BECKMAN MODEL DU SPECTROPHOTOMETER, 0.30 mm SLIT WIDTH
Ru CONCENTRATIONS = 1.8 gm./l

absorbance at 475 mμ and the value of the absorbance at the maximum increasing with increasing nitric acid concentration.

In order to obtain some idea of the amount of time required for the aqueous solutions to reach equilibrium with regard to the distribution of the complexes in solution, spectrophotometric studies were made of the solutions at various solution ages.

Figures 3.7 and 3.8 show the spectra of a solution of RuNO-nitrato complexes (Batch B) in 4.75N HNO_3 (no salting) with a ruthenium concentration of 1.78 gm/liter as a function of solution age at room temperature. At any wave length up to about 500 mμ, the absorbance exhibits a maximum with increasing age. However, the maximum absorbance occurs at about 475 mμ, regardless of solution age. In Figure 3.7, the solution age is shown from 1-2 hours to 22 days. Little change is seen between 16 days and 22 days. Figure 3.8 shows solution ages of 22 days and 31 days. Essentially no change is discernible between the two.

Figure 3.9 shows spectra of a solution of RuNO-nitrato complexes (Batch A) in 1.2N HNO_3 (no salting) with a ruthenium concentration of 1.73 gm/liter at two solution ages, one month and six

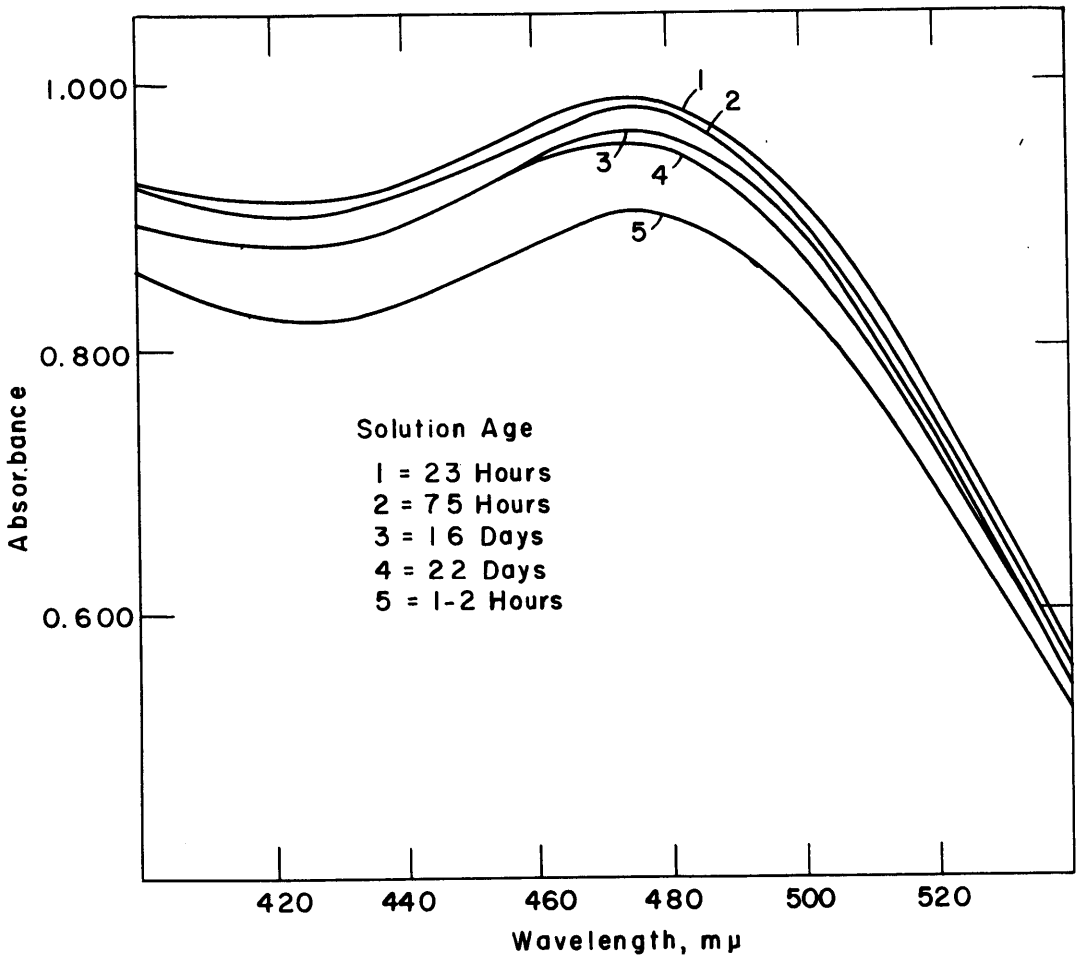

FIG. 3.7 THE EFFECT OF SOLUTION AGE ON ABSORPTION SPECTRA OF RuNO - NITRATO COMPLEXES SOLUTIONS (BATCH B)

RuNO - NITRATO COMPLEXES IN 4.75 N HNO_3
Ru = 1.78 gm / liter

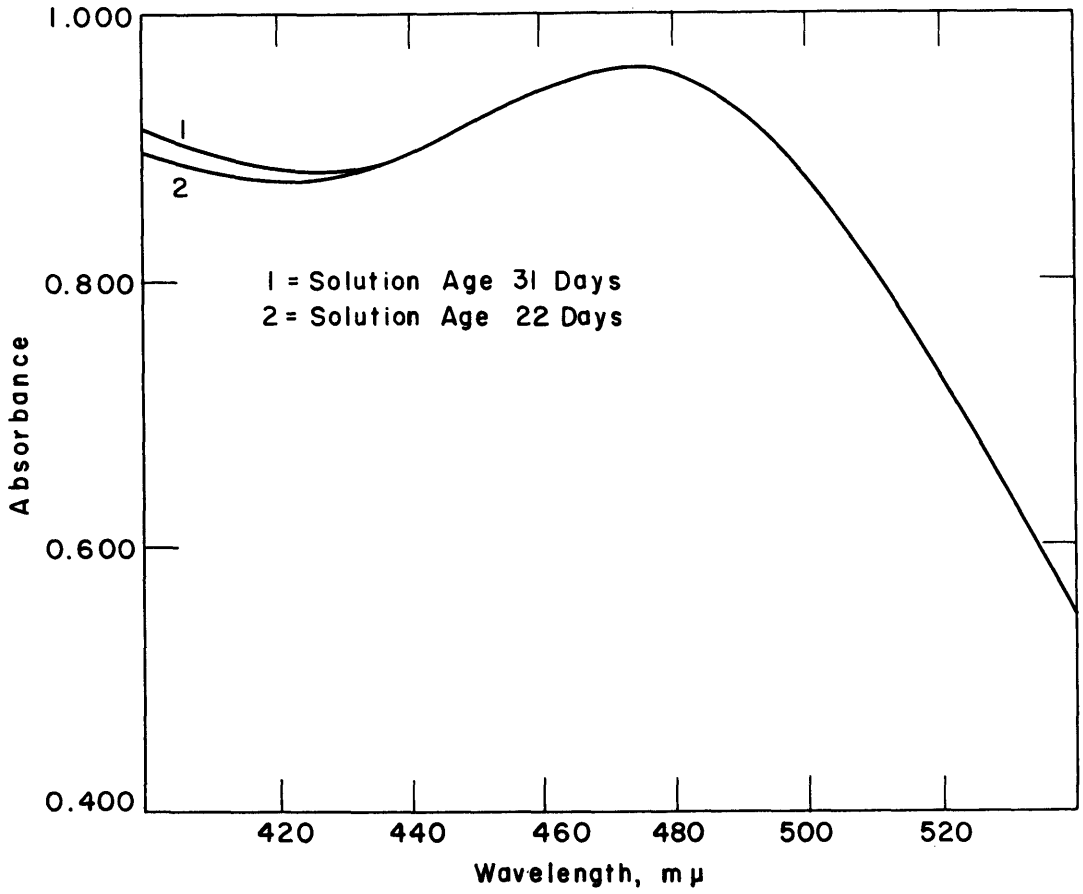

FIG. 3.8 THE EFFECT OF SOLUTION AGE ON ABSORPTION SPECTRA OF RuNO - NITRATO COMPLEXES SOLUTIONS (BATCH B)
RuNO - NITRATO COMPLEXES IN 4.75 N HNO_3
Ru = 1.78 gm / liter

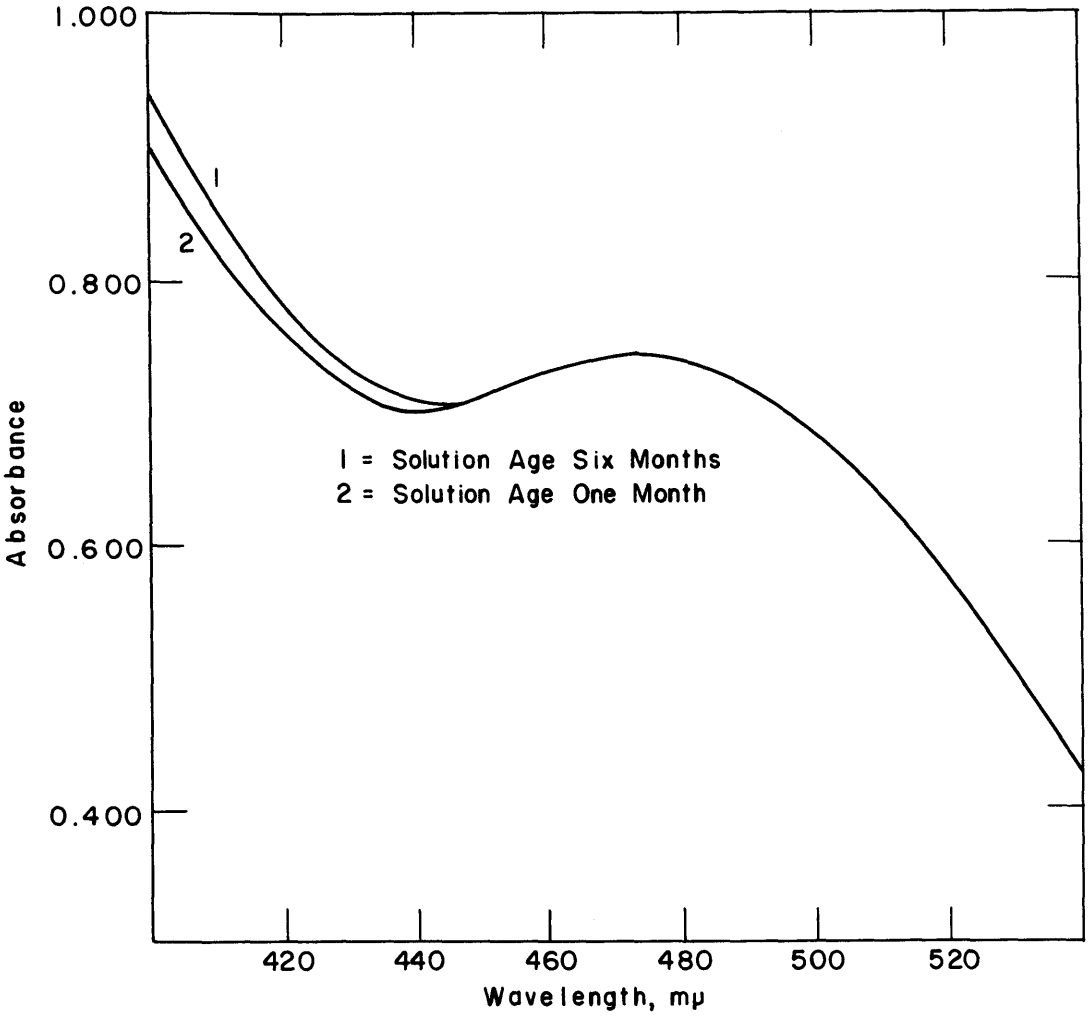

FIG. 3.9 THE EFFECT OF SOLUTION AGE ON ABSORPTION SPECTRA OF RuNO-NITRATO COMPLEXES SOLUTIONS (BATCH A)

Ru NO - NITRATO COMPLEXES IN 1.2N HNO_3
Ru = 1.73 gm/liter

months. Once again, no appreciable change is noticeable. The conclusion to be reached from the previous spectra is that equilibrium has been attained in less than 31 days and probably in the range of 16 to 22 days.

Confirming the work of Vaughen and Mason (24), the organic phase spectra of nitrosyl ruthenium nitrato complexes extracted into 0.26M TLA in toluene at MIT (16) exhibit an absorption maximum at about 490 mμ. (See Figure 3.10) A quantitative relationship between the absorbance at 490 mμ and the ruthenium concentration in the organic phase seems possible, (Figure 3.11) although the slope of the line evidently depends upon the organic phase unbound nitric acid concentration and/or the relative amounts of extractable nitrosyl ruthenium nitrato complexes in the organic phase.

Fletcher (7) has shown that the spectra in the near ultra-violet region of all aqueous solutions containing greater than 0.2M HNO_3 and less than 10^{-2}M Ru are very similar and that the distribution ratio of ruthenium between aqueous and organic phases is independent of the total ruthenium concentration. The work at MIT (16) has shown the same to be true for solutions of greater than 0.3M HNO_3 and ruthenium

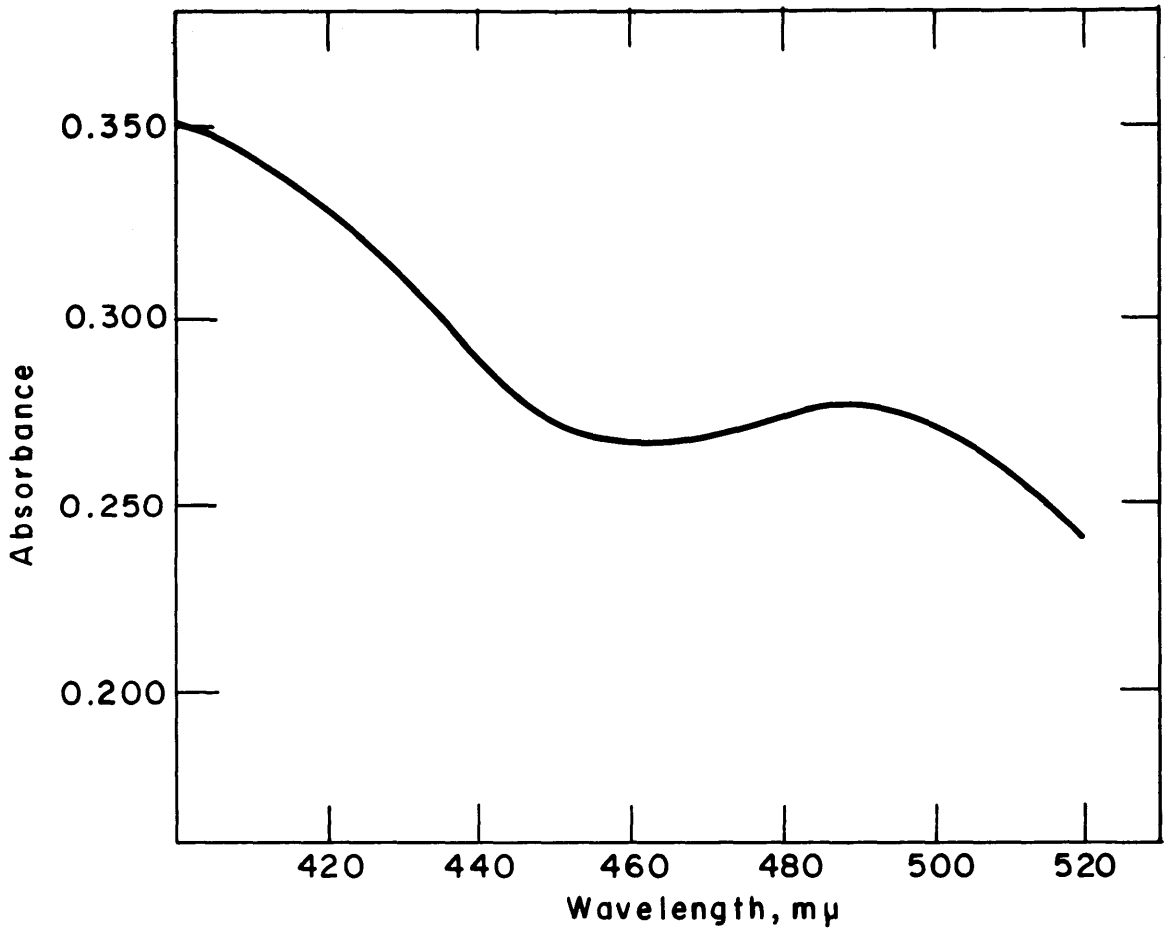

FIG. 3.10 ORGANIC PHASE SPECTRUM OF SAMPLE II
(ABSORBANCE OF RUTHENIUM-FREE SOLUTION HAS BEEN SUBTRACTED)

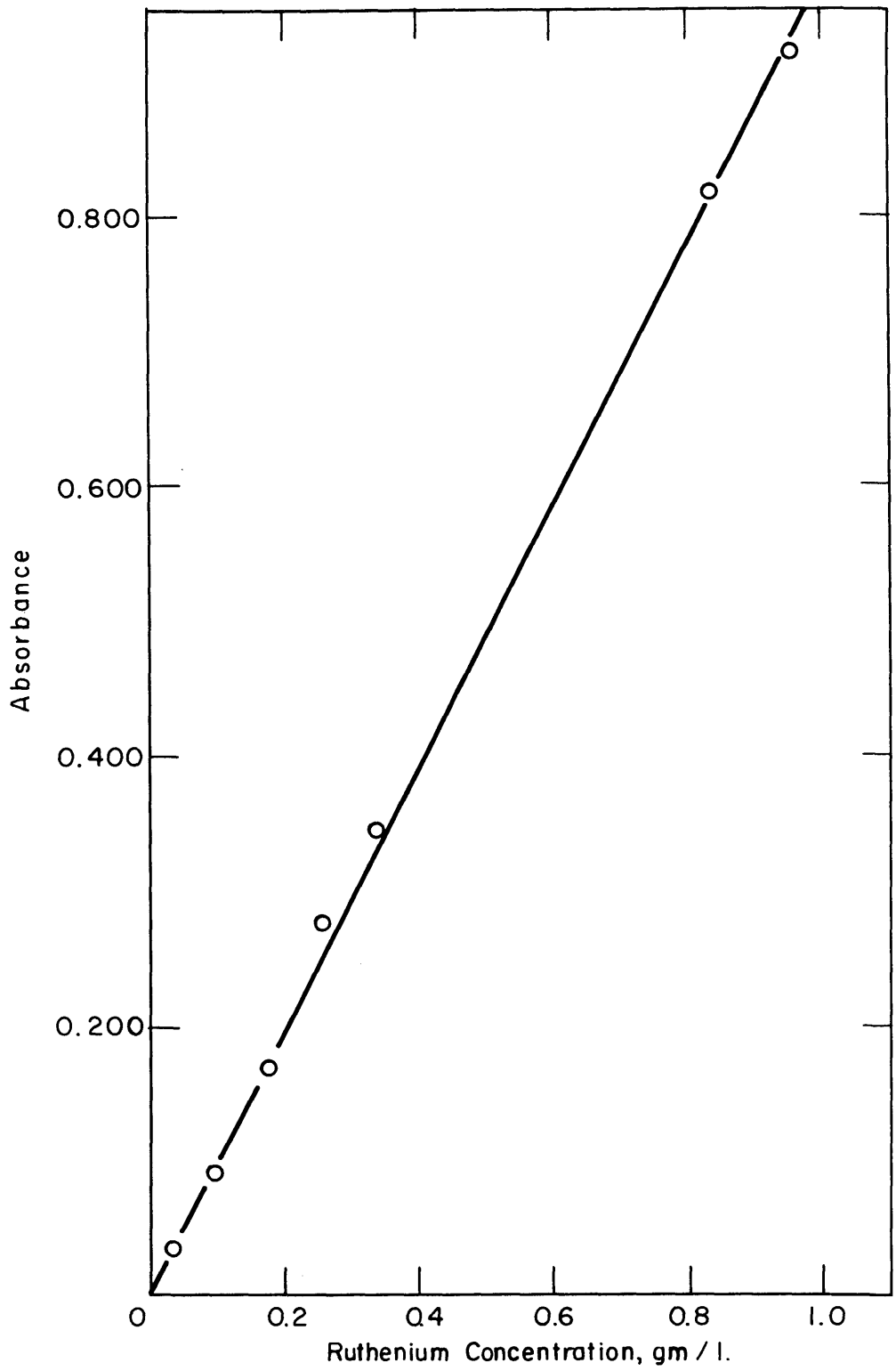

FIG. 3.11 DIRECT READING OF ORGANIC PHASE AT 490mμ, 0.3 mm SLIT WIDTH 1.2N HNO_3 IN AQUEOUS PHASE (ABSORBANCE OF RUTHENIUM-FREE SOLUTION HAS BEEN SUBTRACTED)

concentrations between 10^{-3}M and 10^{-1}M. For these reasons, it appears that there is no detectable polymer formation in the aqueous solutions. Tyndall beam tests performed at MIT on several aqueous solutions of the RuNO-nitrato complexes have indicated no detectable colloid formation.

3.2.2 Reaction Rates of the RuNO-Nitrato Complexes

Because of the slow rates at which the nitrato complexes are converted into one another in aqueous solutions, relatively long times are required to establish equilibrium after it has been disturbed. Three major factors influencing the reaction rates that are to be considered are the initial nitric acid concentration, the final nitric acid concentration, and the temperature. Fletcher (7) has found that of the three, the most important factor is temperature, of secondary importance is the final nitric acid concentration, and of practically no consequence is the initial nitric acid concentration.

The experiments performed by Fletcher (7) involved the dilution of equilibrium stock solutions to a final nitric acid concentration of 0.5M and 3.0M and aging at 0°C and 25°C. During the aging process, paper chromotography was used to determine the

concentrations of the Group D complexes as a function of aging time. It was found that there was essentially no dependence upon initial nitric acid concentration for aging in 3M HNO_3 at 0°C. The results of dilution of a stock solution of 11.1M HNO_3 are summarized in Table 3.2. The rate constants (k) for the disappearance of Group D complexes are first order with respect to ruthenium.

TABLE 3.2

DISAPPEARANCE RATES OF GROUP D COMPLEXES

Initial Stock Solution at Equilibrium in 11.1M HNO_3.

Final Nitric Acid Conc.	Temp°C	k(min^{-1})	Half Time (min)
3M	0	0.0013	550
3M	25	0.024	30
0.5M	0	0.0024	300

The current solvent extraction studies at MIT have yielded disappearance rate constants for the tetra-nitrato and penta-nitrato complexes at room temperature. The results are tabulated in Table 3.3 and are to be interpreted in more of a qualitative aspect than a quantitative aspect.

TABLE 3.3

DISAPPEARANCE RATE CONSTANTS OF TETRA- AND PENTA-NITRATO COMPLEXES AT ROOM TEMPERATURE (~25°C.)

Initial HNO_3 Conc., N	Final HNO_3 Conc., N	k(min^{-1}) Tetra	k(min^{-1}) Penta	Half Time (min) Tetra	Half Time (min) Penta
9.7	1.0	0.065	1.0	11	0.7
6.8	1.0	0.065	1.0	11	0.7
9.7	3.0	0.055	0.50	13	1.4
9.7	4.9	0.045	0.25	15	2.8

The method of experiment and mathematical interpretation are discussed more fully in Chapter IV; however, a short description of the experimental procedure is as follows:

Nitric acid stock solutions of the RuNO-nitrato complexes that had been aged to equilibrium were diluted rapidly to various final nitric acid concentrations and shaken for 30 seconds. Values of the distribution ratio were determined as a function of delay time, where delay time is defined as the time elapsed between the start of addition of stock solution and the start of shaking.

The delay time was only varied between 30 seconds and 5 1/2 minutes since the original intention of the set of experiments was to determine the correction

factor for extrapolation back to zero delay time. Subsequent mathematical correlation yielded the results of Table 3.3 and since the values of the delay times were not large compared to the disappearance half-times, their quantitative accuracy is questionable. However, when compared with the data of Fletcher, it is interesting to speculate that his values are possibly the disappearance rates of only the tetra-nitrato complex. Since his measurements were made over the space of several hours, during which the penta-nitrato complex could have rapidly denitrated to the tetra-nitrato complex, the long-time disappearance rate measured could have been that of only the tetra-nitrato complex.

3.2.3 Preparation of the RuNO-Nitrato Complexes at MIT

The method of preparation employed was essentially that outlined by Fletcher, et al (9), with a slight modification. The general method of Fletcher, et al (9) is as follows:

1. Conversion of commercial $RuCl_3$ to nitrosyl ruthenium chloride by passing an $NO-NO_2$ mixture into a solution of $RuCl_3$.
2. Conversion of $RuNOCl_3$ to $RuNO(OH)_3$ by boiling with addition of NaOH, maintaining pH > 11.

3. Centrifuging at pH 6.4 to remove colloidally - suspended $RuNo(OH)_3$, after aging for several days to allow complete precipitation.
4. After washing and drying, the $RuNO(OH)_3$ is dissolved and boiled in sufficient nitric acid to leave the solution about 8M HNO_3 (Boiling with concentrated acid gives slow oxidation to RuO_4).
5. Evaporating solution to dryness at room temperature in a vacuum desiccator over solid caustic soda leaves the trinitrato complex, $RuNO(NO_3)_3 \cdot 2H_2O$, as a dark red mass.
6. Dissolution of the solid in various nitric acid solutions and aging for several weeks gives the equilibrium distributions of the RuNO nitrato complexes.

In the preparations performed at MIT, it was found necessary to substitute the use of sodium nitrate for the $NO-NO_2$ mixture in order to more adequately form the nitrosyl ruthenium.

Three batches of the nitrosyl ruthenium nitrato complexes were made utilizing two different starting materials.

3.2.3.1 Preparation of Batch A

The starting material for Batch A was $RuCl_3$ purchased from Metals and Controls Division, Texas Instruments Inc., Attleboro, Massachusetts.

A portion of the $RuCl_3$, 53.2 grams, was dissolved in 155 ml of 1N HCl. Over the course of one hour and 11 minutes, 58.4 grams of $NaNO_2$ were added to the boiling solution. The hot solution was filtered through a sintered glass suction filter to remove RuO_2. The solution was a very clear plum color. After evaporating nearly to dryness, the still wet solid (about 116 grams) was dissolved in water. Then 25.3 grams of NaOH were added and the solution brought to 350-400 ml. of volume with distilled deionized water (DDW). More NaOH, 27.0 grams, was then added and the mixture put on a heater to boil. After boiling for 31 minutes, approximately 100 ml had been evaporated and the pH = 10.75. The pH was brought to 6.35 by adding 413 ml of 2M $HClO_4$. A light brown precipitate formed at pH = 9.6.

After standing for 6 1/4 days, a brown precipitate filled the lower half of a 1000 ml beaker. The top liquor was very dark colored and had a pH = 6.10. The liquor was decanted and the bulk mixed with 400 ml of 9:1 acetone-water mixture.

The suspension was allowed to stand overnight and then was centrifuged, washed, and centrifuged three times with acetone-water. After drying in a current of air, about 41 grams of dark brown solid resulted. The solid was added to 300 ml of DDW in a 600 ml beaker along with 75 ml of 0.88N NaOH and boiled for six minutes. The next day another 100 ml of 0.88N NaOH was added along with the solids from one last centrifugation and reboiled. After setting overnight, the pH was adjusted to 6.40 with 57 ml of 2M $HClO_4$ and 6ml of 0.88N NaOH. The precipitate was a dark brown this time. The suspension was allowed to settle for 3 1/6 days, then washed with acetone-water and centrifuged a total of six times. After the sixth wash and with about 100 ml of acetone-water solution left, about 200 ml of approximately 8N HNO_3 was added. The solution was simmered at about 95-100°C for approximately 1 1/2-2 hours, cooled to about 30°C, then placed in a vacuum desiccator over solid NaOH. The solution had a deep red color.

After evaporation, an attempt was made to analyze the resultant dark red mass for ruthenium content. However, the material was very hygroscopic and became moist and difficult to handle upon coming in contact with the air even for the duration of weighing a sample.

The solid was therefore dissolved in DDW and the solution analyzed for ruthenium. This solution was then diluted to form a series of solutions varying in nitric acid content from 0.3N to 10.7N and having a ruthenium concentration of approximately 9 grams per liter. The solutions are listed in Table 3.4

TABLE 3.4

RUTHENIUM NITROSYL NITRATO COMPLEXES SOLUTIONS (BATCH A)

Nitric Acid Conc., N	Ruthenium Conc. gm/l
0.32	9.10
0.71	9.05
1.21	8.63
3.13	8.79
5.03	8.87
7.09	8.86
9.12	9.22
10.68	9.04

The solutions had the deep red color characteristic of the ruthenium nitrosyl nitrato complexes. After aging for one month at room temperature, an absorption spectrum was taken of each solution (diluted 1:5 in the appropriate nitric acid concentration) using a Beckman Model

DU Spectrophotometer. The spectra are those shown plotted in Figure 3.6.

3.2.3.2 Preparation of Batch B

Subsequent to the preparation of Batch A, it was found possible to purchase nitrosyl ruthenium hydroxide and thus eliminate much time and effort consumed in its synthesis and purification. The hydroxide was purchased from A. D. Mackay, Inc. New York City.

For Batch B, 45 grams of the hydroxide were added to 500 ml of 9.2N HNO_3 and boiled for approximately two hours, the liquid level being kept constant by intermittent additions of DDW. After cooling, the solution was filtered through a sintered glass funnel and placed in an evaporating dish inside a vacuum oven and evaporated almost to dryness, yielding $RuNO(NO_3)_3 \cdot 2H_2O$. The solution had the characteristic deep red color, as did the resultant sticky mass which was formed upon evaporation.

The red mass was dissolved in DDW and the solution diluted to 250 ml in a volumetric flask. A quantitative analysis showed the stock solution to have a ruthenium concentration of 84.6 gm/liter.

A set of solutions was then prepared by adding the appropriate amount and concentration of nitric acid and/or sodium nitrate to aliquot portions of the stock solution. A summary of the solutions is listed in Table 3.5.

3.2.3.3 Preparation of Batch C

Using a portion of the same batch of nitrosyl ruthenium hydroxide as employed in the preparation of Batch B and using the same preparation procedure, a third batch of RuNO-nitrato complexes was made. A summary of the solutions is listed in Table 3.6

3.3 Nitro Complexes of Nitrosyl Ruthenium

The chemistry of these complexes is not so well known as that of the RuNO-nitrato complexes, but probably the best compilation of this subject obtainable in the published literature is the paper by Brown (1). The discussion that follows is essentially a summary of Brown's paper supplemented by work done at MIT.

3.3.1 Solution Chemistry of the Complexes

The general class of individual nitro complexes, or mixture of nitro complexes, that have been isolated as solids have the general formula

TABLE 3.5

RUTHENIUM NITROSYL NITRATO COMPLEXES SOLUTIONS (BATCH B)

HNO_3 Conc., N	$NaNO_3$ Conc., M	Ruthenium Conc., gm/liter
0.52	-	6.45
0.89	-	6.45
1.32	-	6.45
3.10	-	6.45
4.91	-	6.45
6.85	-	6.45
8.74	-	6.45
10.08	-	6.45
0.50	0.72	6.45
0.48	2.80	6.45
0.46	4.91	6.45
0.47	5.73	6.00
1.27	1.89	6.45
1.29	3.89	6.45
1.27	4.92	6.00
3.09	1.91	6.45
3.10	3.07	6.00
5.05	1.30	6.00

TABLE 3.6

RUTHENIUM NITROSYL NITRATO COMPLEXES SOLUTIONS (BATCH C)

HNO_3 Conc., N	$NaNO_3$ Conc., M	Ruthenium Conc., gm/liter
0.61	-	8.46
0.99	-	8.46
1.45	-	8.46
3.23	-	8.46
5.02	-	8.46
6.96	-	8.46
8.89	-	8.46
9.78	-	8.46
0.62	0.40	3.47
0.61	2.40	3.47
0.59	4.40	3.47
0.60	5.50	3.36
1.41	1.56	3.47
1.37	3.56	3.47
1.34	4.84	3.47
3.17	1.76	3.47
3.11	3.08	3.47
5.08	1.28	3.47

$[RuNO(NO_2)_x(NO_3)_y(OH)_{3-x-y}(H_2O)_2]$ with $x \geq 1$. Although each of the solids has a different solution chemistry when considered in detail, the general picture of the solution chemistry of the nitro complexes can be obtained by referring to one of the more important of the complexes rather than considering each in turn. The complex so chosen is the dinitromonohydroxy-nitrosylruthenium, $RuNO(NO_2)_2OH(H_2O)_2$. This complex was chosen for several reasons, one of them being its importance in the processing of spent nuclear reactor fuels. Siddall (23) has said:

"A large fraction, probably a majority, of the ruthenium is nitrosyl ruthenium by the time it reaches the solvent extraction contactors.... The nitro complexes are quite stable and are in the majority. The complex $RuNO(NO_2)_2(H_2O)_2OH$ is considered to be the dominant complex."

A second reason for its choice is the relative ease of its preparation.

The species existing in aqueous nitric acid solutions of the complex are not known, either qualitatively or quantitatively, as well as those resulting from the dissolution of $RuNO(NO_3)_3 \cdot 2H_2O$ in aqueous nitric acid. The nitro complexes are characterized by very slow reaction rates (relative to the RuNO- nitrato complexes) and it is difficult,

if not impossible, to speak of equilibrium distribution.

When the dinitro complex ($RuNO(NO_2)_2OH(H_2O)_2$) is first dissolved in aqueous nitric acid, any detectable changes that take place do so after a solution age of at least 1-2 hours. (Except for the possible immediate substitution of a NO_3^- ligand for the OH^- ligand.) In particular, Brown (1) has shown, by the equivalence of forward and backward extration distribution ratios, that at a solution age of five minutes, only one species is in solution. A portion of his data is summarized in Table 3.7.

TABLE 3.7

SOLVENT EXTRACTION OF FRESHLY PREPARED AQUEOUS NITRIC ACID-SODIUM NITRATE SOLUTIONS OF $RuNO(NO_2)_2OH(H_2O)_2$

Age of complex in solution approximately five minutes,
Ru conc. 5×10^{-3} M
Organic Phase = 30% TBP in kerosene, 30 second equilibration at 20°C.

Aqueous Phase		Distribution Ratio	
HNO_3,N	$NaNO_3$,M	Forward	Backward
1.0	-	1.70	1.66
3.0	-	0.506	0.514
3.0	2.5	0.215	0.214

Solvent extraction studies performed at MIT (to be discussed in Chapter V) support this statement up to solution ages of 1-2 hours.

The probable changes that take place in the aqueous solutions are the substitution of nitrato ligands for the nitro and/or hydroxyl ligands, thus forming a mixture of nitro, nitro-nitrato, and nitrato complexes.

3.3.2 Reaction Rates of the RuNO-Nitro Complexes

Several experiments indicate the slow reaction rates, for ligand substitution, of the nitro complexes. The previously mentioned observation that no detectable change occurs during the first hour or two after dissolution is one indication.

Brown (1) applied paper chromotography to a solution of the dinitro complex aging at 20°C in 3M HNO_3 containing excess (0.07N) ceric sulfate and showed that there is a slow decomposition which gives at least two products. The results indicated two consecutive reactions occurring:

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Where A represents the dinitro complex and B and C the reaction products. The values of the reaction

rate constants that were found were $k_1 = 0.7\ day^{-1}$ and $k_2 = 0.034\ day^{-1}$, which are equivalent to reaction half-times of approximately 1 day and 20 days, respectively. These are to be considered in relation to the reaction half-times of approximately 1 to 30 minutes for the disappearance rates of the tetra-and penta-nitrato nitrosyl ruthenium complexes.

A third indication of the slow reaction rates, and also of their qualitative nature, is to be derived from the study (at MIT) of the absorption spectra of the aqueous nitric acid solutions of the dinitro complex.

Figure 3.12 shows the absorption spectra of three aqueous nitric acid solutions of the dinitro complex as a function of solution age. Of interest are several points:

(1) The spectra of the RuNO-nitro complexes at all three solution ages (7 weeks, 4 months, 5 1/2 months) are similar to the aged RuNO-nitrato complexes from the aspect of exhibiting a minimum in the value of the absorbance between 400 mμ and 450 mμ and a maximum between 450 mμ and 500 mμ. They are also similar in that the absorbance at the maximum increases with increasing nitric acid concentration.

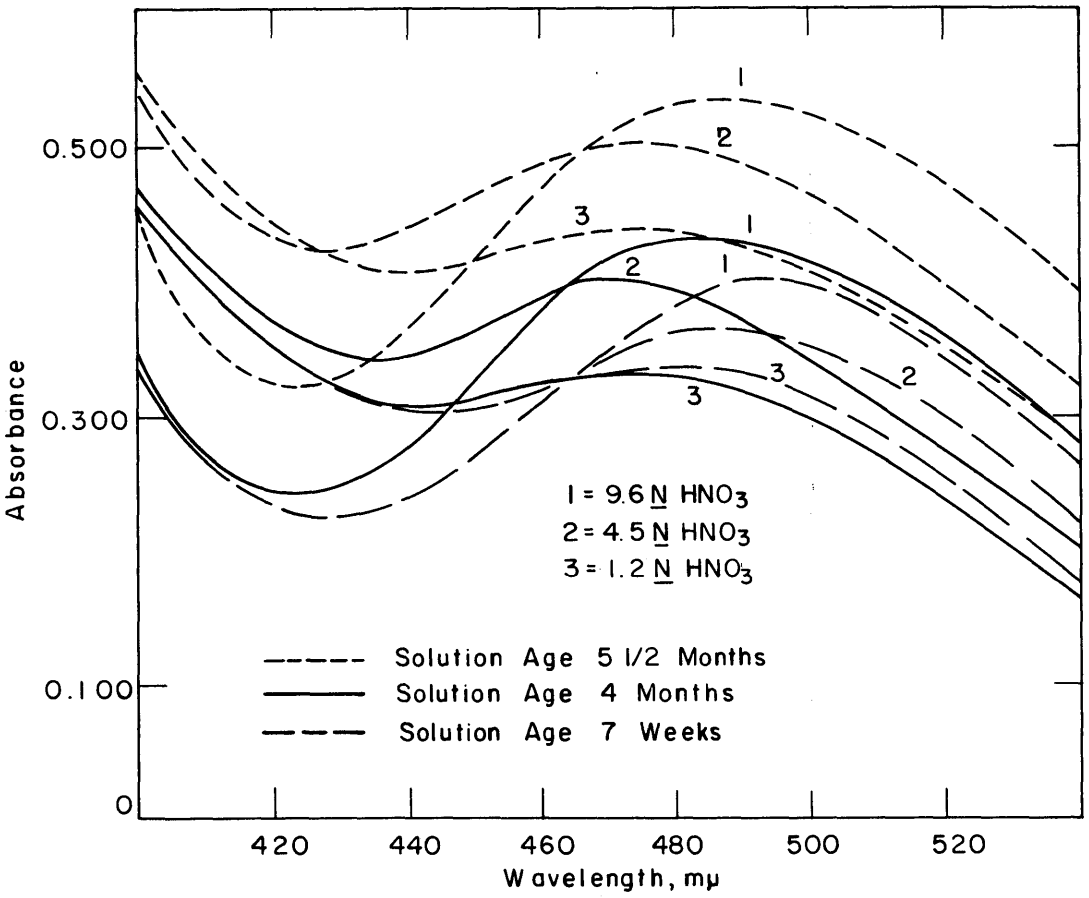

FIG. 3.12 THE EFFECT OF SOLUTION AGE ON ABSORPTION SPECTRA OF RuNO - NITRO COMPLEXES

(2) A significant difference is that the position of the maximum shifts with acid concentration. Whereas in the RuNO-nitrato complexes solutions the position of the maximum remained at 475 mμ, in the seven weeks aged RuNO-nitro solutions the position of the maximum moves from 485 mμ at 1.2N HNO_3 to 500 mμ at 9.6N HNO_3. Although the absorbance at the maximum increases with acid strength, it does not increase nearly so much as does the peak absorbance for the RuNO nitrato solutions.

(3) The effect of aging is generally to increase the absorbance over the entire range of 400 mμ to 540 mμ and to shift the position of the maximum to lower values of wave length.

(4) The rate of change of the spectra seems to increase with increasing solution age.

The general conclusions to be reached are:

(1) The RuNO-nitro complexes solutions are very slow in attaining equilibrium (relative to the RuNO-nitrato complexes). Equilibrium has not been reached after 4 months aging and possibly not after 5 1/2 months aging.

(2) From the appearance of the manner of the change in the spectra with solution aging, it appears that the RuNO-nitro complexes are slowly being transformed, either wholly or in part, to the RuNO-nitrato complexes and/or mixed RuNO-nitro-nitrato

complexes. Supporting this, also, is the increased rate of change with solution age, since the increased rate could be due to increased nitrato-complexes concentrations.

3.3.3 Preparation of the RuNO-Nitro Complexes

The method of preparation of these complexes has been reported previously (1, 9, 14) and is summarized as follows:

1. Conversion of commercial $RuCl_3$ to $RuNO\ Cl_3$ by addition of $NaNO_2$ to a solution of $RuCl_3$.
2. Conversion of $RuNOCl_3$ to $Na_2\ [RuNO(NO_2)_4OH]$ by adding slowly additional $NaNO_2$ at 80^oC and $pH \approx 7$.
3. Conversion of $Na_2\ [RuNO(NO_2)_4OH]$ to $RuNO(NO_2)_2OH(H_2O)_2$ by addition of dilute acid.
4. Removal of Na^+ and acid anion by equilibration with mixed cation and anion exchange resins.
5. Vacuum evaporation over phosphorous pentoxide to yield solid $RuNO(NO_2)_2OH(H_2O)_2$.
6. Dissolution of the solid in various aqueous nitric acid-sodium nitrate solutions.

3.3.3.1 Preparation I

In the preparation performed at MIT, 124.3 grams of $RuCl_3$ (same batch of $RuCl_3$ from which Batch A of nitrato complexes was prepared) were dissolved in 500 ml of 2.96N HCl. A total of 175.8 grams of $NaNO_2$ were added to the boiling solution during the period of one hour and seven minutes. The solution was cooled to between 75-80°C, and while being held at that temperature, 211.5 grams of $NaNO_2$ were added over the course of one hour and nine minutes. The solution was held at 75-80°C for another one hour and 31 minutes to ensure completion of reaction, then it was removed from the heater and allowed to cool to room temperature. After crystallizing from this solution and recrystallizing from water, vacuum evaporation at 30°C yielded the orange-yellow needles of $Na_2RuNO(NO_2)_4OH$ (hereafter referred to as "yellow salt"). The yellow salt was analyzed for ruthenium content and was found to contain 24.1% Ru; theoretical Ru content is 24.5%.

After being dried completely in vacuum, 74.3 grams of the solid were added to 180 ml of 2.11N $HClO_4$ and 500 ml of water and boiled for 30 minutes. After cooling to room temperature, the solution was contacted for one to two minutes with a mixture of ion exchange resins. The mixture contained

197.9 grams of Permutit "Q" (H^+ form, 1.88 milli-equivalents per gram) and 510.0 grams of Permutit "S-1" (OH^- form, 0.71 milli-equivalents per gram).

Subsequent evaporation to dryness over P_2O_5 in vacuum at 30°C yielded 17.9 grams of solid. The odor of nitrous fumes was evident upon opening the vacuum chamber. The solid was analyzed for Ru content and was found to contain 28.6% Ru. Theoretical ruthenium content of the dinitro complex $RuNO(NO_2)_2OH(H_2O)_2$, is 36.7%. The solid was placed in a bottle for storage and possible future use.

3.3.3.2 Preparation II

It was believed that the poor agreement between theoretical and actual Ru content of the previous preparation was possibly due to insufficient $HClO_4$ in the last step of the reaction and therefore another preparation was made.

The 400 ml of 2.96N HCl were added 124.4 grams of $RuCl_3$. Over the course of 44 minutes, 124.5 grams of $NaNO_2$ were added to the boiling solution. After cooling to 70-80°C, and holding at that temperature, 215 grams of $NaNO_2$ were added during the period of 2 hours and 40 minutes. The solution was held at 70-80°C for another hour and 50 minutes to ensure completion of reaction, and allowed to cool to room

temperature. After crystallizing from this solution and recrystallizing from water, vacuum evaporation at room temperature again yielded the orange-yellow needles of the yellow salt. The ruthenium analysis showed 25.5% ruthenium content as compared to the theoretical Ru content for the yellow salt of 24.5%, which was considered good agreement.

Thirty-seven grams of the above compound and 15.5 grams of the result of Preparation I were dissolved in 300 ml of water and 125 ml of 2.11N $HClO_4$. The solution was heated to boiling and additional 2.11N $HClO_4$ was added intermittently until further addition showed no signs of reaction. The additional $HClO_4$ amounted to 105 ml, the sum total of 2.11N $HClO_4$ being 230 ml.

The solution, after cooling to room temperature, was contacted for three minutes, with frequent shaking, with a mixture of 307.6 grams of Permutit "Q" (H^+ form) and 800 grams of Permutit "S-1" (OH^- form). The solution, after contacting, had a clear orange color, such as reported in reference (1).

The solution was placed in a vacuum oven at 30°C and evaporated nearly to dryness, yielding the deliquescent brown-orange solid $RuNO(NO_2)_2OH(H_2O)_2$. The solid was dissolved in DDW and diluted to 250 ml

in a volumetric flask. Analysis showed the ruthenium concentration to be 55.3 grams/liter.

A set of solutions was then prepared by adding the appropriate amount and concentration of nitric acid and/or sodium nitrate to aliquot portions of the stock solution. A summary of the solutions is listed in Table 3.8.

TABLE 3.8

RUTHENIUM NITROSYL NITRO COMPLEXES SOLUTIONS

HNO_3 Conc., N	$NaNO_3$ Conc., M	Ruthenium Conc., gm/liter
0.42	-	5.43
0.77	-	5.43
1.22	-	5.43
2.94	-	5.43
4.51	-	5.43
6.29	-	5.43
8.22	-	5.43
9.60	-	5.43
0.42	0.58	5.43
0.41	2.58	5.43
0.38	4.58	5.43
0.36	5.98	4.94
1.16	1.78	5.43
1.07	3.78	5.43
1.01	5.25	4.94
2.97	0.10	5.43
2.76	2.10	5.43
2.60	3.73	4.94
4.60	0.50	5.43
4.31	1.27	4.94

IV. EXTRACTION OF NITROSYL RUTHENIUM NITRATO COMPLEXES BY TRILAURYLAMINE

4.0 General Discussion

4.0.1 Purpose

The purpose of this study was to determine the more extractable species of the nitrosyl ruthenium nitrato complexes. The desired results were both the qualitative identification of these species, and some quantitative information regarding the amount of each species in solution and its degree of extractability.

4.0.2 State of the Art

As of the date of writing of this report, there is no single treatise available in the published literature covering the RuNO-nitrato complexes from the aspect of the study of the effect of variation of the many possible parameters existing in the solution and solvent extraction chemistry of these complexes.

It is possible to gather a certain amount of this type of information from the consideration of the publications covering certain portions of the

work. However, the differences in the systems utilized make comparison and/or analysis difficult. A sample of some of the conclusions at which other workers have arrived is listed below.

(1) Wallace (26) says that the most extractable species (by TBP) is the neutral trinitrato complex.

(2) Fletcher, et al (7) say that "tributyl phosphate extracts preferentially the tetra- and penta-nitrato acids rather than the uncharged trinitrato complex."

(3) Knoch (11) finds the most highly extractable species (by tri-iso-octylamine) to be the anionic tetra-nitrato complex.

(4) Zvyagintsev (27) states that the most extractable species (in general) are the result of "...the formation of nitroso complexes of bivalent ruthenium." That is, he says that the **nitrosyl ruthenium** group, RuNO, has a net charge of +2, rather than the customarily accepted +3. According to that, the neutral compound would be $RuNO(NO_3)_2 \cdot 3H_2O$ rather than $RuNO(NO_3)_3 \cdot 2H_2O$.

Although the above references do not cover all of the work on ruthenium, they are sufficient, it is believed, to indicate the lack of agreement. The results of the work performed at MIT are in qualitative agreement with Fletcher, et al (7) but are not in quantitative agreement, as shown, for example, by Figure 3.4.

As previously mentioned in Chapter II, however, there is widespread agreement that the extractable ruthenium species are in the nitrosyl ruthenium form and that non-nitrosyl ruthenium need not be considered a problem in ruthenium decontamination when solvent extraction is employed.

4.0.3 Experimental Approach

The variables that were considered important, or possibly important, in the RuNO-nitrato complexes systems and that were consequently studied are discussed in this chapter.

The general approach was to investigate each of these variables in a certain limited depth initially and then if any of them showed exceptional importance or promise, a more thorough study was undertaken.

Two important results of the latter were the more detailed study of sodium nitrate salting, with its resultant investigation of nitric acid extraction and organic phase titrations, and the more thoroughly applied technique of rapid dilution experiments. The former enabled the qualitative determination of the more extractable species and the latter enabled the quantitative determination of their mole fraction distribution in aqueous

solutions and their respective partition coefficients between those aqueous solutions and TLA in toluene.

4.1 Parameter Variation Experiments

4.1.1 Effect of Contact Time

4.1.1.1 Batch A

It was thought necessary to determine the length of time which the two phases must be in intimate contact before the value of the distribution ratio (E_A^o) could be considered to be the "equilibrium" value.

In order to study the effect of contact time on the distribution ratio, three of the solutions of Batch A were chosen and run in parallel for varying contact times. The solutions chosen were the aged, non-salted solutions of nitric acid concentrations of 0.3, 1.2, and 10.7N, and were so chosen as to represent the low, intermediate, and high acid regions, respectively.

It should be noted, that when used in connection with the RuNO-nitrato complexes, the term "aged" always refers to aqueous solutions that have been aged for at least 22 days at room temperature and are therefore assumed to be at equilibrium conditions with regard to the relative

distributions of the complexes (see Section 3.2.1). When discussing "aged" RuNO-nitro complexes, it is necessary to specify the length of aging time since no apparent equilibrium aging time was detectable.

When discussing either set of complexes, the terms "salted" and "non-salted" refer, respectively, to aqueous solutions that do and do not contain additional nitrate (above that associated with the HNO_3) in the form of sodium nitrate.

The contact time was varied from one minute to 96 hours and the results are shown in Figure 4.1. There are no data points for the 0.3N HNO_3 solution below a contact time of five minutes because of the lower limit of reliable detection of ruthenium in the organic phase. The data for the 10.7N HNO_3 solution are only shown for the points of one minute, 15 minutes, one hour, and 24 hours due to non-reproducibility of analysis at the other points.

As can be seen from the plot, the value of the distribution ratio appears to be increasing noticeably even at the 96 hour contact time and does not show any definite trend to level off, except perhaps for the high acid solution. The rate of increase can be seen to be dependent on the acid concentration and to vary inversely with it.

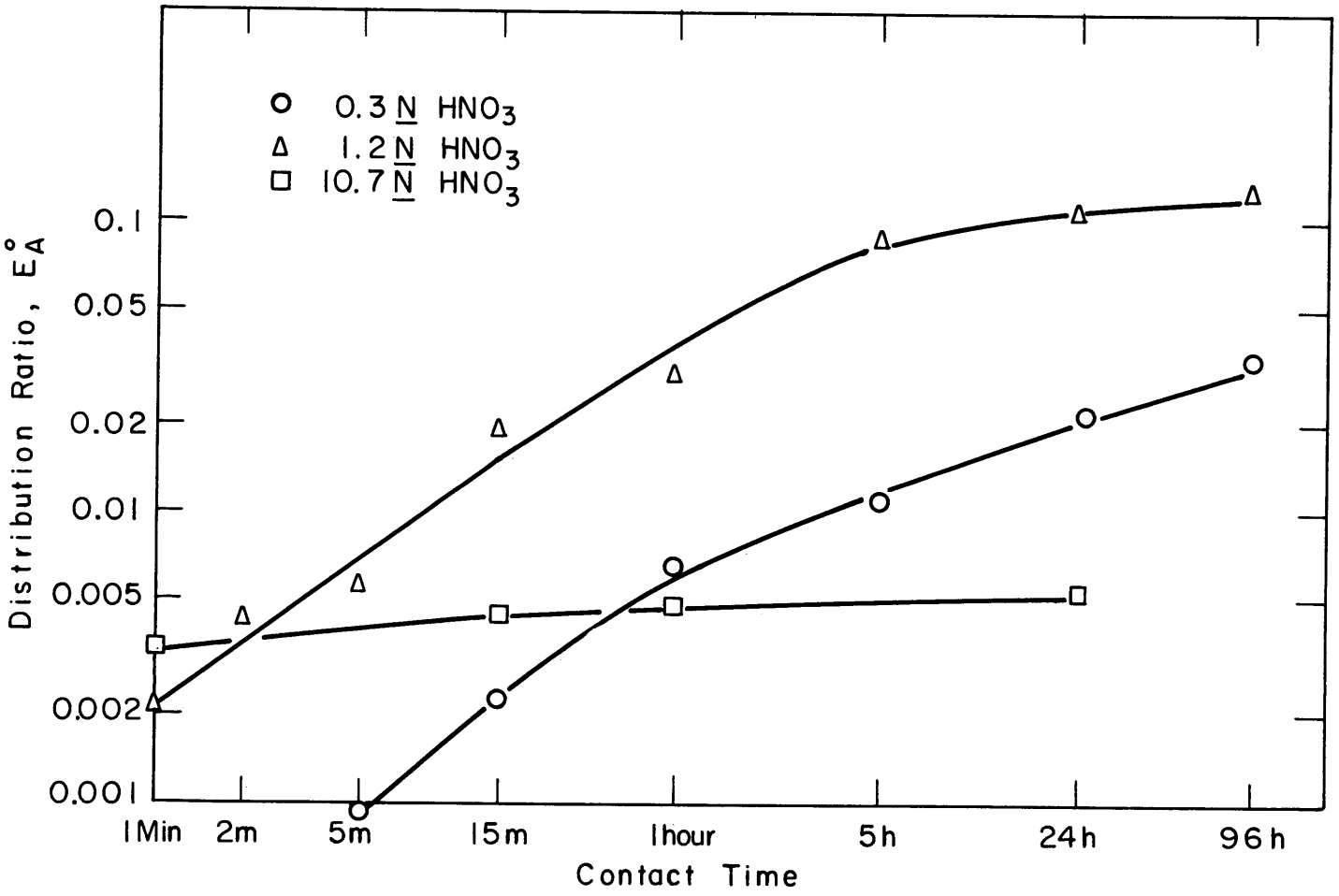

FIG. 4.1 EXTRACTION OF AGED RuNO-NITRATO COMPLEXES (BATCH A) AT 25°C WITH 0.26M TLA IN TOLUENE

It seems possible that at longer contact times, the value of E_A^o for the 0.3N HNO_3 solution would be higher than that for the 1.2N HNO_3 solution.

4.1.1.2 Batch B

A similar study of the effect of contact time was performed for the aged, non-salted solutions of Batch B, with some slight variation. The number of different contact times employed was reduced but the number of different nitric acid concentrations studied was increased. Figure 4.2 shows the results of the study. Once again, the rate of increase of E_A^o with contact time appears greater at the lower acid concentrations.

The primary reason for the type of contact-time-behavior observed is the slow rate of redistribution of the nitrato complexes in the aqueous phase (see Section 3.2.1). As the more extractable species are removed from the aqueous phase by the extraction process, redistribution must act to attempt to restore the equilibrium balance among the five nitrato complexes. The lengths of time required to bring the aqueous solutions to equilibrium is on the order of 22 days for the undisturbed system; therefore, when the system is being continuously disturbed, as in the extraction

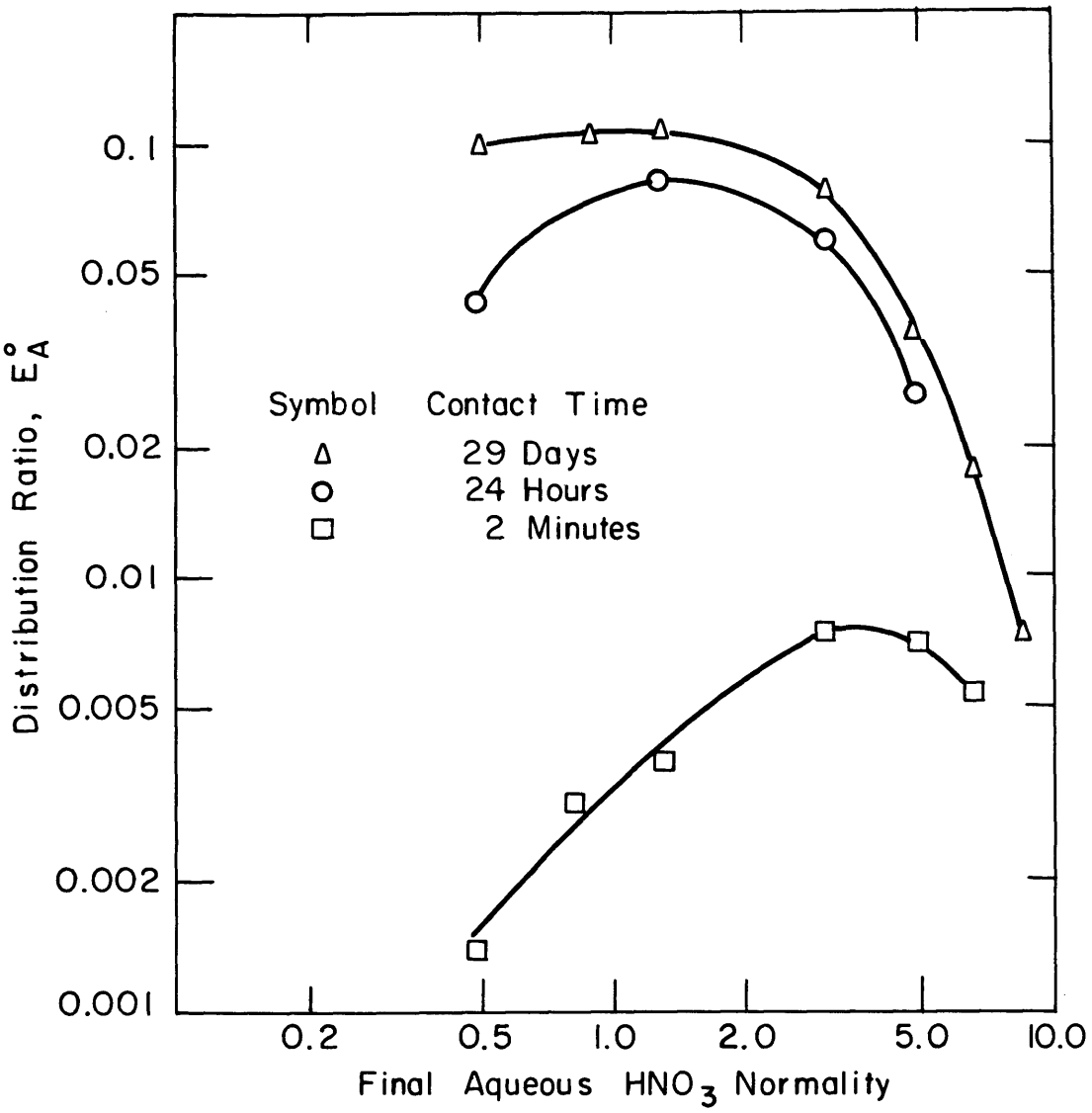

FIG. 4.2 EXTRACTION OF AGED RuNO-NITRATO COMPLEXES (BATCH B) AT 25°C WITH 0.26 M TLA IN TOLUENE

process, it is possible to visualize very long "equilibrium" contact times. The actual "equilibrium" contact time has not been determined in this study.

A second important consideration is the possible "fixing" of a portion of the extractable species in the organic phase by coordination with the extractant. It appears that a degree of irreversibility results when the extracted RuNO-nitrato complexes are allowed to remain in the organic phase for a length of time. It is difficult to isolate this phenomenon, however, since allowing the extracted RuNO-nitrato complexes to age in the organic phase also allows them to redistribute among themselves in a similar fashion to the aqueous phase solutions. The effect of fixation would be to give higher values of the back-extraction distribution ratio than would be the case if no fixation occurred, but the effect of redistribution would be to give lower values of the back-extraction distribution ratio if no redistribution occurred. Since the more extractable species are extracted into the organic phase, any redistribution that would take place in the organic phase must necessarily involve the formation of less extractable species which would subsequently be extracted into the aqueous phase during back-extraction. It is suggested that future

work on the nitrosyl ruthenium complexes include a study of these phenomena occurring in the organic phase.

4.1.2 Effect of Nitric Acid Concentration

It is apparent from Figure 4.2 that the value of E_A^o passes through a maximum with regard to the aqueous nitric acid concentration. At all three values of contact time studied, a maximum is seen in the value of the distribution ratio, the position of the maximum being dependent upon contact time and moving from higher to lower acid concentration with increasing contact time.

An explanation of this behavior can be obtained if one considers the amount of a complex available for extraction and the individual partition coefficient of that complex. An individual partition coefficient is defined as the ratio of the concentration of a particular complex in the organic phase to the concentration of that same complex in the aqueous phase. In the simplest case, it would be possible to measure a partition coefficient directly if several conditions were satisfied. These conditions are: (1) The aqueous phase contains only one species, (2) that species is not affected by time (either aging or contact),

concentration (of either the species or its medium), or any other variable that could change the form or amount of species in aqueous solution, (3) the extraction of the species into the organic phase has an "equilibrium" contact time, and (4) the extraction is reversible. Under these conditions, the value of the distribution ratio (E_A^o) measured for the equilibrium contact time would also be the value of the partition coefficient (P).

If the aqueous solution contains more than one species and if each of the species has a different concentration and a different partition coefficient, then the value of E_A^o measured under any variety of conditions must be a function of the number of species, the concentration of each species, and the partition coefficient of each species.

As will be shown later in this chapter, the partition coefficients for the more extractable species (the tetra-and penta-nitrato complexes of nitrosyl ruthenium) decrease with increasing acid concentration. As shown by Figure 3.4, the mole fractions of the more extractable species increase with increasing acid concentration. Although the amount of each extractable species in aqueous solution at equilibrium is small at low acid concentrations, the fraction of the species that is

extracted into the organic phase is greater at low acid concentrations than at high acid concentrations. Initially, at small values of contact time, the absolute amount of the complexes extracted is higher for high acid concentrations, but as contact time increases and redistribution takes place in the aqueous phase, a larger percentage of the newly formed complexes is extracted from low acid solutions than is extracted from high acid solutions. The position of the maximum of E_A^o vs acid concentration is then seen to be a measure of the product of the partition coefficients times the total amount of extractable species existing in both the aqueous and organic phases.

4.1.3 Effect of Solution Age

4.1.3.1 Freshly Prepared Solutions

Extractions of most of the fresh solutions of batch B (age after dissolution of the $RuNO(NO_3)_3 \cdot 2H_2O$ in DDW approximately 1 -2 hours) were made for a two minute contacting time. The data are plotted in Figure 4.3. The curve for the nitric acid system with no salting is fairly flat with a maximum at about 3N nitric acid. The values of E_A^o range from 0.0060 at 3N HNO_3 to 0.0028 at 8.8N HNO_3; the acid concentration was varied from 0.5N to 8.8N HNO_3.

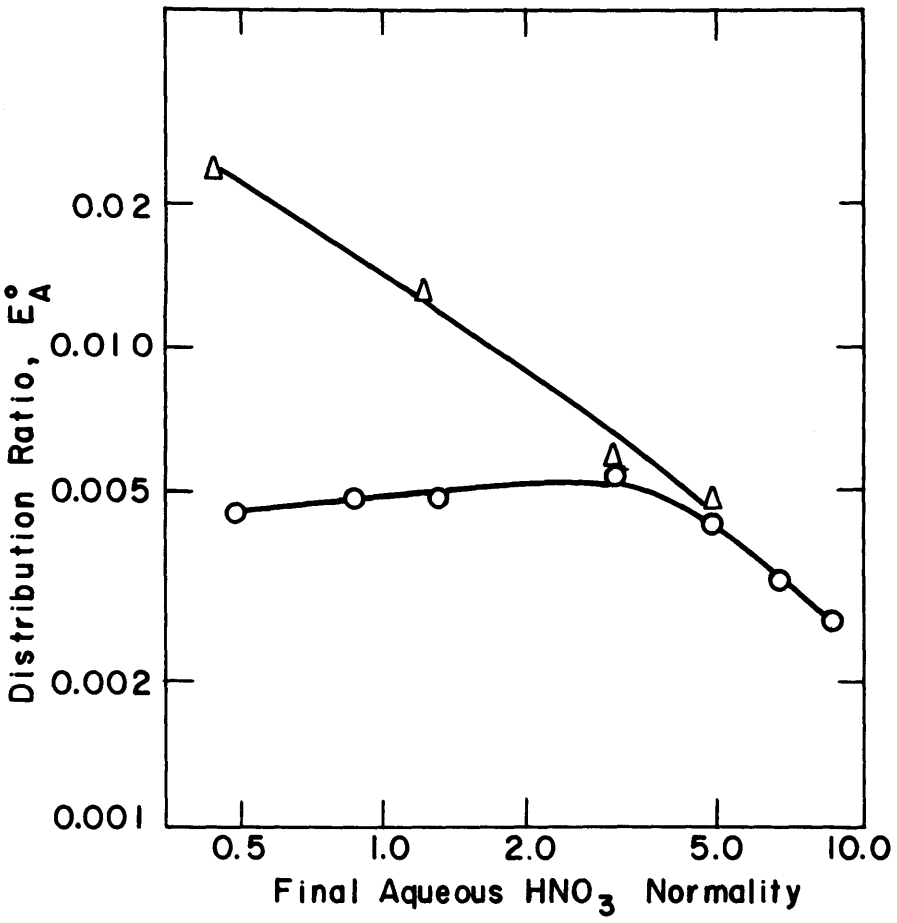

FIG. 4.3 EXTRACTION OF FRESHLY PREPARED RuNO-NITRATO COMPLEXES (BATCH B)
2-MINUTE CONTACTING AT 25°C WITH 0.26 M TLA IN TOLUENE

O = NITRIC ACID SYSTEM (NO SALTING)
Δ = NITRIC ACID-SODIUM NITRATE SYSTEM (TOTAL NITRATE = 6.2 M)

The data for a constant total nitrate concentration of approximately 6.2M show a decrease in E_A^o from 0.025 at 0.45N HNO_3 to 0.0050 at 5.0N HNO_3, the data falling on a straight line on a log-log plot with a slope of about -0.7. The increase in the extraction of ruthenium with nitrate salting can be explained by an increase in the nitrate complexing, especially at the lower acid concentrations. At 0.5N HNO_3, the addition of nitrate salting to form a total nitrate concentration of 6.2M raises the values of E_A^o by a factor of five.

4.1.3.2. Aged Solutions

In order to determine the effect of solution age on the extraction characteristics of the RuNO-nitrato complexes, extractions repeating the conditions of Figure 4.3 were carried out after the solutions had aged for one month. Figure 4.4 shows the two sets of data. Of interest are several points. For the nitric acid system with no salting, distribution ratios of the aged solutions varied in a manner consistent with the observation of Fletcher et al (7) that nitrate complexing decreases with aging at the low acid concentrations and increases with aging at the higher

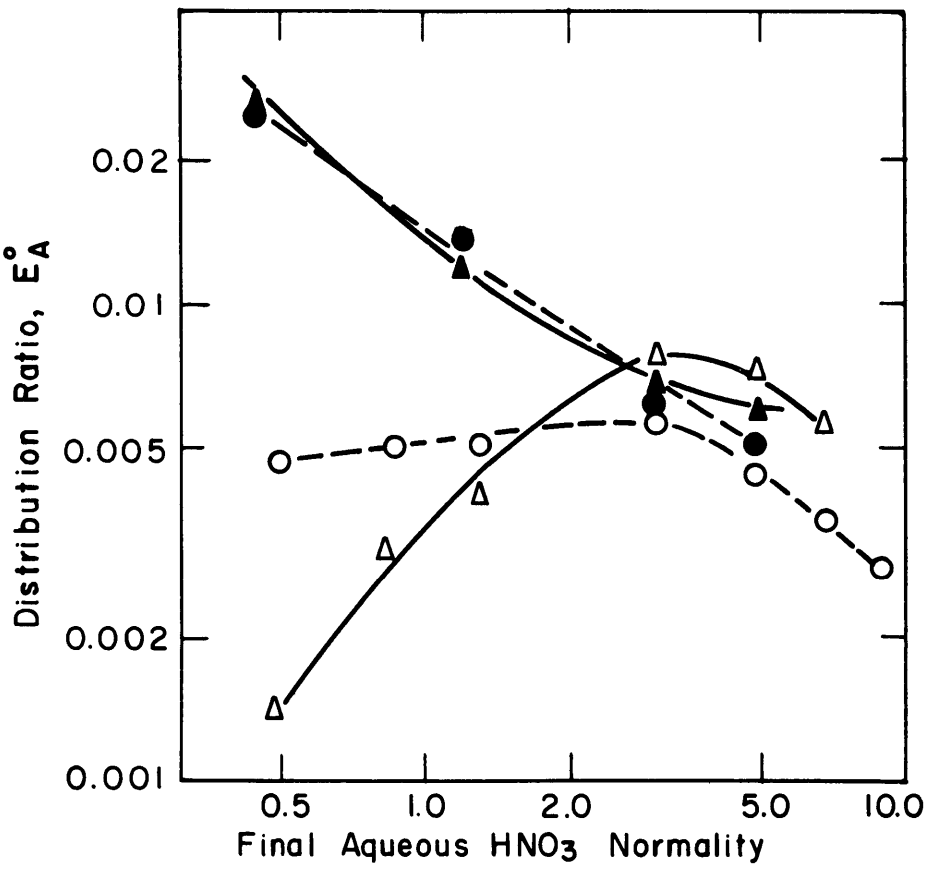

FIG. 4.4 THE EFFECT OF AGE OF SOLUTION ON THE EXTRACTION OF RuNO-NITRATO COMPLEXES
SOLUTIONS AGED AT ROOM TEMPERATURE (BATCH B)
2-MINUTE CONTACTING AT 25°C WITH 0.26 M TLA IN TOLUENE

O = NITRIC ACID SYSTEM, NO SALTING, SOLUTION AGE = 1-2 HOURS

Δ = NITRIC ACID SYSTEM, NO SALTING, SOLUTION AGE = ONE MONTH

● = TOTAL NITRATE CONCENTRATION CONSTANT AT 6.2 M, SOLUTION AGE = 1-2 HOURS

▲ = TOTAL NITRATE CONCENTRATION CONSTANT AT 6.2 M, SOLUTION AGE = ONE MONTH

SALTING AGENT = $NaNO_3$

acid concentrations. Aging had little effect on the salted solutions at a total nitrate concentration of 6.2M., indicating that the freshly prepared salted solutions were more nearly at equilibrium conditions with regard to the distribution of the RuNO-nitrato complexes than were the non-salted solutions. Above about 2.5N HNO_3 the data show the salted solutions to be less extractable than the non-salted solutions, a condition which is inconsistent with the usual findings that salting increases nitrate complexing and therefore increases the degree of extractability. However, the increase in nitrate complexing due to the salting is more than offset by an increase in the unbound nitric acid concentration in the organic phase which is caused by the nitrate common ion effect (see Section 4.1.4 for discussion). (The "unbound" nitric acid in the organic phase is the physically dissolved nitric acid. The "bound" nitric acid is the nitric acid chemically bound by the amine to form the amine nitrate, $TLA \cdot HNO_3$.) Thus, the net result is a decrease in the extraction of the complexes.

4.1.3.3 Comparison of Batch A and Batch B

The second batch (Batch B) of solutions was aged at room temperature for one month and then

sample extractions were made to determine if this batch resembled batch A with respect to its extraction characteristics. Variations in the preparation methods of the two batches, in particular the two different starting materials ($RuCl_3$ for batch A and RuNO-hydroxide for batch B) could possibly result in products with dissimilar values of NO_3: Ru ratios and concentrations of nitro complexes, if any exist. A second important variable is the method and speed of evaporation of the solution to yield $RuNO(NO_3)_3 \cdot 2H_2O$. In the two cases, the method of evaporation was very similar, in that the same equipment was employed and the temperature of evaporation was the same (30°C.)

Extractions were made for a 2 minute contacting time and a 24 hour contacting time and varying nitric acid concentration with no salting. The results are shown in Figure 4.5. It can be seen that, in general, the values of E_A^o are slightly lower for Batch B than for Batch A. The maximum variation occurs at 1.3N HNO_3 for the 24 hour contact time and shows the value of E_A^o to be approximately 20% lower for Batch B. For the two minute contact time, the maximum variation occurs at 4N HNO_3, when the Batch B value is 35% below that of Batch A. It appears that an even greater

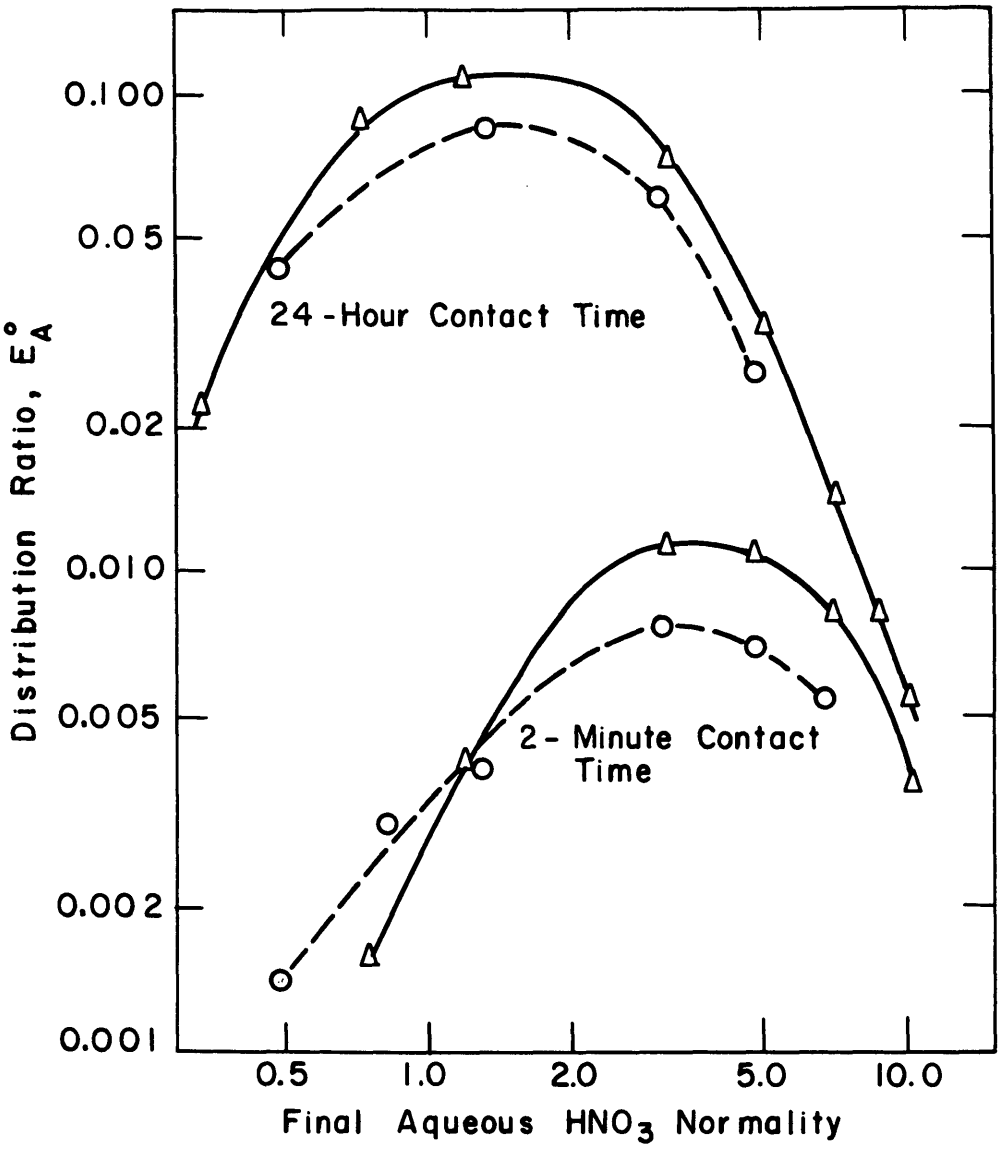

FIG. 4.5 COMPARISON OF THE EXTRACTION CHARACTERISTICS OF TWO BATCHES OF RuNO-NITRATO COMPLEXES SOLUTIONS SOLUTIONS AGED FOR ONE MONTH AT ROOM TEMPERATURE CONTACTED AT 25°C WITH 0.26 M TLA IN TOLUENE

Δ = BATCH A
O = BATCH B

variation may occur at very low acid concentration and that the Batch B values may be appreciably greater than the Batch A values. However, analytic limitations prevent a closer investigation of this point, in that the ruthenium concentration in the resultant organic phase would be too small for accurate analysis by the KOH-KNO_3 fusion method. In addition, the differences between the batches seems to disappear, or at least reduce in magnitude, at the longer contact time.

4.1.4 Effect of Nitrate Salting Concentration

Using 24 hour contacting times, extractions were made to determine the effect of sodium nitrate salting on the extractability of RuNO-nitrato complexes. The data are plotted in Figure 4.6 so as to show the effect of varying aqueous nitric acid concentration at various levels of constant total nitrate concentration. As a result of cross plotting, Figure 4.7 shows the effect of varying total nitrate concentration with constant nitric acid concentration.

In Figure 4.6 above a nitric acid concentration of about 2.5N, salting appears to cause a slight decrease in the value of E_A^o. This apparent inconsistency can possibly be explained by

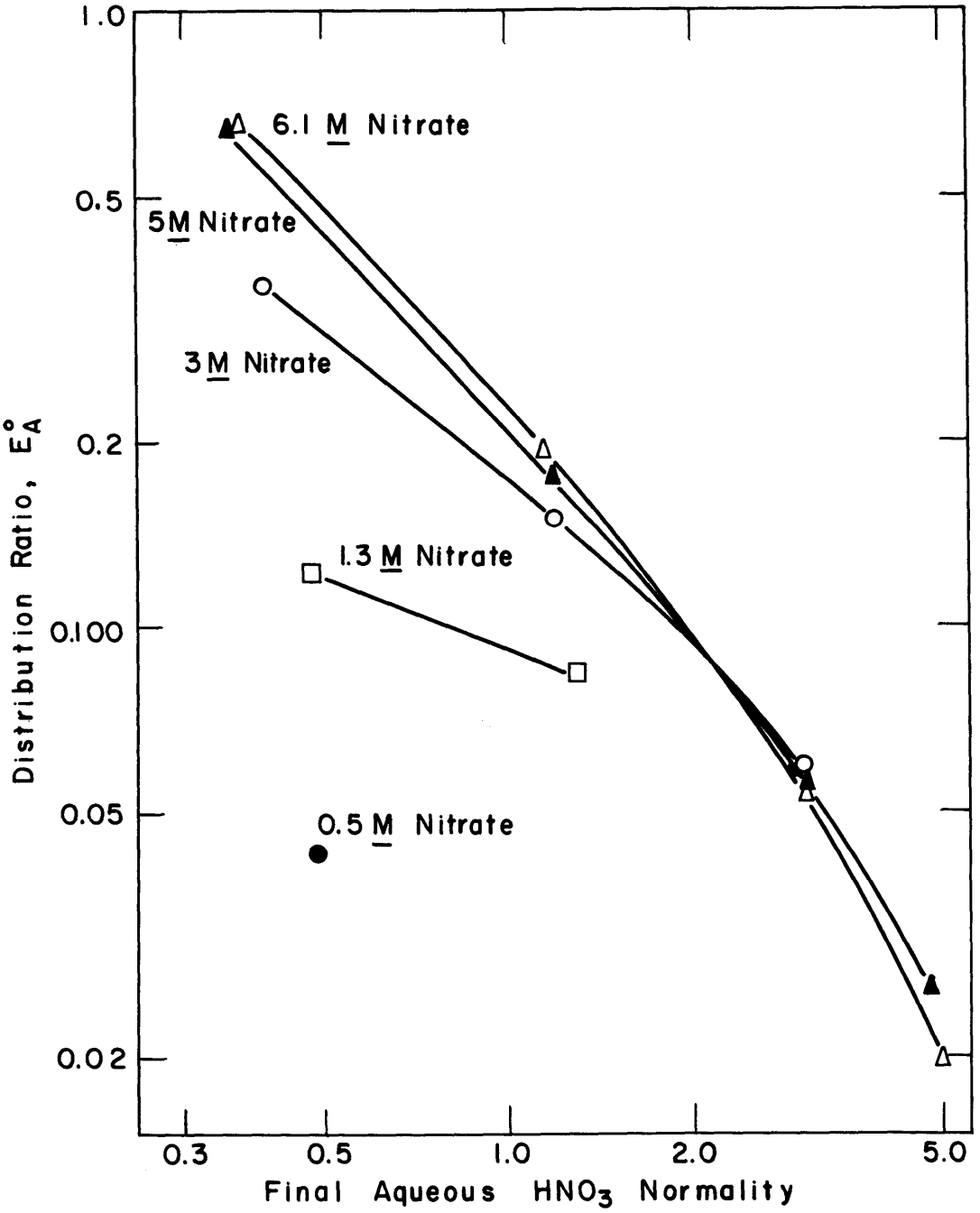

FIG. 4.6 THE EFFECT OF NITRATE SALTING ON EXTRACTION OF RuNO - NITRATO COMPLEXES
SOLUTIONS AGED FOR ONE MONTH AT ROOM TEMPERATURE (BATCH B) 24-HOUR CONTACTING AT 25 °C WITH 0.26 M TLA IN TOLUENE
SALTING AGENT = $NaNO_3$

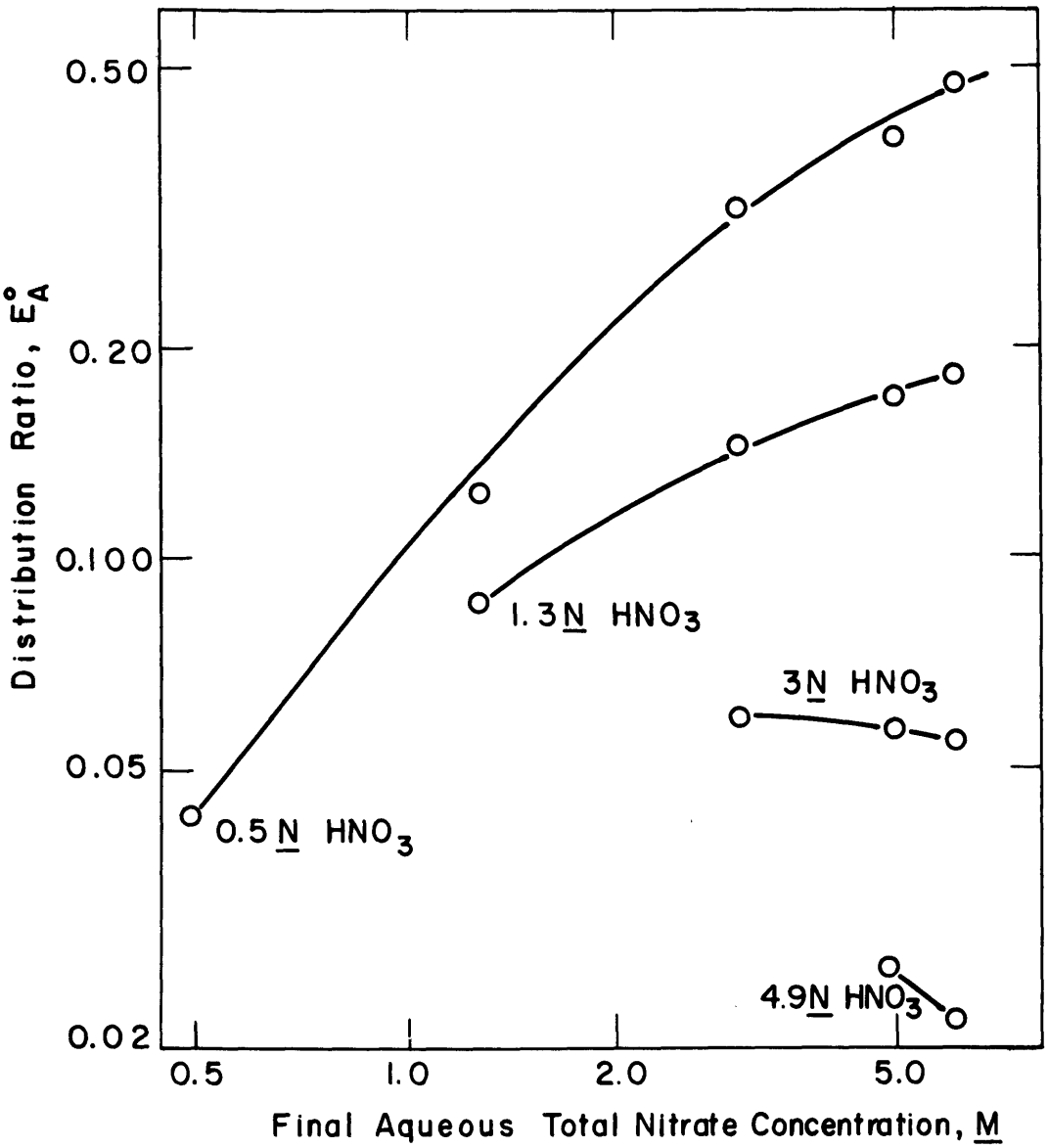

FIG. 4.7 THE EFFECT OF NITRATE SALTING ON EXTRACTION OF RuNO-NITRATO COMPLEXES
SOLUTIONS AGED FOR ONE MONTH AT ROOM TEMPERATURE (BATCH B)
24-HOUR CONTACTING AT 25°C WITH 0.26 M TLA IN TOLUENE
SALTING AGENT = $NaNO_3$

considering the effect of changes in the concentration of nitric acid in the organic phase on the distribution ratios. The addition of $NaNO_3$ to an aqueous nitric acid solution results in an increase in the concentration of nitric acid in the contacting organic phase; see the data of Figure 4.8 which were obtained by titration of various organic phase samples. Nitrate salting can be seen to cause a substantial increase in the amount of unbound nitric acid in the organic phase.

A more meaningful correlation of the ruthenium extraction data can be obtained by plotting E_A^o as a function of the final concentration of the organic phase unbound nitric acid at various levels of total aqueous nitrate concentration (see Figure 4.9). Of significant interest and importance is the fact that this method of correlation yields the more logically expected trend, i.e. as total nitrate increases at constant unbound HNO_3, E_A^o increases. The inference is that the values of the partition coefficient of the individual complexes are dependent on the concentration of the unbound HNO_3 in the organic phase rather than on the concentration of HNO_3 in the aqueous phase. Therefore, in order to more fully investigate the effect of nitrate salting at constant HNO_3 concentration, the organic phase unbound nitric acid should be held

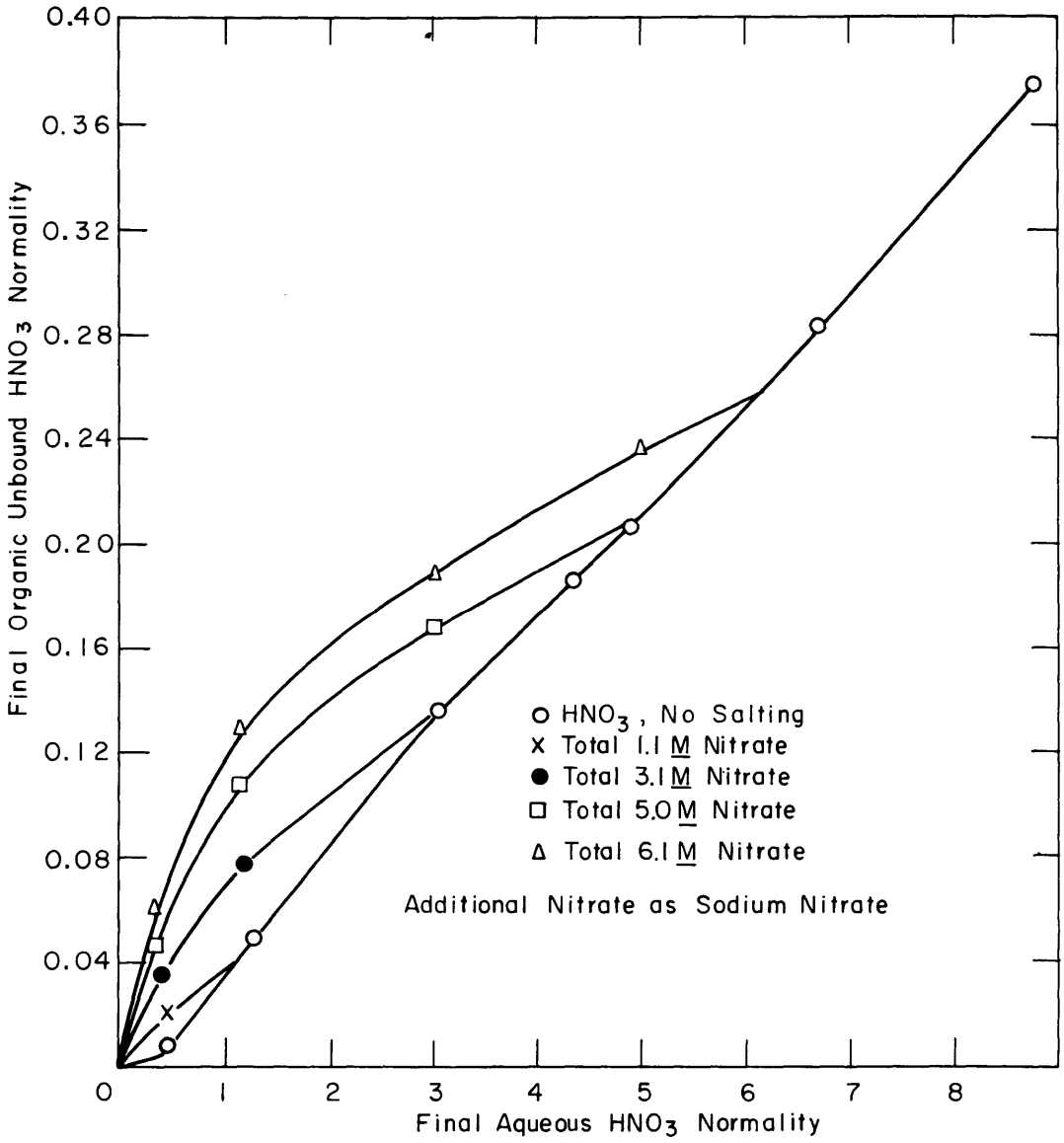

FIG. 4.8 EXTRACTION OF NITRIC ACID BY 0.26M TLA IN TOLUENE AT 25°C

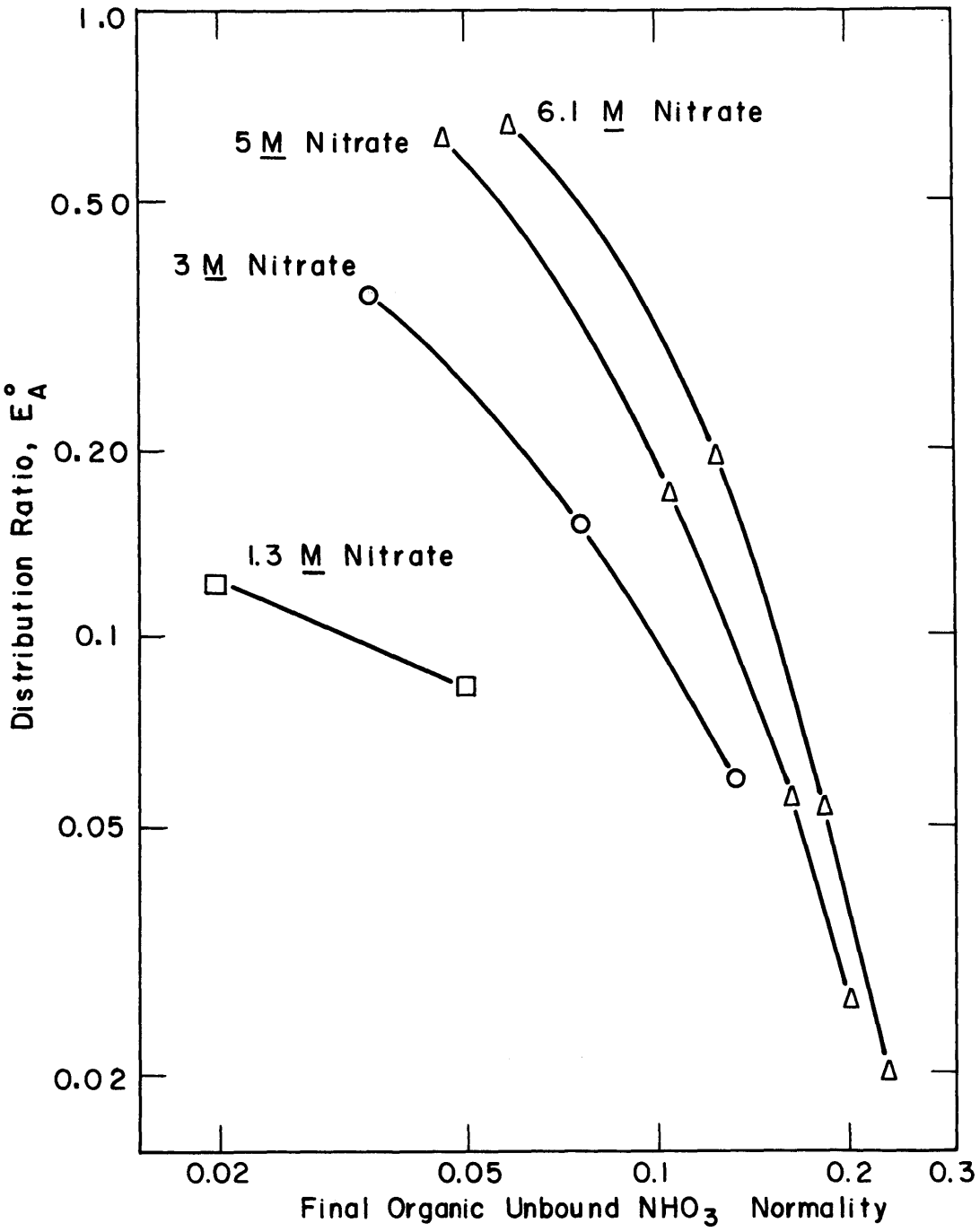

FIG. 4.9 THE EFFECT OF NITRATE SALTING ON EXTRACTION OF RuNO-NITRATO COMPLEXES
SOLUTIONS AGED FOR ONE MONTH AT ROOM TEMPERATURE (BATCH B)
24-HOUR CONTACTING AT 25°C WITH 0.26 M TLA IN TOLUENE
SALTING AGENT = $NaNO_3$

constant rather than the aqueous phase nitric acid, as was done in Figure 4.7. Figure 4.10 illustrates this point by presenting the ruthenium extraction data for both constant aqueous phase nitric acid concentrations and constant organic phase unbound nitric acid concentrations. The values plotted were obtained from Figures 4.7 and 4.9. When compared on the basis of constant concentration of unbound nitric acid in the organic phase, ruthenium extraction is seen to increase with increasing nitrate salting of the aqueous phase. The slope of the E_A^o vs total aqueous nitrate curve on log-log paper is approximately 1.3 to 1.7 for the condition of constant concentration of unbound nitric acid in the organic phase.

4.1.5 Organic Phase Titration of Extractable Ruthenium

A very interesting result of the organic phase titrations discussed in the previous section was the apparent titration of extractable ruthenium in the organic phase. This was observed for samples having a relatively large concentration of ruthenium (approximately 2.5 gm/liter).

The phenomenon was first noticed when the organic phase of sample number 128 was titrated and gave a value of 0.103M for the difference between

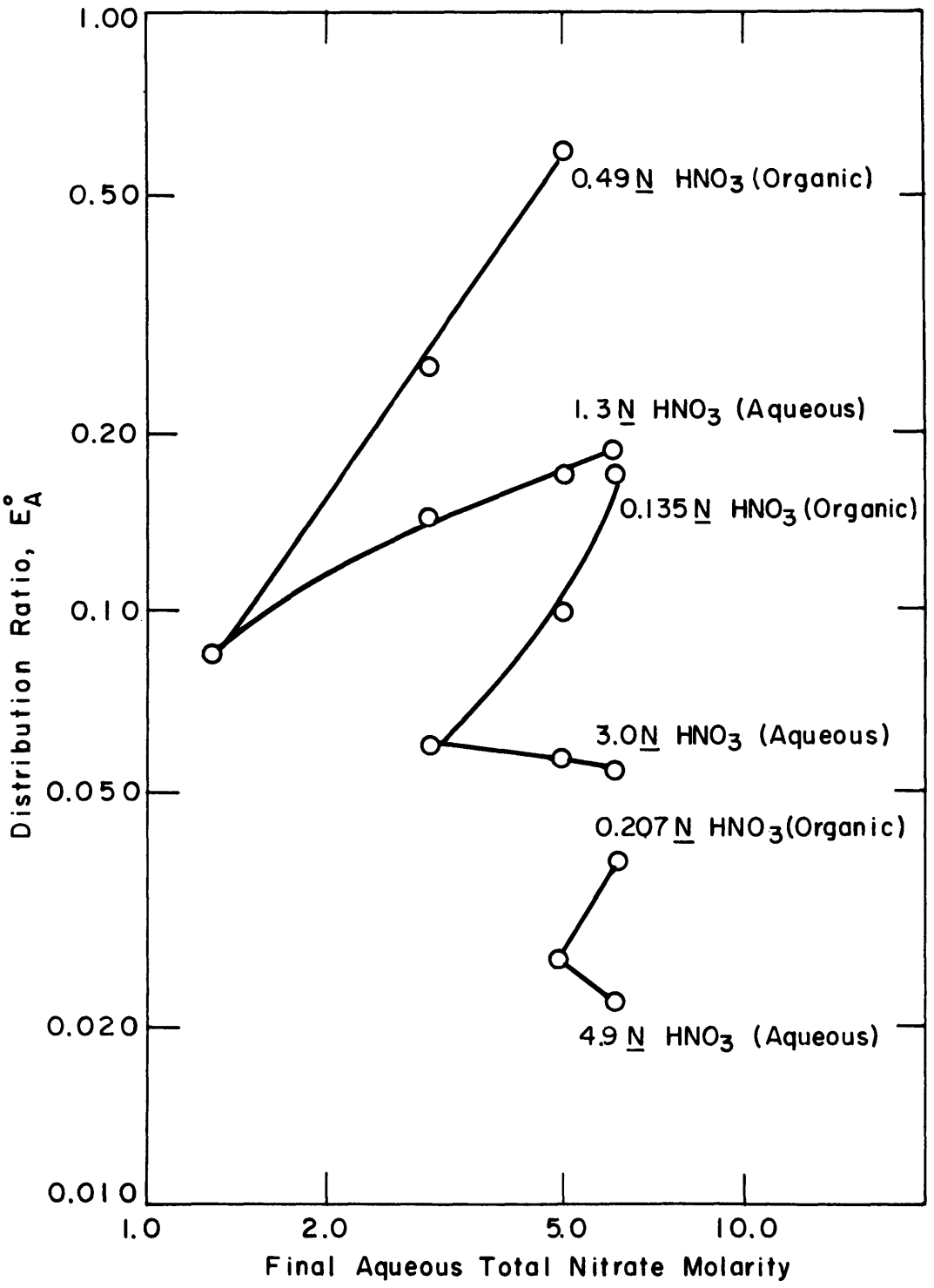

FIG. 4.10 THE EFFECT OF SODIUM NITRATE SALTING ON EXTRACTION OF RuNO-NITRATO COMPLEXES (BATCH B) AGED FOR ONE MONTH 24-HOUR CONTACTING AT 25°C WITH 0.26M TLA IN TOLUENE

total acid and amine nitrate concentration. This difference is normally taken to represent the unbound nitric acid concentration. Sample 128 had a final aqueous nitric acid concentration of 0.38N and a final aqueous nitrate concentration of 6.1M. From Figure 4.8 the expected unbound HNO_3 concentration would be about 0.055M, a factor of about two less than the 0.103M value. Closer inspection of the titration curve (Figure 4.11) revealed that a total of four inflection points rather than the customary two points of inflection were possibly present.

In order to investigate this phenomenon, the sodium hydroxide was diluted by a factor of five (from 0.0875N to 0.0175N) and the sample titrated again. Figure 4.12, which shows the result of the re-titration, covers the range corresponding to 0-1.3 ml on Figure 4.11. As can be seen from Figure 4.12, the first portion of the curve yields at least two inflection points and possibly more. The first corresponds to a concentration of 0.059M, as would be expected if this were the unbound nitric acid inflection point. The difference between the first and second inflection points corresponds to a concentration of 0.038M. By previous quantitative analysis, the ruthenium concentration was found to be 2.38 gm/liter, 0.024M.

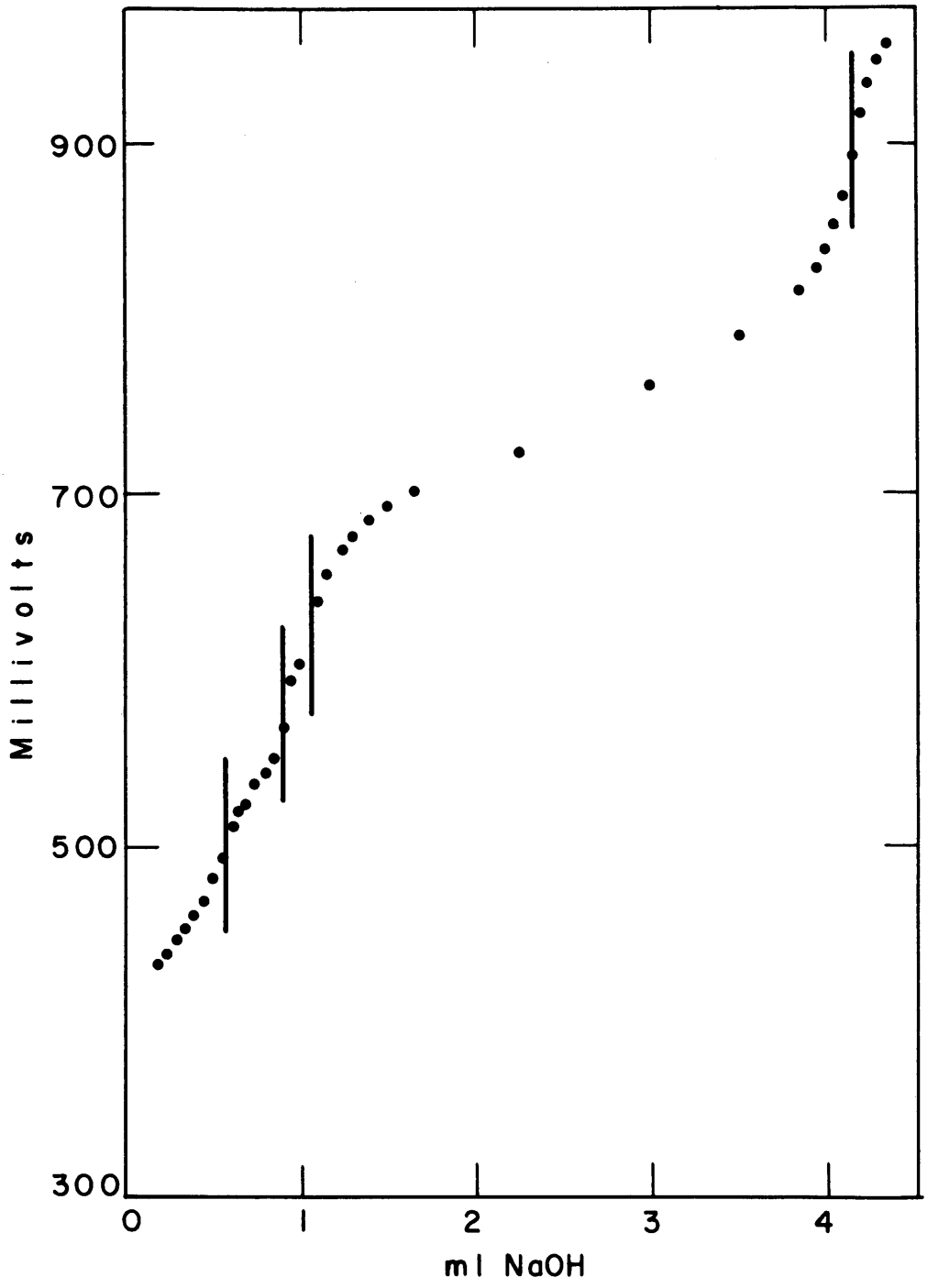

FIG. 4.11 ORGANIC PHASE TITRATION OF SAMPLE 128
1 ml OF SAMPLE VS 0.0875 N NaOH

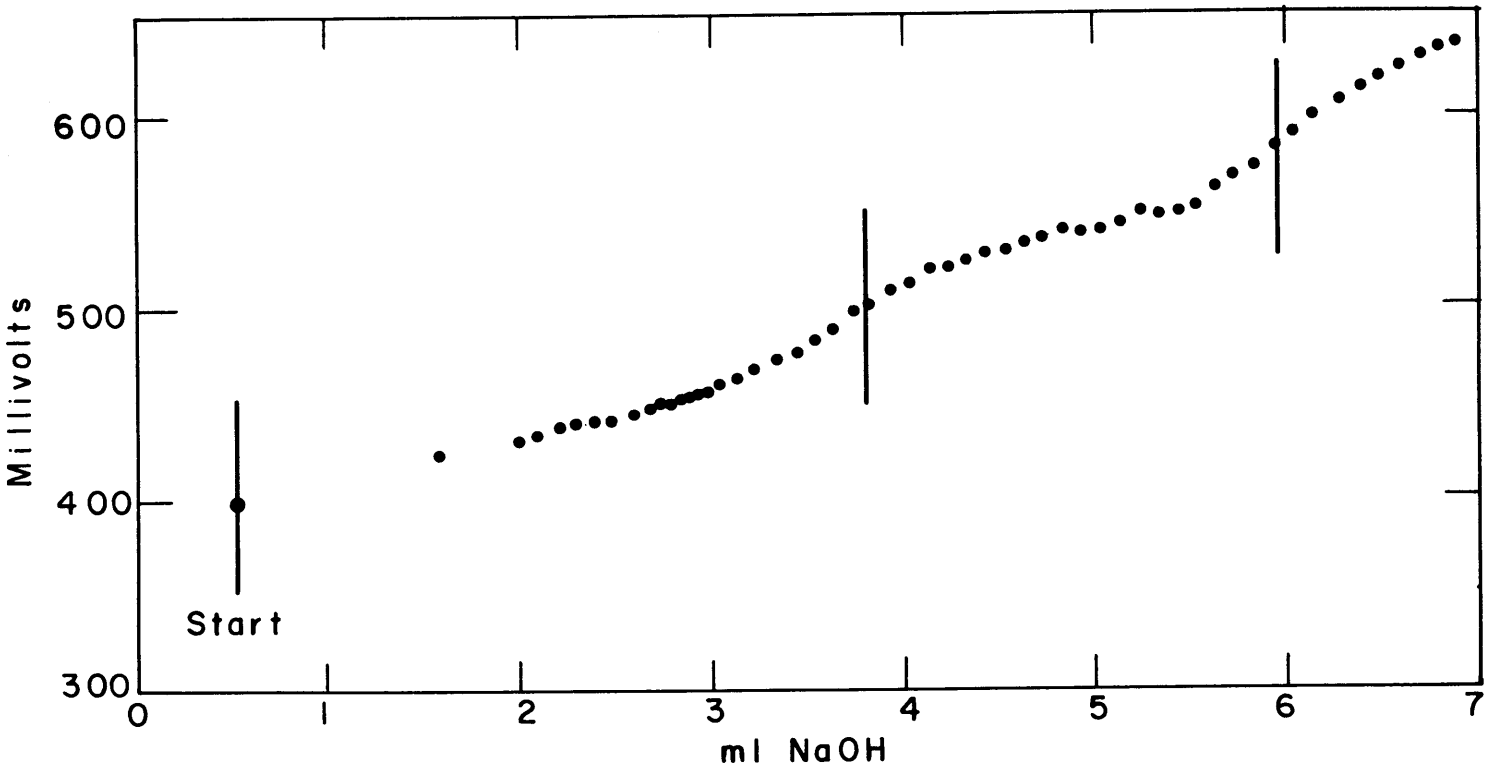

FIG. 4.12 ORGANIC PHASE TITRATION OF SAMPLE 128 1ml OF SAMPLE VS 0.0175 N NaOH

If it assumed that the ruthenium in the organic phase is mostly in the form of the acids of the tetra- and penta-nitrato complexes of nitrosyl ruthenium (i.e., $HRuNO(NO_3)_4(H_2O)$ and $H_2RuNO(NO_3)_5$) which are neutralized between the two and points marked on Figure 4.12 and if the mole fraction of the penta-complex is represented by x, then

$$2\ x\ (0.024) + (1-x)\ 0.024 = 0.38$$

and x then is equal to 0.58. The resultant concentration of the complexes are 0.10M and 0.014M for the tetra- and penta-, respectively. Even closer inspection of Figure 4.12 shows an irregularity in the titration curve at about 5.25 ml. If it is assumed that the entire penta-complex would be titrated before the tetra-complex, then for a concentration of 0.014M, its neutralization would be calculated to occur at 5.40 ml (which is very close to the inflection found at 5.25 ml).

Other samples with large ruthenium concentrations in the organic phase were also titrated. At concentrations of less than approximately 1 gm/liter, the results of the titrations are inconclusive. However, sample number 127, with an organic phase Ru concentration

of 2.51 gm/liter (0.025M), gave very similar results to those of sample 128. The aqueous phase of sample 127 was 0.35N HNO_3 and a total nitrate of 5.26M. From Figure 4.8, the unbound nitric acid concentration in the organic phase would be about 0.044M. Titration of the organic phase (Figure 4.13) yielded end points at 2.55 ml and 4.60 ml. The first end point gives a concentration of 0.045M and the difference between the end points corresponds to a concentration of 0.036M. Again, assuming the Ru to be mostly in the form of the acids of the tetra- and penta-complexes, the mole fraction of the penta complex is calculated to be 0.44 and the concentrations of the complexes are calculated to be 0.014M and 0.011M for the tetra- and penta-complexes, respectively.

Although the titrations of samples 127 and 128 and their resultant interpretations do not present conclusive evidence for the more extractable forms of the RuNO-nitrato complexes, the indications are that the tetra- and penta-nitrato complexes of the nitrosyl ruthenium nitrato system are more highly extractable than the lower complexes. This subject will be discussed in more detail in Section 4.3.

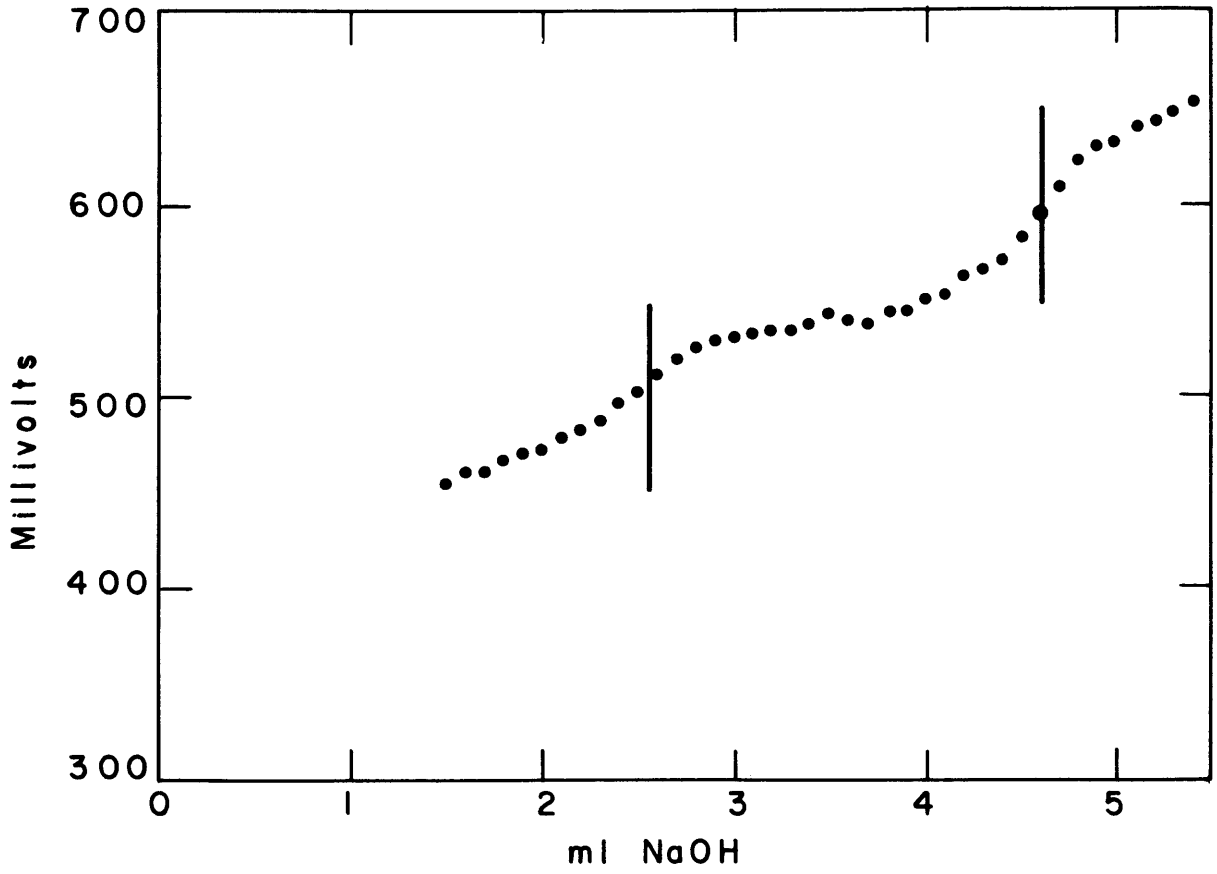

FIG. 4.13 ORGANIC PHASE TITRATION OF SAMPLE 127 1ml OF SAMPLE VS 0.0175 N NaOH

4.1.6 Effect of Ruthenium Concentration

In order to determine the effect of ruthenium concentration on the extraction of the RuNO-nitrato complexes, the initial aqueous ruthenium concentration of the 1.2N HNO_3 stock solution (Batch A) was varied in steps by dilution with appropriate amounts of 1.2N nitric acid and then extractions performed.

The results are shown in Figure 4.14 and are reported as final organic ruthenium concentration versus final aqueous ruthenium concentration. The slope is seen to be essentially 1.0, indicating no effect of ruthenium concentration on the extraction process, at least in this range of concentrations. The final aqueous ruthenium concentrations varied from about 0.3 gm/l to about 8 gm/l.

4.1.7 Effect of Amine Concentration

A variation of TLA concentration was made to determine the effect of amine concentration on ruthenium extraction. The amine concentration was varied from 0.053M to 0.26M. The extractions were made for 24-hour contacting time at 25°C. The aqueous phase contained aged RuNO-nitrato complexes in 1.3N HNO_3 solution with no salting (Batch B). The data is presented in Figure 4.15. The value of E_A^o is seen to be initially dependent upon the 1.5 power of the

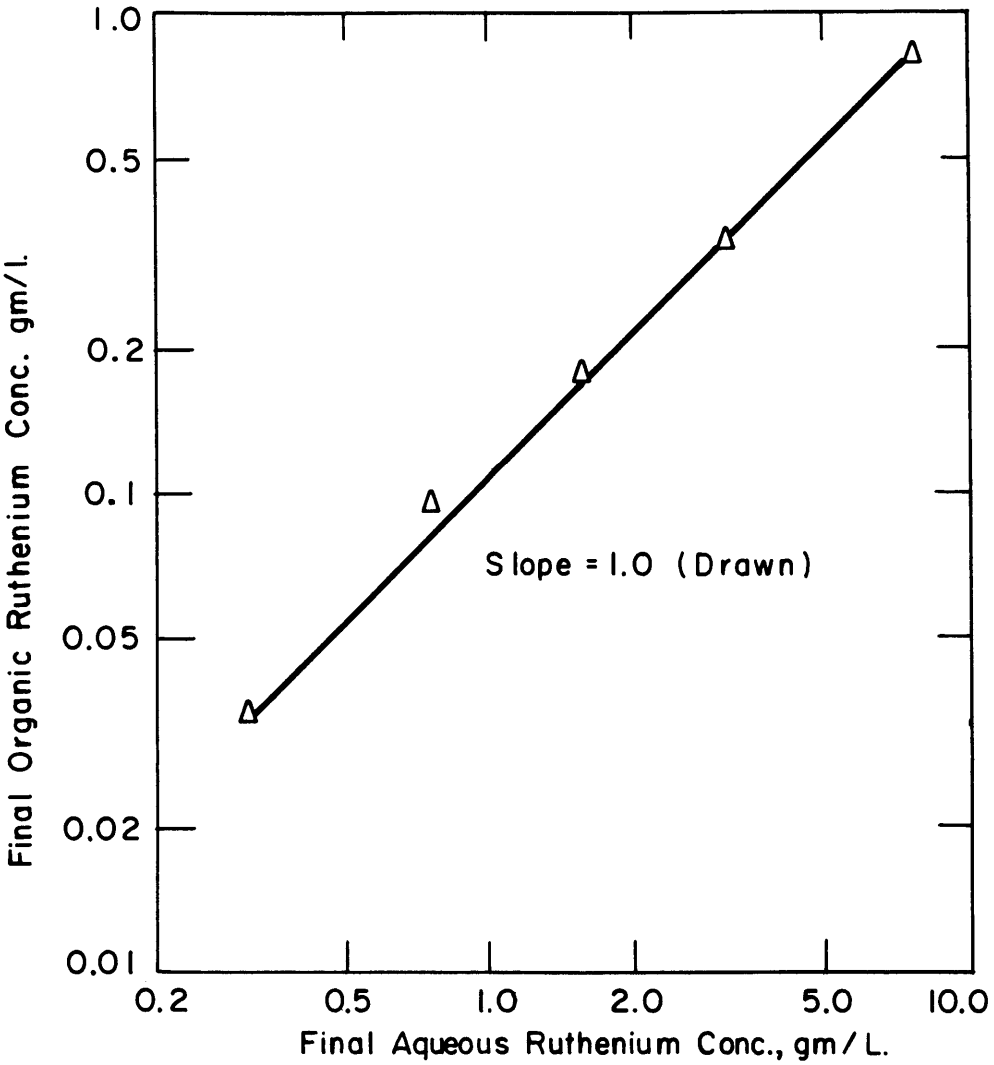

FIG. 4.14 THE EFFECT OF RUTHENIUM CONCENTRATION ON THE EXTRACTION OF AGED RuNO - NITRATO COMPLEXES (BATCH A) 24 -HOUR CONTACTING AT 25 °C. WITH 0.26 M TLA IN TOLUENE 1.2 N HNO_3 IN AQUEOUS PHASE

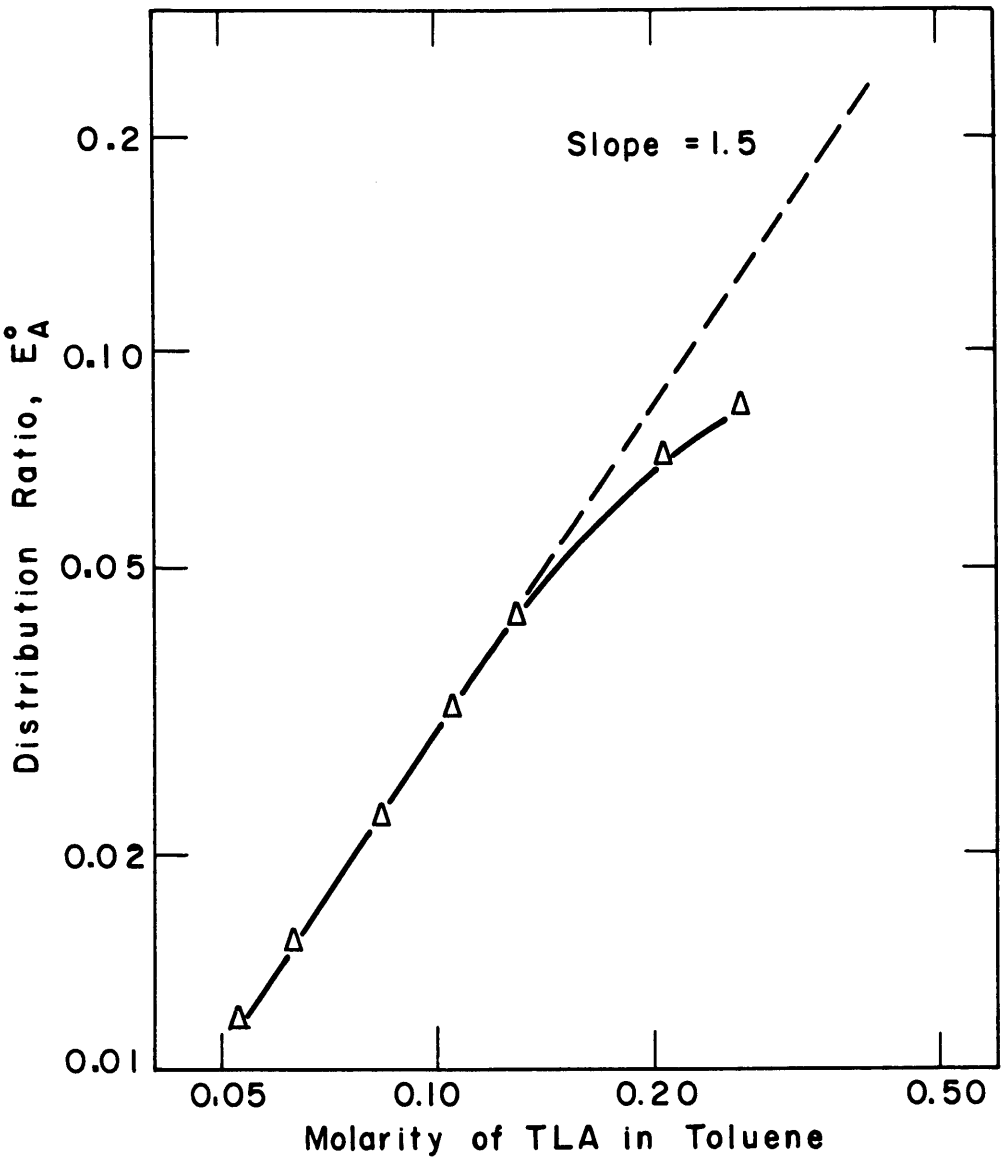

FIG. 4.15 THE EFFECT OF AMINE CONCENTRATION ON EXTRACTION OF RuNO-NITRATO COMPLEXES SOLUTION AGED FOR ONE MONTH AT ROOM TEMPERATURE (BATCH B)
24-HOUR CONTACTING AT 25°C WITH 1.3 N HNO_3 AQUEOUS SOLUTION OF RuNO-NITRATO COMPLEXES; INITIAL AQUEOUS Ru = 6.45 gm/liter

amine concentration. Above an amine concentration of approximately 0.13M, the values of E_A^o fall below the line of slope 1.5. The slope of 1.5 agrees with that observed by Wilson (18).

4.2 Rapid Dilution Experiments

4.2.1 Experimental Method

An experimental technique that proved to be of great use was the rapid dilution method. In this method, an aged, non-salted, nitric acid stock solution of the RuNO-nitrato complexes of relatively high acid concentration was diluted rapidly to a lower acid concentration, immediately contacted with TLA for a short period of time (usually 30 seconds), and then the phases quickly separated. The advantage of this type of experiment is that it was possible to accomplish the dilution with several different initial (before dilution) acid concentrations and with a single final (after dilution) acid concentration and thereby obtain a semi-quantitative idea of the effect of the initial acid concentration upon the relative amount of extractable species at equilibrium in the aqueous solutions. The method can be more clearly explained by the use of an example. The following is a summary of sample 165:

The desired final aqueous nitric acid concentration was 1.0N. The initial acid concentration was 4.9N HNO_3. (Only non-salted solutions were used in these experiments). The desired total volume of each phase (the phase volume ratio is also a possible variable) was approximately 20 ml. The dilutions and contactings (for the phase volume ratio of one) were done in 50 ml centrifuge tubes and therefore the total volume was necessarily less than this value. It was also desirable that the stock solution volume be a whole number of milliliters to facilitate easy and rapid addition of the stock solution to the centrifuge tube. If a stock solution volume of 4 ml is used, then 15.6 ml of DDW must be mixed with it to reduce the HNO_3 concentration from the initial 4.9N to the final 1.0N. The total volume of each phase must then be 4+ 15.6= 19.6 ml. Therefore, 15.6 ml of DDW and 19.6 ml of 0.26M TLA in toluene were pipetted into the centrifuge tube in that order, care being taken not to pre-mix the phases. The TLA phase had been precontacted with an equal volume of 1.3N HNO_3 to form the amine nitrate and extract the unbound nitric acid. In all of the experiments, precontacting of the organic phase was accomplished by equal volumes of aqueous phase whose acid concentration was

approximately 0.3-0.4N greater than the desired final aqueous phase acid concentration. This allowed for extraction of HNO_3 by TLA to form the TLA·HNO_3 and also a slight amount of unbound acid extraction and still leave the final aqueous acid concentration very close to the desired value.

The stock solution was then taken up in a 4 ml pipette and the pipette placed in position for delivery to the centrifuge tube. The stock solution was run into the centrifuge tube down the wall of the tube and not directly through the organic phase so as to reduce the precontact time to a minimum. At the same time that the stock solution started down the wall of the centrifuge tube, an electric timer was started. As soon as the stock solution had all been added, the tube was capped, handshaken for 30 seconds, and then placed in a centrifuge for rapid phase separation. The length of time elapsed between the start of addition of stock solution and the start of shaking is defined as the "delay time" and for all samples was on the order of 20-30 seconds, unless otherwise specified.

The main purpose of these experiments was to attempt to derive a quantitative idea of the amount of extractable species in solution and the extractability

of the species. As has been shown previously, the reaction rates and redistribution rates of the complexes are neither fast nor slow, but somewhat intermediate. In particular reference to the previous example, it was thought that although the stock solution was diluted from 4.9N HNO_3 to 1.0N HNO_3, the mole fractions of the extractable species existing during extraction in the 1.0N HNO_3 were those that existed previously in the 4.9N HNO_3, since the redistribution rates were relatively slow considering the delay time of only 20 or 30 seconds. Under that assumption, it can be seen to be possible to obtain an idea of the effect of initial acid concentration on the mole fractions of the extractable species by performing a series of these experiments with different initial acid concentrations diluted to one, similar final acid concentration. Since the partition coefficients are believed to depend on the final conditions, it is also possible to obtain an idea of their dependence on acid concentration by diluting one, similar initial acid concentration to a series of different final acid concentrations.

4.2.2 Effect of Initial Acid Concentration

In Figure 4.16 are plotted values of the distribution ratio for various initial and final acid concentrations. The initial acid concentrations are those for aged stock solutions of Batch B and Batch C. The three points shown for Batch C show the similarity between the two batches.

As can be seen, in all three cases of final acid concentration (1.0, 3.0, and 4.9N HNO_3) the distribution ratio increases with increasing initial acid concentration. It can be concluded that the mole fraction of at least one of the more extractable species increases with increasing acid concentration of the aged stock solutions. This is in qualitative agreement with Fletcher et al (6).

4.2.3 Effect of Final Acid Concentration

From Figure 4.16, it can also be seen that at each initial acid concentration (4.9, 6.8, 8.7, 9.7, and 10.1N HNO_3) the value of the distribution ratio decreases with increasing final acid concentration. It can therefore be concluded that the partition coefficients decrease with increasing final acid concentration.

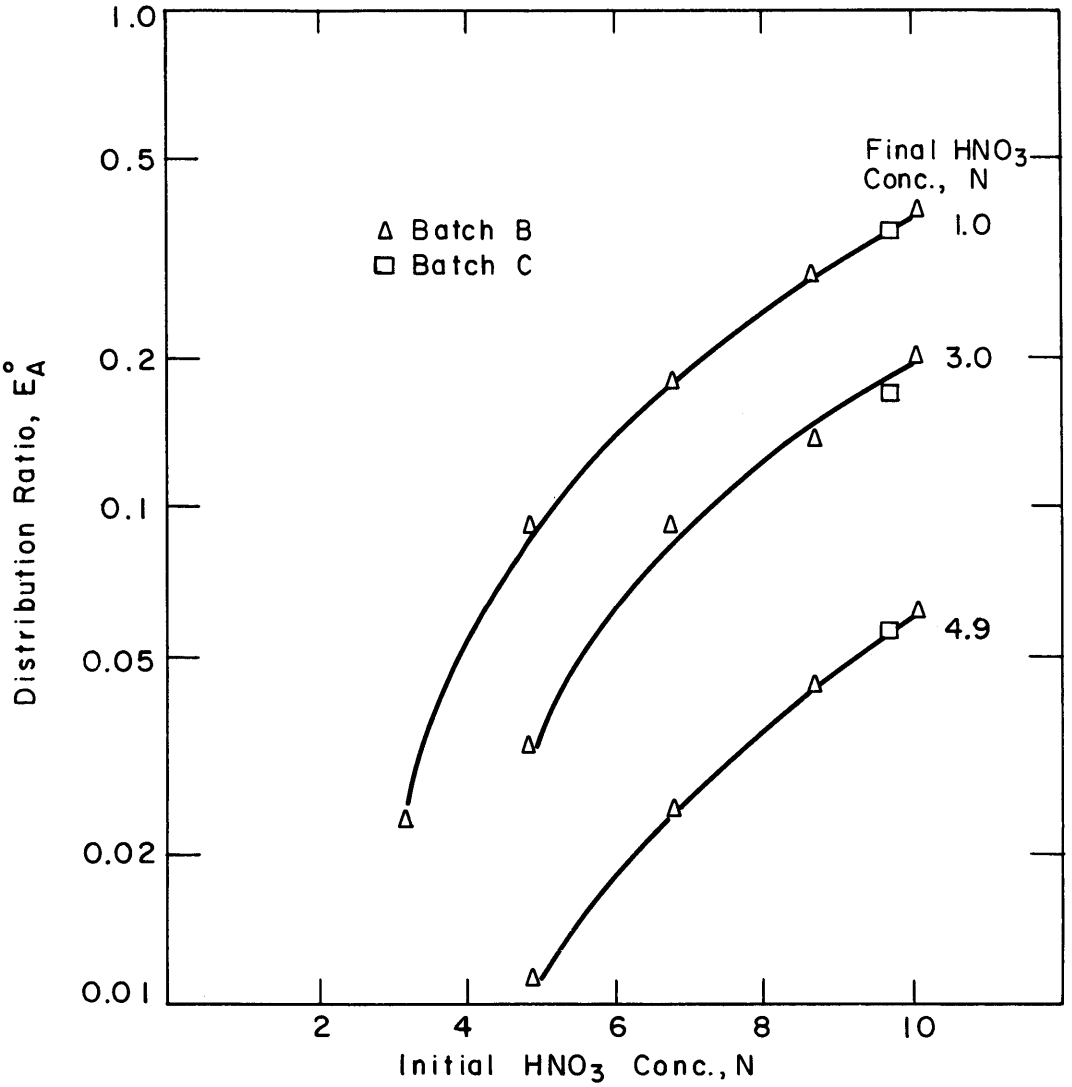

FIG. 4.16 AGED NITRIC ACID SOLUTIONS OF RuNO-NITRATO COMPLEXES DILUTED RAPIDLY AND CONTACTED FOR 30 SECONDS AT ROOM TEMPERATURE WITH 0.26 M TLA IN TOLUENE

4.2.4 Effect of Phase Volume Ratio

If there are more than one species in solution and if at least two of them have different partition coefficients, it is possible to observe values of the distribution ratio that are functions of the phase volume ratio. Equation (4-1) expresses the value of the distribution ratio (E_A^o) for the rapid dilution experiments as a function of the partition coefficients (P_x), the aqueous phase mole fractions before contacting (M_x), and the phase volume ratio (T, $=\frac{\text{aqueous}}{\text{organic}}$). (See Appendix for derivation).

$$E_A^o = T \left[\frac{\sum_x \left(\frac{M_x P_x}{T+P_x} \right)}{1 - \sum_x \left(\frac{M_x P_x}{T+P_x} \right)} \right] \qquad (4\text{-}1)$$

In the simplest case, where only one species is the solution, $M_1 = 1.0$ and all other M's are identically zero. Then:

$$E_A^o = T \left[\frac{\left(\frac{P_1}{T+P_1} \right)}{1 - \left(\frac{P_1}{T+P_1} \right)} \right] = T \left[\frac{\left(\frac{P_1}{T+P_1} \right)}{\left(\frac{T+P_1-P}{T+P_1} \right)} \right] = P_1$$

which is consistent with the discussion in Section 4.1.2.

As a means of determining the minimum value of the partition coefficient of the most extractable species, a series of rapid dilution experiments was performed for varying phase volume ratios. The results are shown in Figure 4.17 and 4.18. The largest value of E_A^o observed is seen in Figure 4.17 and is for an initial acid concentration of 8.7N HNO_3, a final acid concentration of 1.0N HNO_3, and a phase volume ratio of 79. The value observed is 5.2, and therefore it must be that the partition coefficient, at this final acid concentration, of the most extractable species is at least equal to, or greater than, 5.2. Since the rate of increase of E_A^o with increasing values of T is rather large and shows no indication of approaching an asymptotic value at the value of T investigated, it can be concluded that at least one extractable species has a large partition coefficient. As mentioned in Section 4.1.2, the value of E_A^o is a measure of the product of the partition coefficient times the mole fractions. Since one of the extractable species has a large partition coefficient ($P \geq 5.2$) at 1.0N· HNO_3, and the value of E_A^o at 1.0N·HNO_3 is relatively small (E_A^o about 0.1), then the value of the mole fraction of

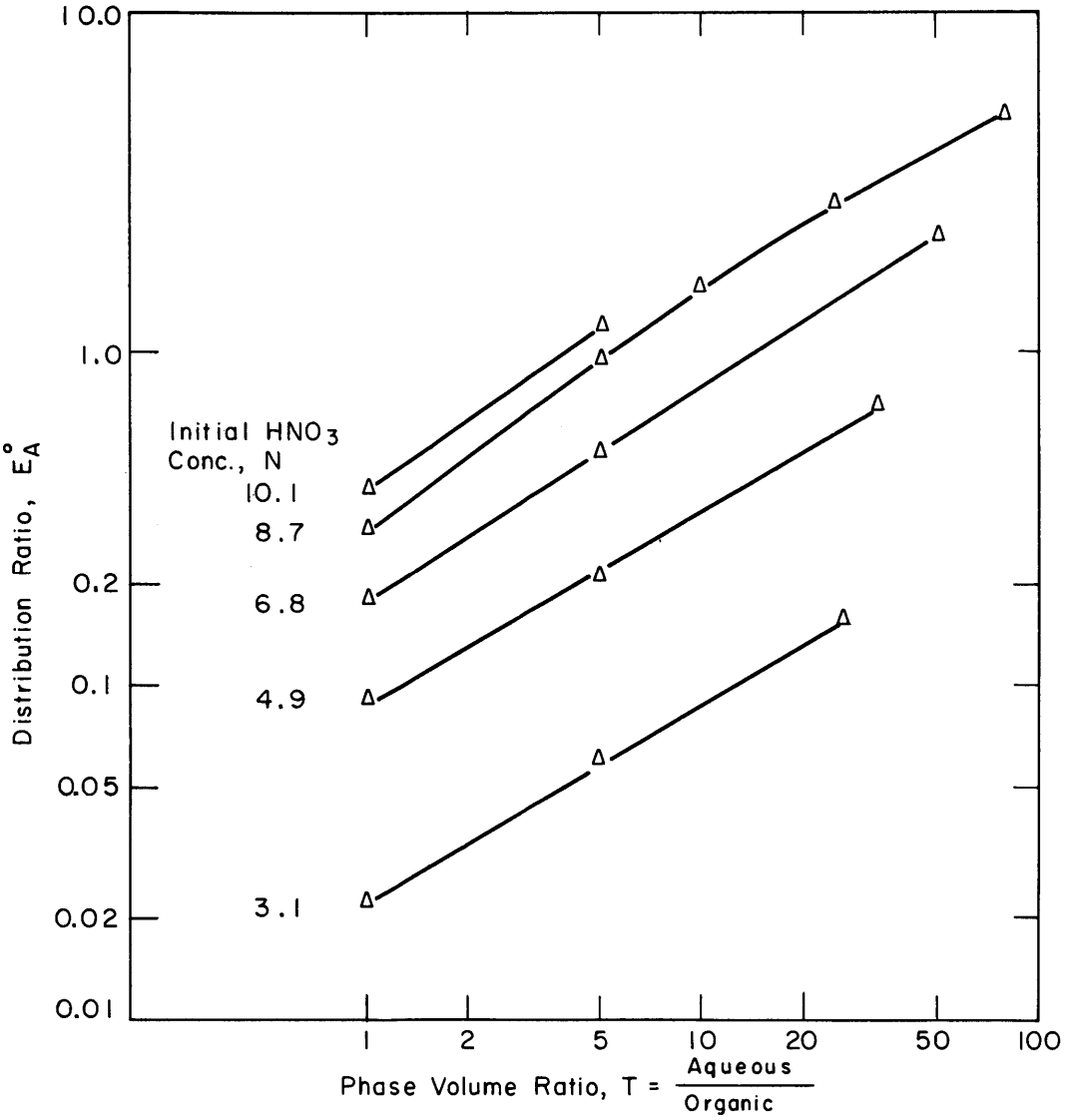

FIG. 4.17 AGED NITRIC ACID SOLUTIONS OF RuNO-NITRATO COMPLEXES (BATCH B) DILUTED RAPIDLY TO 1.0 N HNO_3 AND CONTACTED FOR 30 SECONDS AT ROOM TEMPERATURE WITH 0.26 M TLA IN TOLUENE

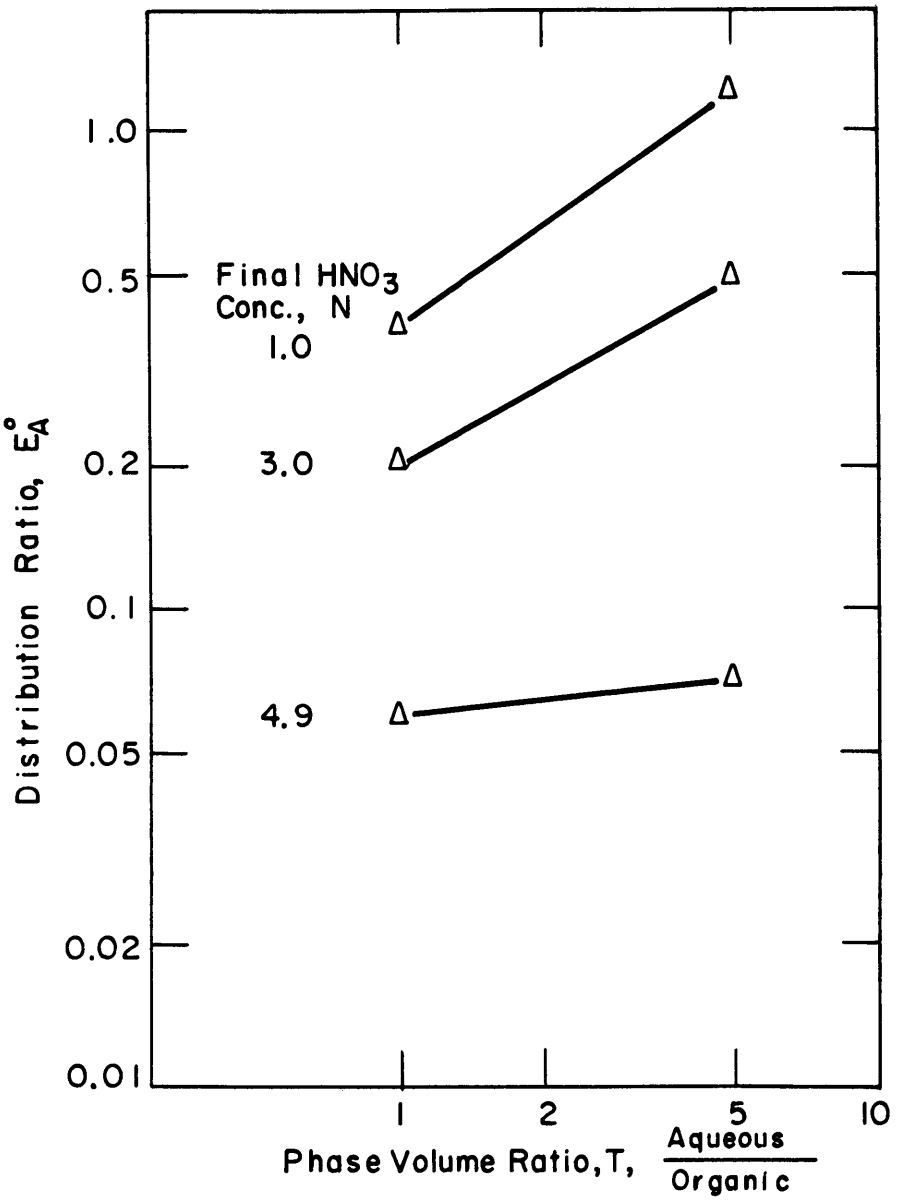

FIG. 4.18 AGED 10.1 N HNO_3 SOLUTION OF RuNO-NITRATO COMPLEXES (BATCH B) DILUTED RAPIDLY AND CONTACTED FOR 30 SECONDS AT ROOM TEMPERATURE WITH 0.26 M TLA IN TOLUENE

that species must be very small, or on the order of 0.1 divided by 5.2, approximately 0.02. The value of 0.02 is an upper limit on the value of the mole fraction, since the value of 5.2 is a lower limit on the partition coefficient.

As seen from Figure 4.18, the rate of increase of E_A^o with phase volume ratio is decreased as final acid concentration is increased. This is to be expected, since it has already been shown that the partition coefficients decrease as final acid concentration is increased.

4.2.5 Effect of Delay Time

It was first assumed that the delay time of 20-30 seconds does not allow sufficient time for any appreciable redistribution of the complexes. In order to either justify or modify this assumption, a series of experiments was conducted using the delay time as a variable.

The experimental procedure was identical to that of the previous dilution experiments except that the period of time between the end of addition of stock solution and start of shaking was varied in a controlled manner. Similar to the other experiments, the electric timer was started as soon as the stock solution from the pipette began running down the

wall of the centrifuge tube. After the stock solution had all been added, a period of waiting a measured length of time was instituted before proceeding with the rest of the experiment. In this manner, a series of distribution ratios could be observed for varying delay times. The results are shown in Figure 4.19 and 4.20.

In Figure 4.19, an initial stock solution of 9.7N HNO_3 (Batch C) was diluted to final acid concentrations of 1.0, 3.0, and 4.9N HNO_3 and the distribution ratios measured as a function of delay time. In each case, extrapolation back to zero delay time results in an increase in the value of E_A^o by about 10% over the 30-second value.

In Figure 4.20, two different initial acid concentrations are diluted to the same final acid concentration and E_A^o observed as a function of delay time. Once again, extrapolation back to zero delay time yields a 10% increase of E_A^o over the 30-second value.

Since all of the rapid dilution experiments (except those of the delay time study) were for delay times of 20-30 seconds, the values obtained by increasing the observed values by 10% would more nearly represent the zero delay time values and more

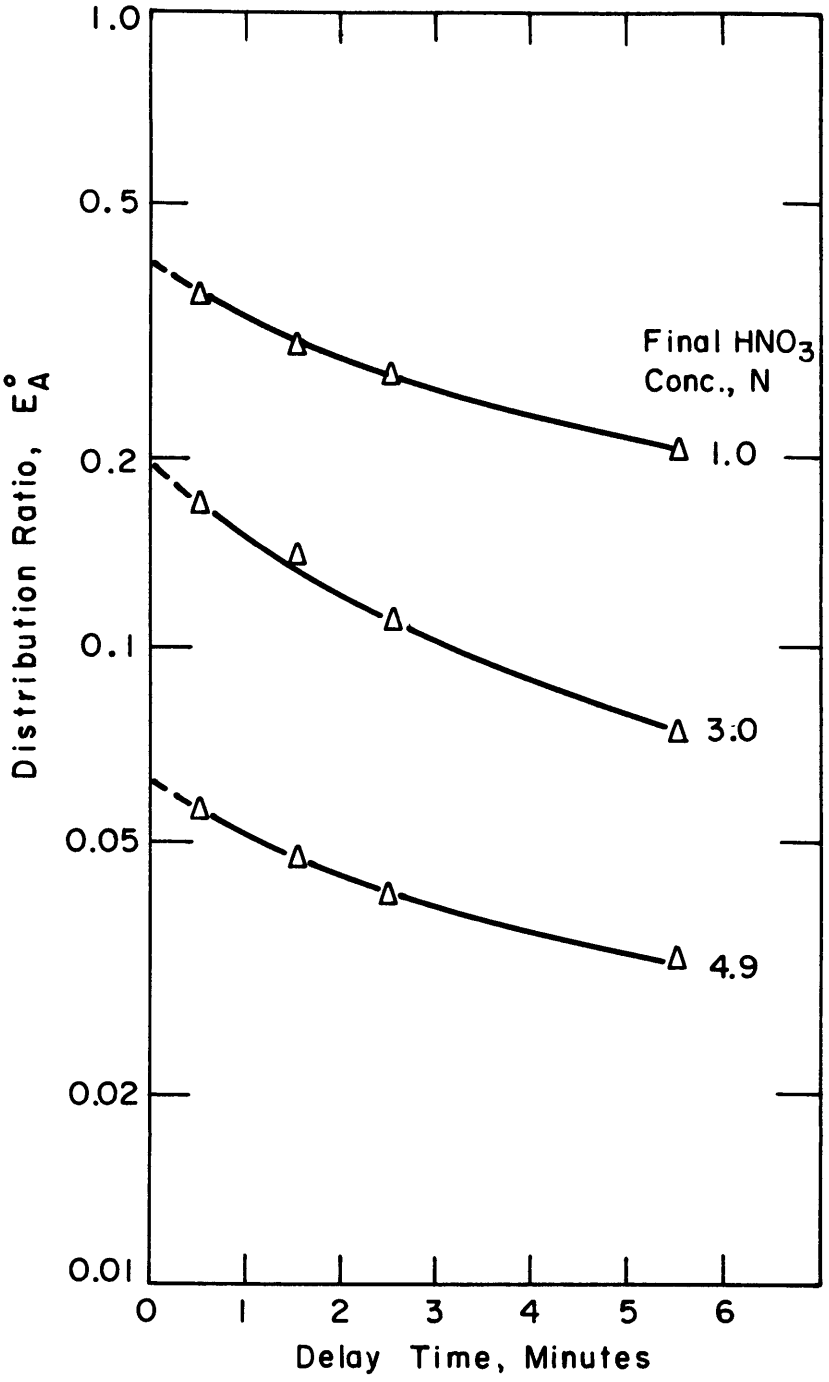

FIG. 4.19 AGED 9.7 N HNO_3 SOLUTION OF RuNO-NITRATO COMPLEXES (BATCH C) DILUTED RAPIDLY AND CONTACTED FOR 30 SECONDS WITH 0.26 M TLA IN TOLUENE AT ROOM TEMPERATURE

DELAY TIME = TIME ELAPSED BETWEEN START OF ADDITION OF STOCK SOLUTION AND START OF SHAKING

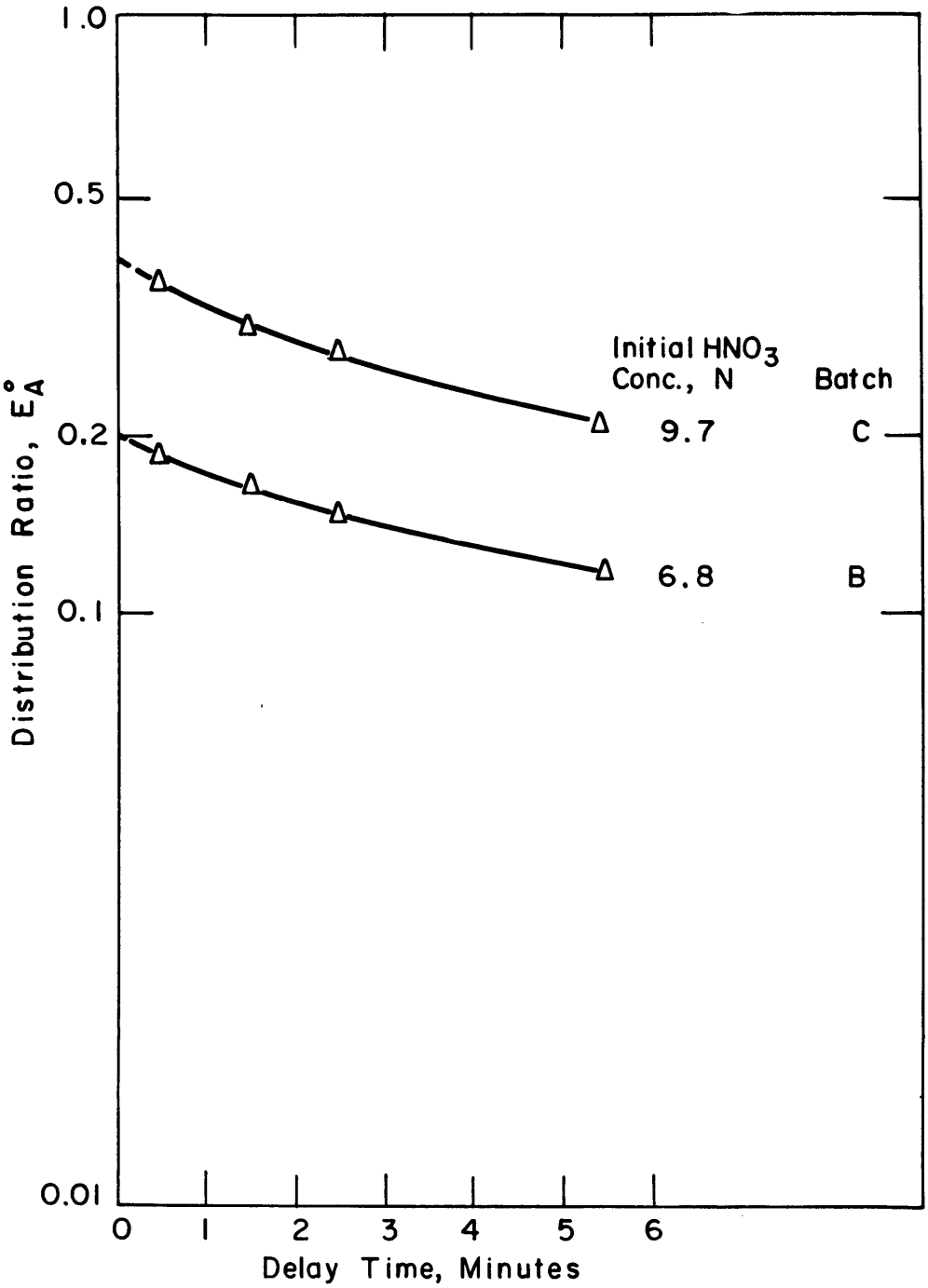

FIG. 4.20 AGED NITRIC ACID SOLUTIONS OF RuNO-NITRATO COMPLEXES DILUTED RAPIDLY TO 1.0N HNO_3 AND CONTACTED FOR 30 SECONDS AT ROOM TEMPERATURE WITH 0.26M TLA IN TOLUENE

DELAY TIME = TIME ELAPSED BETWEEN START OF ADDITION OF STOCK SOLUTION AND START OF SHAKING

nearly approximate the desired condition of non-redistribution of the complexes.

4.3 Correlation of Experimental Results

4.3.1 General Discussion

The rapid dilution experiments have given some qualitative and semi-quantitative results that afford an insight into the nitrosyl ruthenium nitrato complexes-TLA in toluene system. It has been rather firmly established that:

(1) The more extractable species increase in relative proportion to the less extractable species as the nitric acid concentration of the aged stock solutions is increased.

(2) The partition coefficients of the species decrease as the final acid concentration after extraction is increased.

(3) The minimum value of the partition coefficient of the most extractable species is 5.2 (For a final acid concentration of 1.0N HNO_3 and a TLA in toluene concentration of 0.26M All of the rapid dilution experiments, and therefore all of the correlations, consider the same TLA in toluene concentration of 0.26M).

(4) The maximum value of the mole fraction of the most extractable species at a stock solution

acid concentration of 1.0N HNO_3 is 0.02 for aged solutions.

The above results lead into a set of questions to which further correlation of the experimental results have supplied some answers. The questions are:

(1) How many of the "more extractable species" are there?

(2) What are the species?

(3) What are the respective quantitative values of the equilibrium mole fractions of each species as a function of the nitric acid concentration of the stock solutions?

(4) What are the respective quantitative values of the partition coefficients of each species as a function of the final nitric acid concentration after extraction?

(5) What are the respective rates of redistribution, or diappearance, of each species upon dilution?

The answers to these questions cannot be obtained clearly by considering each in turn by itself. There is a considerable amount of interplay, assumption, and feedback necessary in their determination.

4.3.2 Number and Forms Extractable Species

There has already been an indication as to the number and form of the more extractable species in the work involving the possible organic phase titration of extractable ruthenium (Section 4.1.5). Preliminary results of that work showed that assumption of a mixture of the acids of the tetra-nitrato and penta-nitrato complexes could account for the observations of the titration experiments. The results of the correlation of the rapid dilution experiments(to be discussed in the next section) and further organic phase titration have added considerable weight to that interpretation.

4.3.3 Mole Fractions and Partition Coefficients

Equation (4-1) expressed the distribution ratio for the rapid dilution extractions as a function of the phase volume ratio (T), the equilibrium mole fraction in the aqueous phase at the time of extraction (M_x), and the partition coefficient (P_x). The total number of variables is seen to be equal to one plus twice the number of species. Therefore, if the extractions are performed in such a manner that the number of data points is equal to or greater than the number of variables, the value of each variable can be derived.

The type of experiment most useful from this standpoint proved to be the experiments involving the variation of phase volume ratio. (Figures 4.17 and 4.18). In these experiments the values of E_A^o were observed as a function of T, therefore the number of unknowns is reduced to twice the number of species. A second important advantage (and requirement as far as correlation is concerned) is that it is possible to obtain many values of E_A^o while holding the M_X's and P_X's constant. It is believed that the M_X's depend on the initial acid concentration and the P_X's depend on the final acid concentration. By varying only T, many values of E_A^o are possible for any particular set of M_X's and P_X's.

The number of possible extractable species in the RuNO-nitrato complexes system appears to be limited to five (mono-nitrato through penta-nitrato complexes). The previous organic phase titrations indicated that the number may be two. From the aspect of mathematical ease, the maximum number that can be handled without the use of a computer is also two. The correlations were done, therefore, assuming first only one extractable species and then two extractable species. The correlation assuming two extractable species was in much better agreement with the observed results than was the correlation for only one species, and therefore only the former is presented here.

Assuming there are two extractable species, the distribution ratio is expressed as

$$E_A^o = T\left[\frac{\left(\frac{M_1P_1}{T+P_1}\right)+\left(\frac{M_2P_2}{T+P_2}\right)}{1-\left[\left(\frac{M_1P_1}{T+P_1}\right)+\left(\frac{M_2P_2}{T+P_2}\right)\right]}\right] \qquad (4\text{-}2)$$

The four unknowns are therefore M_1, M_2, P_1, and P_2. Referring to Figure 4.17, there are seen to be five data points for the initial acid concentration of 8.7N HNO_3. Using any four of these five points in conjunction with Equation (4-2) would result in four simultaneous equations in the four unknowns M_1, M_2, P_1 and P_2. By solving the four simultaneous equations, the values of the four unknowns can be obtained. The unused fifth point can be used as a check. It was found to be more satisfactory, however, to include the fifth point in the calculations as a means of feedback information. The actual mathematical procedure used was to first solve the four simultaneous equations for the four unknowns. Using the values obtained for the mole fractions and partition coefficients, the fifth point was calculated. By comparing the observed value with calculated value, it could be seen whether the values of the unknowns were "sufficiently" accurate or were either too small or too large. The values of the mole

fractions and/or partition coefficients were then adjusted to bring the calculated value of the fifth point into closer agreement with the observed value. This adjustment could then have caused a deviation in the calculated values of some or all of the other four points. Therefore, the previous four points were re-calculated, and the re-calculated values compared with the observed values. Correspondingly, adjustments in the values of the mole fractions and/or partition coefficients were made again, if necessary, and the mathematical process continued. By this reiterative method, a "best fit" set of values for the mole fractions and partition coefficients was determined. It was somewhat arbitrarily established than an agreement between observed and calculated values within about 5-10% was "sufficient", and that adjustments were ceased when all calculated values agreed with all observed values within that range of deviation.

The set of "best fit" values that were determined for the initial acid concentration of 8.7N HNO_3 and final acid concentration of 1.0N HNO_3 were $M_1 = 0.107$, $M_2 = 0.167$, $P_1 = 100$, and $P_2 = 2.5$. The indentification of species "1" and species "2" was done by organic phase titration (to be discussed in the next section) and showed that species "1" is the acid of the penta-

nitrato complex ($H_2RuNO(NO_3)_5$) and species "2" is the acid of the tetra-nitrato complexes ($HRuNO(NO_3)_4(H_2O)$).

Since all of the data points in Figure 4.17 were at the same final acid concentration of 1.0N HNO_3, the values of P_1 and P_2 are the same for all data points and are equal to the previously calculated values of 100 and 2.5, respectively. Therefore, for the other sets of data at the remaining initial acid concentrations of 10.1, 6.8, 4.9, and 3.1N HNO_3, it is necessary only to solve for the values of the two mole fractions at each acid concentration.

Employing the same type of reiterative method to each set of data points, the values of M_1 and M_2 were calculated. The values of the mole fractions are shown in Figure 4.21. It should be noted that the values of the mole fractions shown in Figure 4.21 are "30-second" values, that is, values of the mole fractions that actually existed in the aqueous phase after having been diluted for a delay time of 30 seconds. The values of the mole fractions shown in the previously discussed Figure 3.4 are the values existing in the stock solutions before dilution and subsequent short-time redistribution. These were obtained by increasing the observed "30-second" values of the distribution ratios by the 10% correction factor mentioned in Section 4.2.5, using

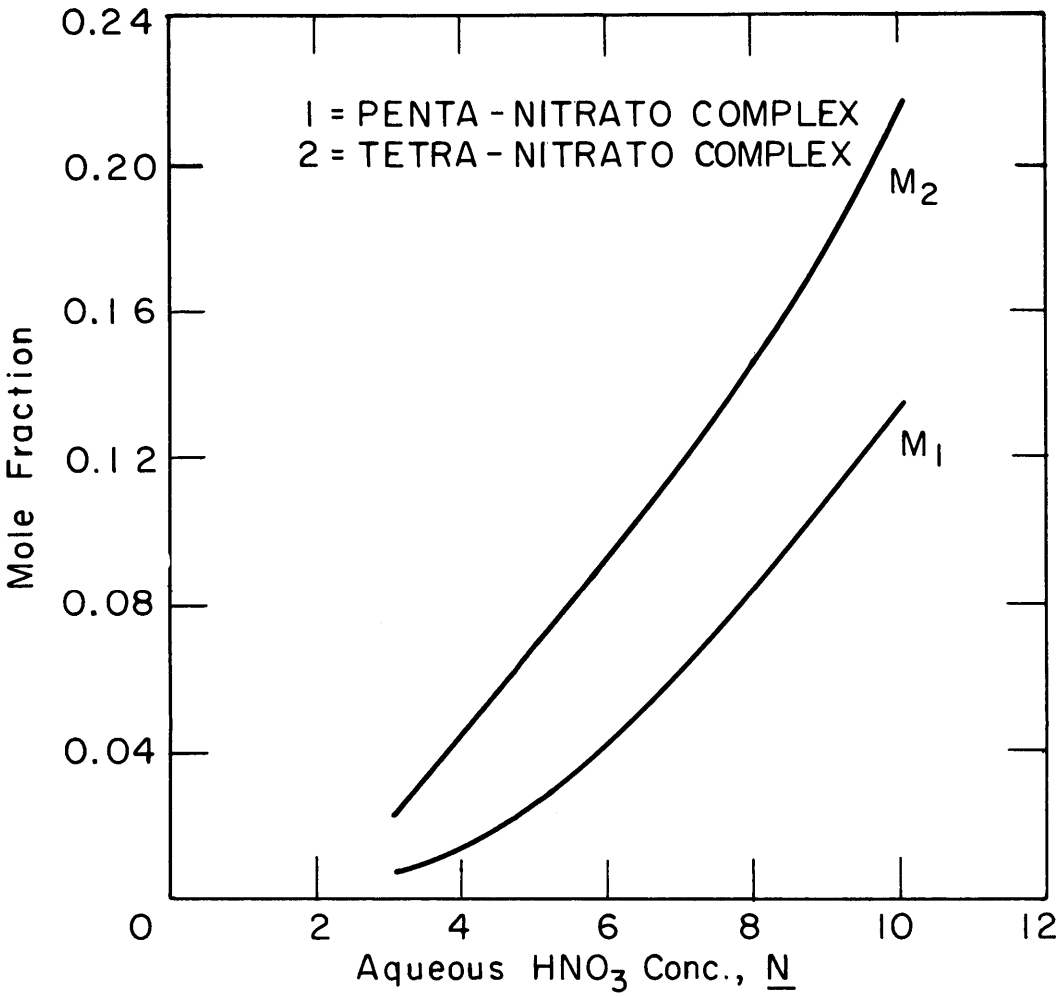

FIG. 4.21 DISTRIBUTION OF EXTRACTABLE SPECIES OF AGED RuNO-NITRATO COMPLEXES IN NITRIC ACID SOLUTIONS ("30-SECOND" VALUES)

the already calculated values of P_1 and P_2 (which are not affected by delay time), and employing the reiterative "best fit" method of calculation.

In Figure 4.22 is shown the comparison between the values of the observed distribution ratios of Figure 4.17 and the values calculated using the stock solution mole fractions of Figure 4.21 and the values of $P_1 = 100$ and $P_2 = 2.5$.

It should be noted that although the other sets of data in Figure 4.17 do not contain four or more data points in a set, it would still be possible to obtain at least four values by drawing a curve through the data points and thereby establishing an infinite number of available points for calculation purposes. By this method, the reiterative "best fit" type of correlation could be performed on sets of data other than just the 8.7N HNO_3 initial acid concentration set.

As a means of checking the values of M_1, M_2, P_1, and P_2 obtained from the 8.7N HNO_3 set, a curve was drawn through the three data points for the initial acid concentration of 6.8N HNO_3, and four values taken at phase volume ratios of 1, 4, 16, and 50. Using those four values and Equation (4-2), the values of M_1, M_2, P_1 and P_2 were calculated. The values were $M_1 = 0.055$, $M_2 = 0.156$, $P_1 = 105$ and

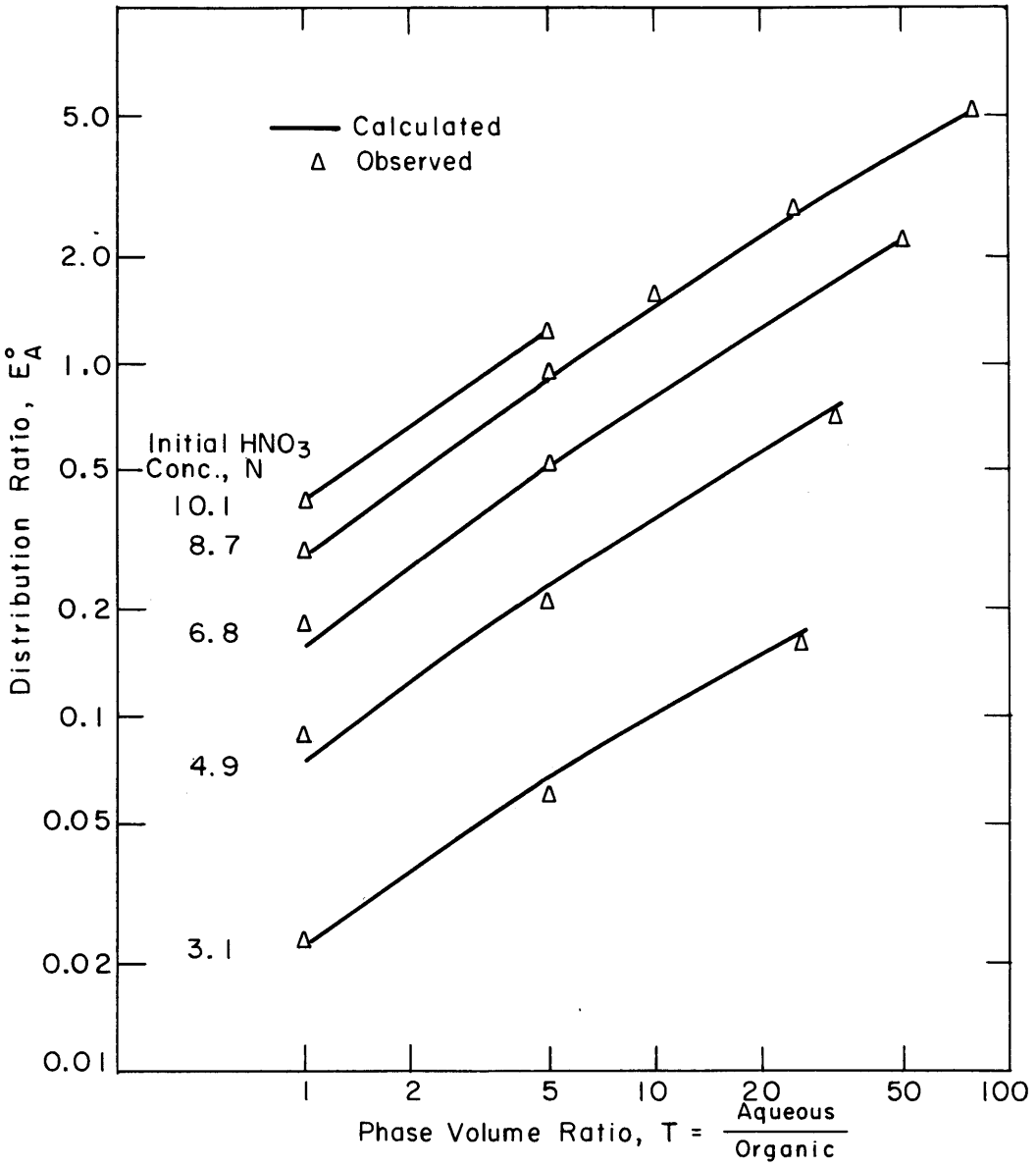

FIG. 4.22 AGED NITRIC ACID SOLUTIONS OF RuNO-NITRATO COMPLEXES (BATCH B) DILUTED RAPIDLY TO 1.0N HNO_3 AND CONTACTED FOR 30 SECONDS AT ROOM TEMPERATURE WITH 0.26M TLA IN TOLUENE

P_2 = 1.7. The values of the partition coefficients were then used in conjunction with the two data points at T = 1 and T = 79 for the 8.7N HNO_3 set, and the mole fractions at the 8.7N HNO_3 and concentration were determined. The values calculated were M_1 = 0.101 and M_2 = 0.198. A comparison of the two systems is summarized below in Table 4.1.

TABLE 4.1

COMPARISON OF VALUES AS DERIVED FROM TWO SETS OF DATA

Values of Mole Fractions are for 8.7N HNO_3

Values of Partition Coefficients are for 1.0N HNO_3

Paramater	Calculated Using 6.8N HNO_3 Set	Calculated Using 8.7N HNO_3 Set
M_1	0.101	0.107
M_2	0.198	0.167
P_1	105	100
P_2	1.7	2.5

The values of M_1 and P_1 are seen to agree very closely. The values of M_2 and P_2 differ in such a manner that the product of M_2P_2 agrees fairly well. By use of a reiterative method the absolute values of M_2 and P_2 could probably be brought into closer agreement; however, the results as they exist are

sufficient to display the qualitative and semi-quantitative reliability of the calculated values. It is believed that any errors in the absolute values of the parameter would be on the order of 10-20% as opposed to 100-200%. Because the data of the 8.7N HNO_3 set covers the largest range of values of the phase volume ratio and because there are five actual data points, that set was used as the basis for calculation.

Having determined the mole fractions as a function of stock solution acid concentration, it is now possible to calculate the partition coefficients at final acid concentrations of 3.0N and 4.9N HNO_3. Referring to Figure 4.16, the lower two sets of data points correspond to rapid dilution experiments at final acid concentrations of 3.0 and 4.9N HNO_3 and initial acid concentrations of 3.1, 4.9, 6.8, 8.7, and 10.1N HNO_3. By increasing the data points of these experiments by the 10% correction factor (except for the point where both the initial and final acid concentrations were 4.9N HNO_3, hence no dilution delay time), using the stock solution mole fractions of Figure 3.4, and applying the reiterative "best fit" method, the values of P_1 and P_2 were obtained for the two final acid concentrations of 3.0 and 4.9N HNO_3. The results are shown in Figure 4.23.

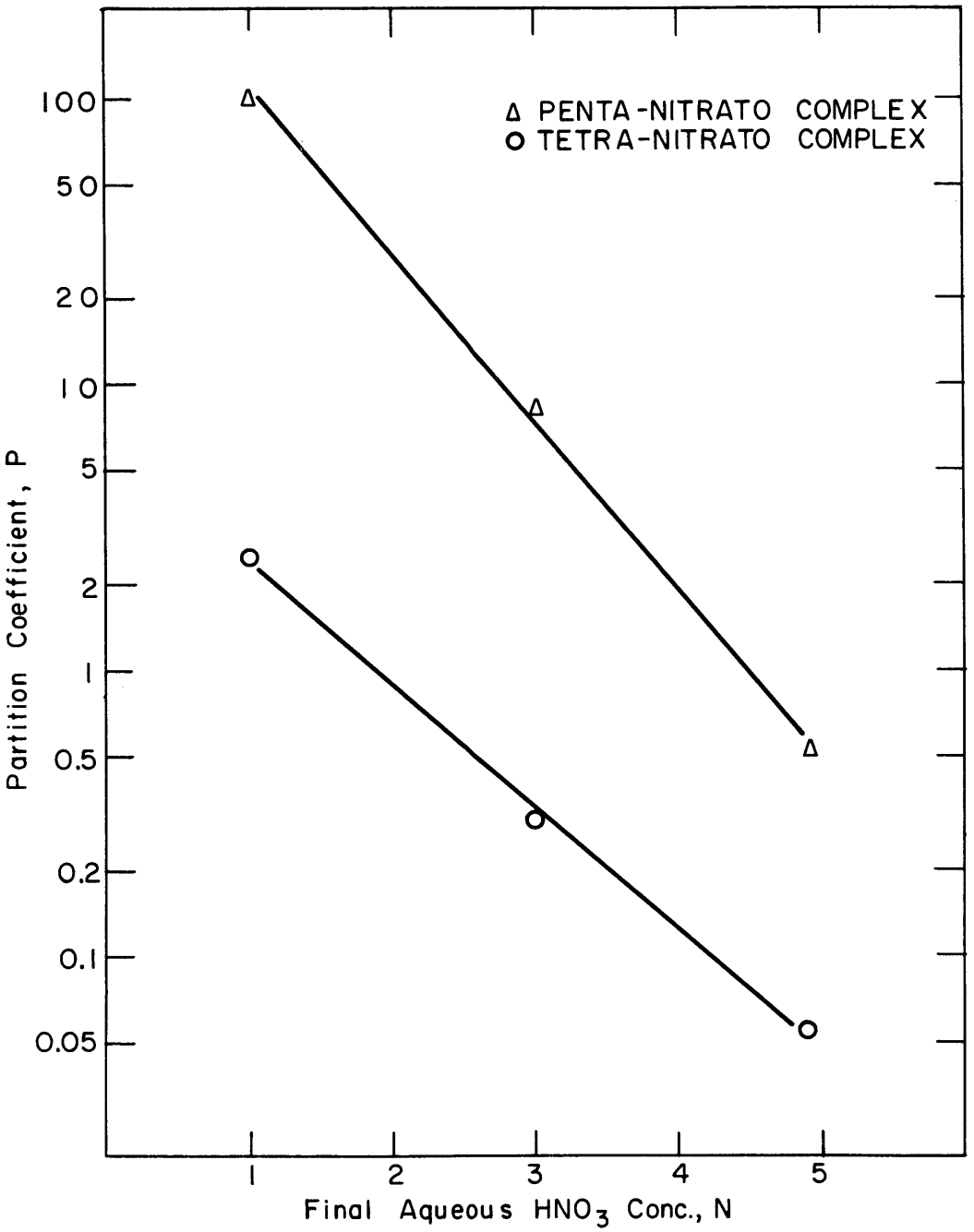

FIG. 4.23 PARTITION COEFFICIENTS OF RuNO - NITRATO COMPLEXES BETWEEN AQUEOUS NITRIC ACID SOLUTIONS AND 0.26M TLA IN TOLUENE AT ROOM TEMPERATURE

In Figure 4.24 is shown the comparison between the corrected data points of Figure 4.16 and the values as calculated from the stock solution mole fractions of Figure 3.4 and the partition coefficients of Figure 4.23.

4.3.4 Organic Phase Titrations

As a means of identifying the two extractable species, organic phase titrations were performed on two of the rapid dilution extraction samples. The samples and the conditions of the extractions are summarized below.

TABLE 4.2

SUMMARY OF EXTRACTION CONDITIONS FOR SAMPLES 178 AND 180

Sample	Initial Aq. HNO_3, N	Final Aq. HNO_3, N	Aq. Ru Conc. after dilution, gm/l	Phase Volume Ratio, T
178	8.7	1.0	0.738	79
180	6.8	1.0	0.942	50

The concentration of each species in the organic phase can be expressed by Equation (4-3). (The derivation of Equation (4-3) can be found in the derivation of Equation (4-1) in the Appendix.)

$$C_{x,o} = \frac{TRM_x P_x}{T + P_x} \qquad (4\text{-}3)$$

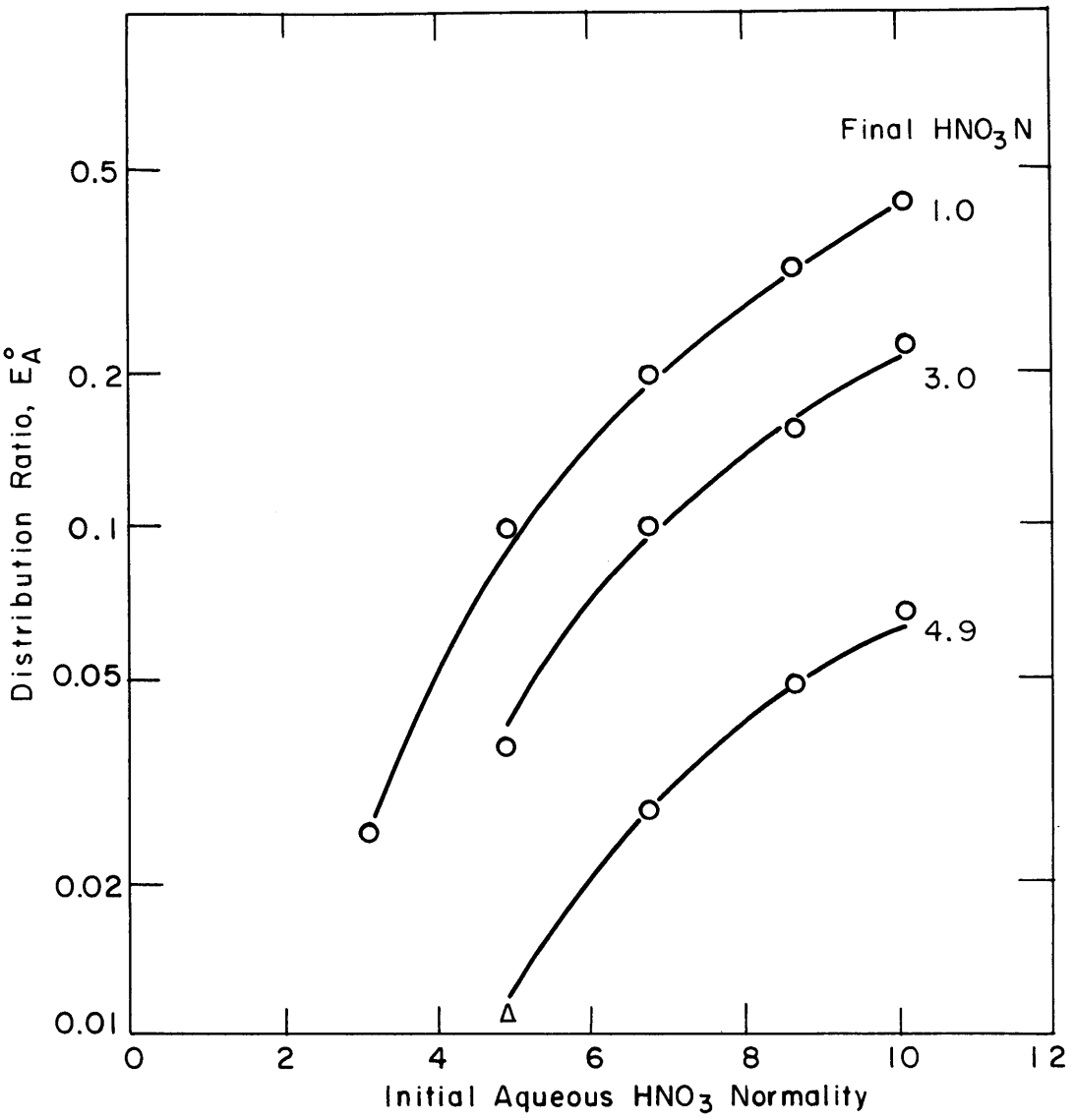

FIG. 4.24 AGED NITRIC ACID SOLUTIONS OF RuNO-NITRATO COMPLEXES DILUTED RAPIDLY AND CONTACTED 30 SECONDS AT ROOM TEMPERATURE WITH 0.26M TLA IN TOLUENE

——— CALCULATED VALUES
o OBSERVED VALUES INCREASED BY 10%
Δ OBSERVED VALUE

Where T, M_x, and P_x have the usual meaning and R is the total ruthenium concentration in the aqueous phase after dilution but before extraction. $C_{x,o}$ is the concentration of species "x" in the organic phase after the rapid dilution extraction.

The values of M_x that must be used in these cases are the "30-second" values, since the concentrations desired are the actual concentrations and not the "corrected" concentrations. Hence the values of M_x will be taken from Figure 4.21 and the values of P_x from Figure 4.23. Using Equation (4-3), the values of M_x and P_x as given in Figures 4.21 and 4.23, respectively, and the values of R and T as given in the previous table, the concentrations of species "1" and species "2" can be calculated. The concentrations are reported in grams per liter of species as ruthenium, not as total complex.

TABLE 4.3

CALCULATED CONCENTRATIONS OF SPECIES IN ORGANIC PHASE (AS GM.Ru/l)

Sample	Calculated Species "1"	Species "2"	Total	Total Observed
178	3.48	0.30	3.78	3.58
180	1.85	0.24	2.09	2.01

Figures 4.25 and 4.26 show the organic phase titrations of samples 178 and 180, respectively. The "titratable ruthenium" concentrations are observed to be about 0.073N for sample 178 and about 0.040-0.042N, depending upon selection of inflection point, for sample 180.

If it is assumed that the titratable ruthenium is in the form of a mixture of a mono-basic and a di-basic acid, then there are two alternatives; (1) species "1" is mono-basic and species "2" is dibasic, or (2) species "1" is dibasic and species "2" is mono-basic.

In Table 4.4 are summarized the results of the calculated values for the two assumptions and the observed values.

TABLE 4.4

CONCENTRATION OF RUTHENIUM IN ORGANIC PHASE OF SAMPLES 178 AND 180

Normality of Titratable Ru in Organic Phases

Sample	Calculated under Assumption (1)	Calculated under Assumption (2)	Observed
178	0.041	0.073	0.073
180	0.023	0.039	0.041

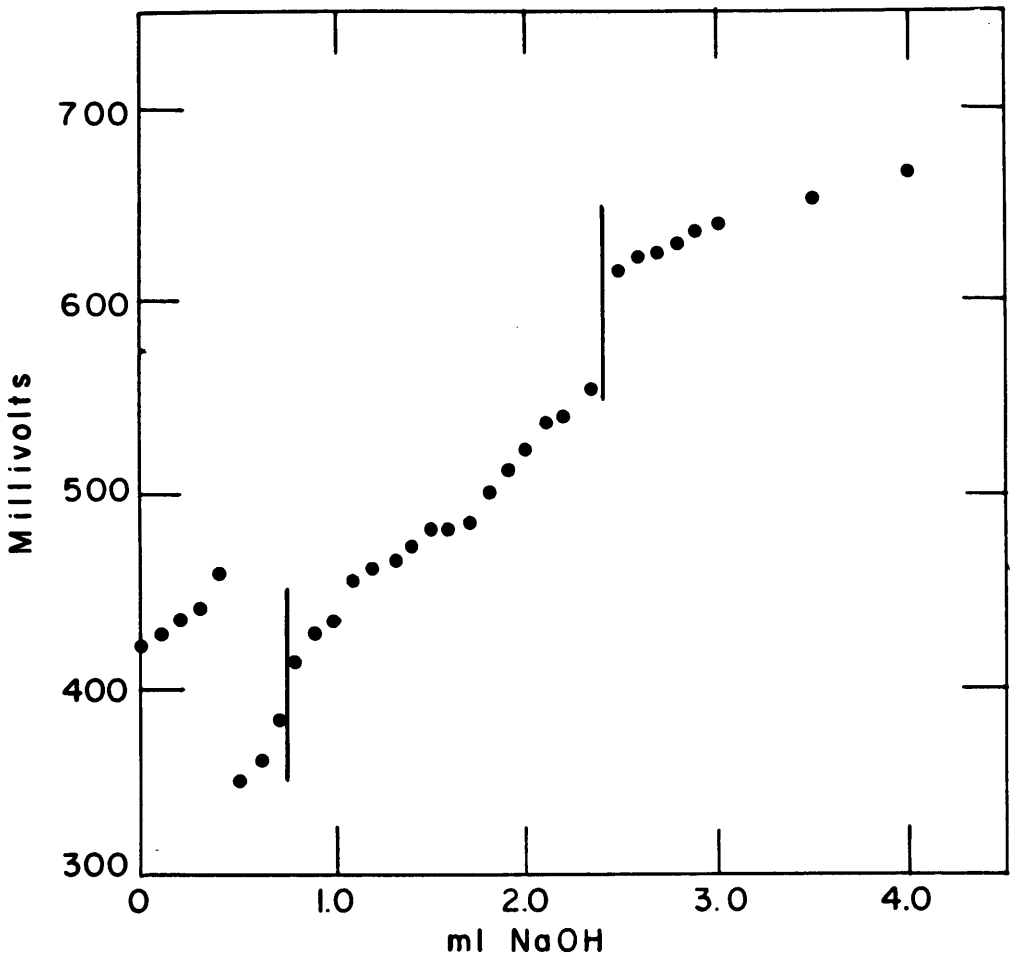

FIG. 4.25 ORGANIC PHASE TITRATION OF SAMPLE 178
0.79 ml. OF SAMPLE VS. 0.0351 N NaOH

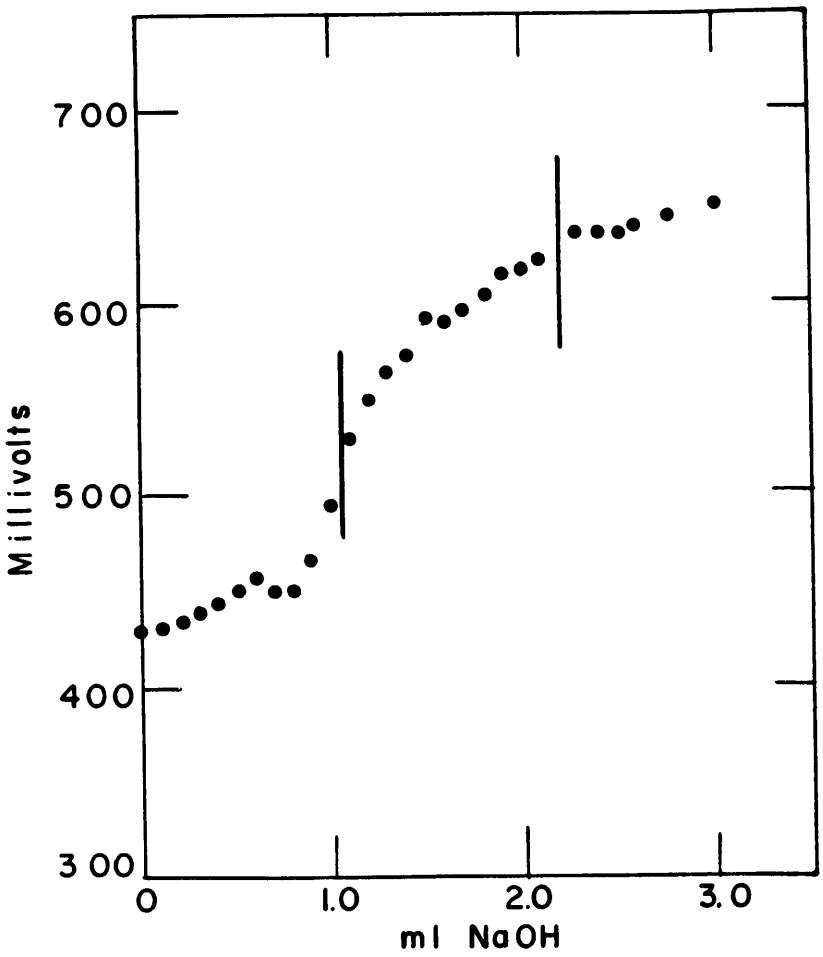

FIG. 4.26 ORGANIC PHASE TITRATION OF SAMPLE 180 1.0 ml. OF SAMPLE VS. 0.0351 N NaOH

It would therefore appear that assumption (2) is correct and the more extractable species of the RuNO-nitrato complexes are the acids of the tetra-nitrato and penta-nitrato complexes ($HRuNO(NO_3)_4(H_2O)$ and $H_2RuNO(NO_3)_5$) and that of the two the penta-nitrato acid complex is more extractable than the tetra-nitrato acid complex.

4.3.5 Prediction of Back-Extraction Distribution Ratio

A further check on the correlation results can be obtained by the comparison of the calculated and observed values of back-extraction distribution ratios. An example is described as follows:

(1) Sample 171 was a rapid dilution extraction performed by diluting an initial acid concentration of 10.1N HNO_3 to a final acid concentration of 3.0N HNO_3 with a phase volume ratio of T = 5.

(2) Immediately after separation of the phases of sample 171, a portion of the organic phase of that sample was contacted for 30 seconds with an equal volume of ruthenium-free 3.0N HNO_3 to obtain the value of the back-extraction distribution ratio, $E_A^o(B) = 3.92$.

For this type of experiment, Equation (4-4) (see Appendix for derivation) expresses the value of the back-extraction distribution ratio, $E_A^o(B)$, in terms of the mole fractions of the extractable species

("30-second" values) for the initial acid condition before the forward extraction (M_1 and M_2), the partition coefficients at the final acid concentration (P_1 and P_2), and the phase volume ratios for the forward (T_F) and backward (T_B) extractions.

$$E_A^o(B) = \frac{\frac{M_1 P_1^2}{(P_1+T_F)(P_1+T_B)} + \frac{M_2 P_2^2}{(P_2+T_F)(P_2+T_B)}}{\frac{M_1 P_1}{(P_1+T_F)(P_1+T_B)} + \frac{M_2 P_2}{(P_2+T_F)(P_2+T_B)}} \qquad (4\text{-}4)$$

Using the following values of the variables, which were obtained from Figures 4.21 and 4.23, the value of $E_A^o(B)$ was calculated to be 4.01, which agrees very well with the observed value of 3.92.

$$M_1 = 0.127 \quad P_1 = 8.0 \quad T_F = 5$$

$$M_1 = 0.216 \quad P_2 = 0.30 \quad T_B = 1$$

4.3.6 Disappearance Rate Constants

From the data obtained for the experiments involving the variation of delay time (Figures 4.19 and 4.20), it was possible to calculate a set of values for the disappearance rate constants of the tetra- and penta-nitrato complexes.

By rearranging Equation (4-2), it is possible to obtain Equation (4-5).

$$\left(\frac{E_A^o}{T+E_A^o}\right) = \left(\frac{P_1}{T+P_1}\right) M_1 + \left(\frac{P_2}{T+P_2}\right) M_2 \qquad (4\text{-}5)$$

By assuming that the following denitration reactions are the cause of the disappearance of the respective species upon dilution, and that they proceed with the indicated reaction rate constants (which are first order with respect to ruthenium), it is possible to derive Equations (4-8) and (4-9) for the value of the mole fractions as a function of time after dilution. (See Appendix for derivation).

$$H_2RuNO(NO_3)_5 + H_2O \xrightarrow{k_1} HRuNO(NO_3)_4(H_2O) + HNO_3 \qquad (4\text{-}6)$$

$$HRuNO(NO_3)_4(H_2O) + H_2O \xrightarrow{k_2} RuNO(NO_3)_3(H_2O)_2 + HNO_3 \qquad (4\text{-}7)$$

$$M_1 = M_1^* + (M_1^o - M_1^*)e^{-k_1 t} \qquad (4\text{-}8)$$

$$M_2 = M_2^* + (M_2^o - M_2^*)e^{-k_2 t} + \frac{k_1 (M_1^o - M_1^*)}{(k_1 - k_2)}\left[e^{-k_2 t} - e^{-k_1 t}\right] \qquad (4\text{-}9)$$

Where M_1^o and M_2^o are the equilibrium stock solution mole fractions at the initial acid concentration, M_1^* and M_2^* are the equilibrium stock solution mole

fractions at the final acid concentration, k_1 and k_2 are the reaction rate constants (min^{-1}), and t is the dilution delay time (minutes).

By substituting Equations (4-8) and (4-9) into Equation (4-5), an equation relating E_A^o and delay time is seen to result in which there are only two unknowns, k_1 and k_2. The values of E_A^o and t can be obtained from Figures 4.19 and 4.20, the values of P_1 and P_2 can be obtained from Figure 4.23, and the values of M_1^o, M_2^o, M_1^*, and M_2^* can be obtained from Figure 3.4. All of the extractions were performed for a phase volume ratio of T=1.

From Figures 4.19 and 4.20, it can be seen that for each set of conditions (dilution from a particular initial acid concentration to a particular final acid concentration) there are four data points. Since there are two unknowns, it becomes possible to solve for the two unknowns at each set of extraction conditions by the same "best fit" reiterative process previously described. The results are those shown in Table 3.3.

In Figures 4.27 and 4.28 is shown the comparison between the observed values of E_A^o and the values as calculated from the disappearance rate constants of Table 3.3, the mole fractions of Figure 3.4, and the partition coefficients of Figure 4.23.

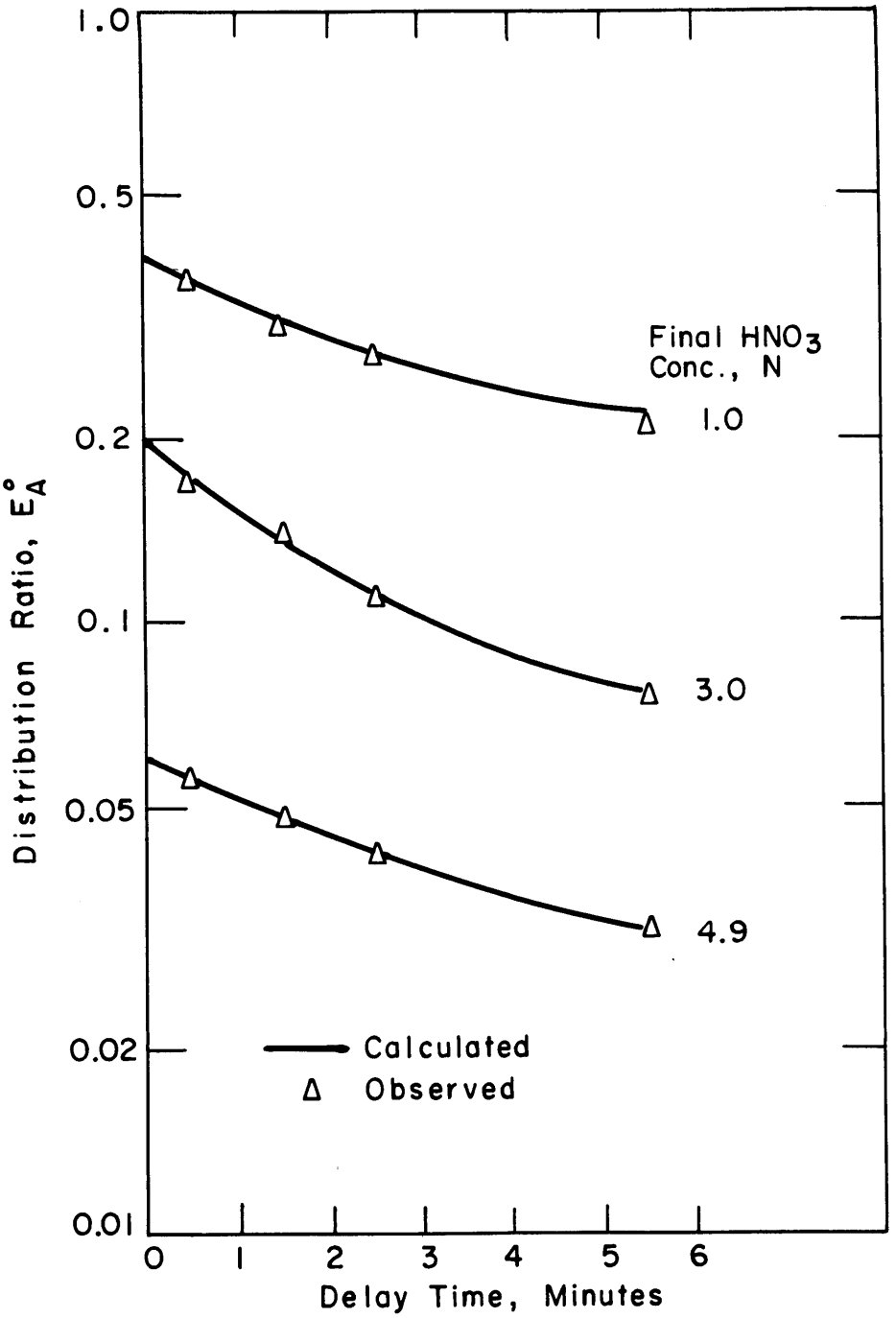

FIG. 4.27 AGED 9.7N HNO_3 SOLUTION OF RuNO-NITRATO COMPLEXES (BATCH C) DILUTED RAPIDLY AND CONTACTED FOR 30 SECONDS WITH 0.26M TLA IN TOLUENE AT ROOM TEMPERATURE

DELAY TIME = TIME ELAPSED BETWEEN START OF ADDITION OF STOCK SOLUTION AND START OF SHAKING

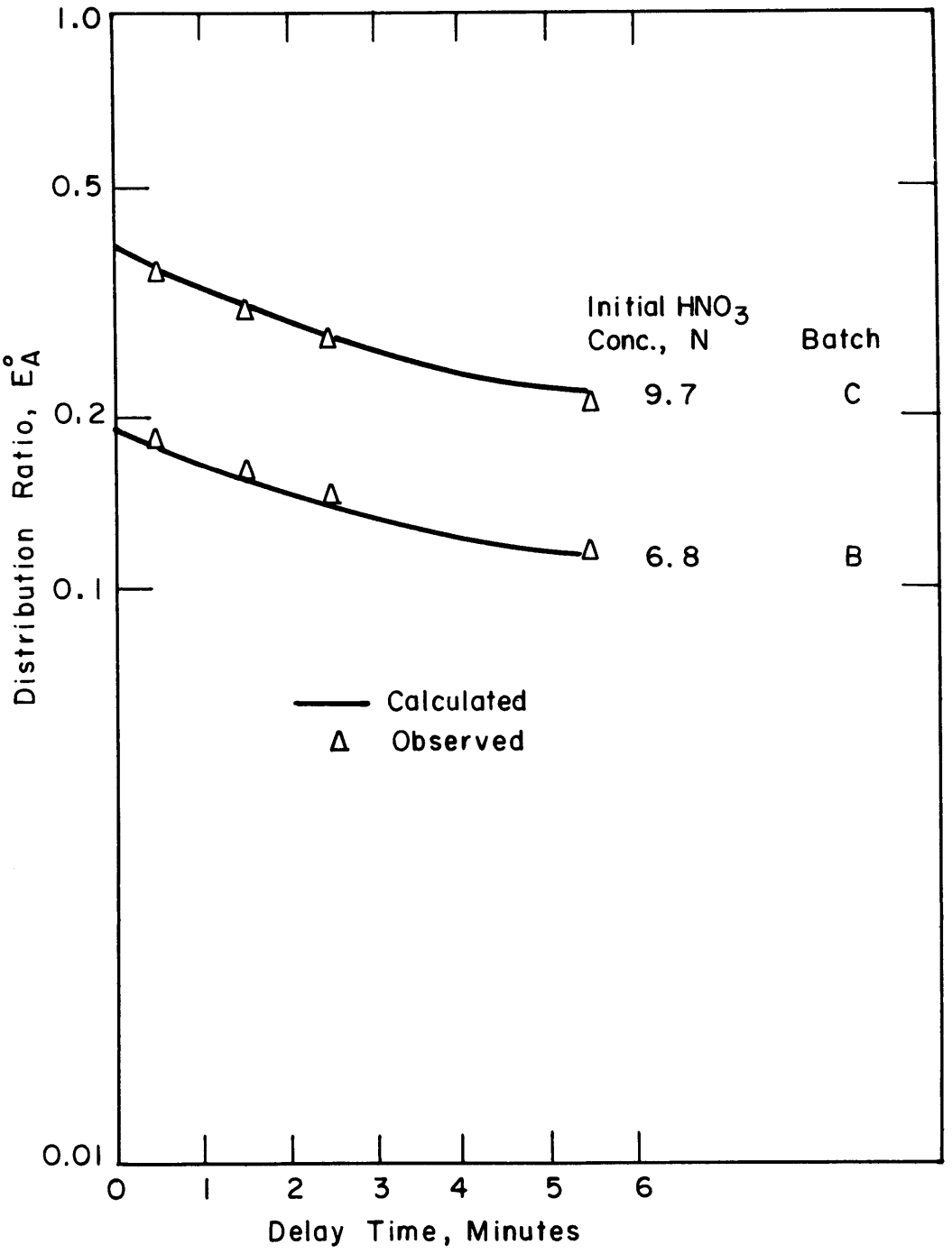

FIG. 4.28 AGED NITRIC ACID SOLUTIONS OF RuNO-NITRATO COMPLEXES DILUTED RAPIDLY TO 1.0N HNO_3 AND CONTACTED FOR 30 SECONDS AT ROOM TEMPERATURE WITH 0.26M TLA IN TOLUENE.

DELAY TIME = TIME ELAPSED BETWEEN START OF ADDITION OF STOCK SOLUTION AND START OF SHAKING

4.3.7 Extraction of Nitric Acid

The data of Figure 4.8 shows a large effect of sodium nitrate salting on nitric acid extraction when the unbound nitric acid concentration in the organic phase is plotted against the aqueous phase nitric acid concentration. At the suggestion of Dr. C. F. Coleman of Oak Ridge National Laboratory (19), an attempt was made to correlate the data on the basis of aqueous phase undissociated nitric acid activity. The result is shown in Figure 4.29. Due to the lack of accurate dissociation data below 2N HNO_3, only five non-salted solution points could be calculated. As can be seen from Figure 4.29, this type of correlation looks very promising.

The activity data used was that of Högfeldt (10); and helpful suggestions regarding method of application were provided by Professor Scatchard of MIT (21).

In Figures 4.30 and 4.31 are shown the dissociation constant and activity coefficient, respectively, for non-salted aqueous nitric acid solutions as presented by Högfeldt (10). The commonly accepted value of the equilibrium constant for nitric acid dissociation is 23.5, i.e.

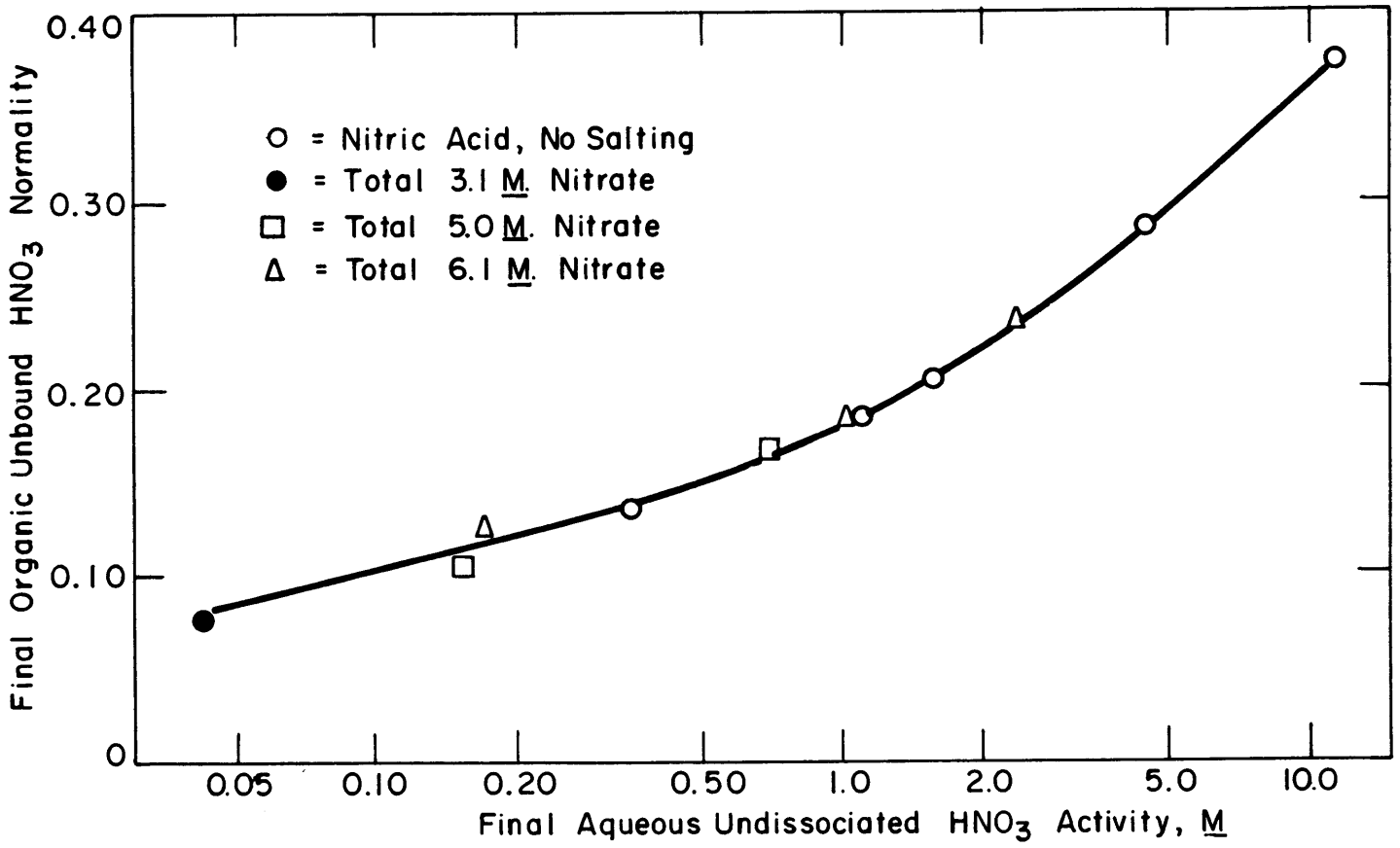

FIG. 4.29 EXTRACTION OF NITRIC ACID BY 0.26 M TLA IN TOLUENE AT 25°C

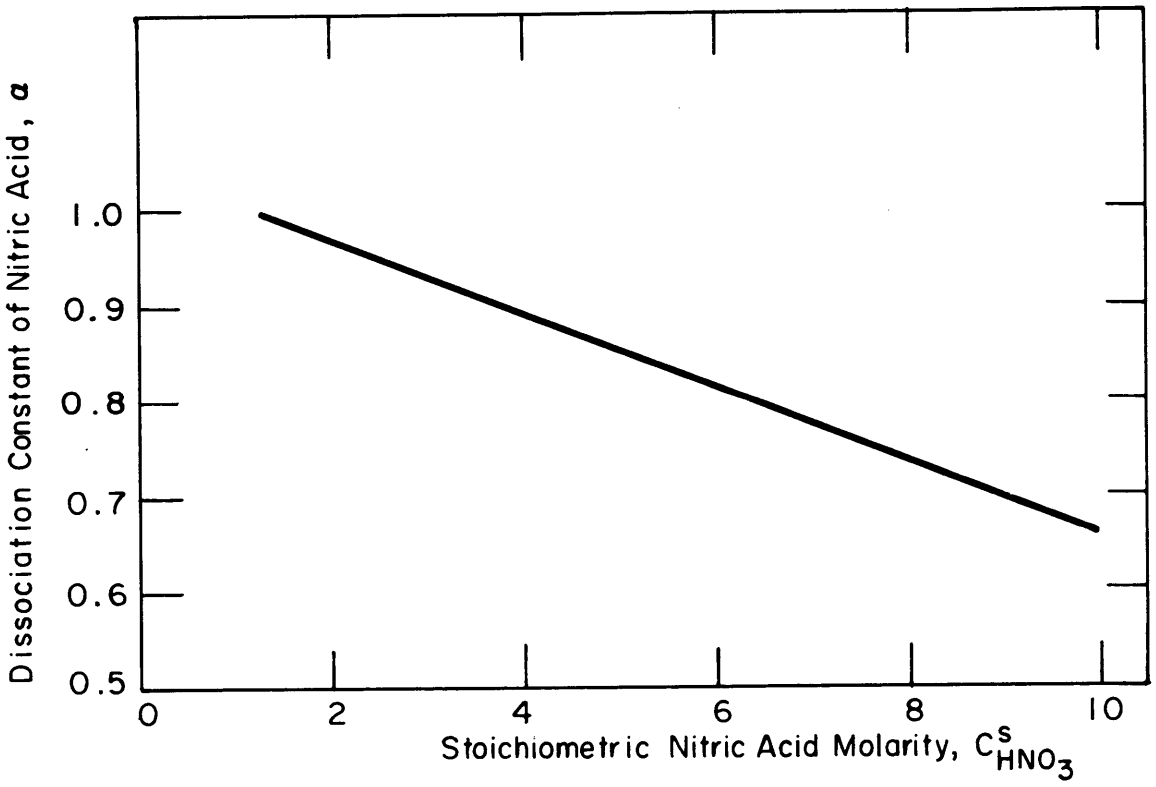

FIG. 4.30 DISSOCIATION CONSTANT OF PURE NITRIC ACID

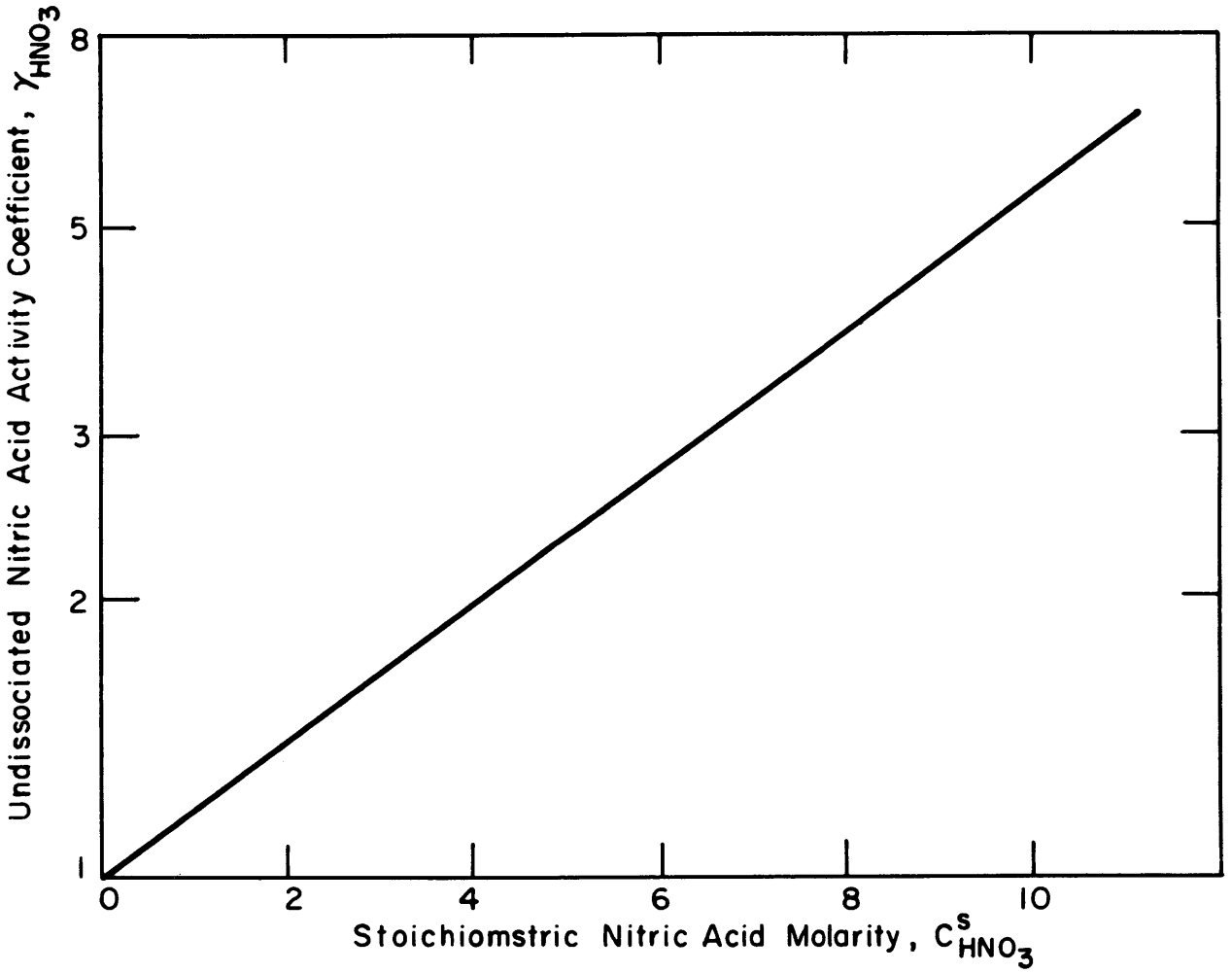

FIG. 4.31 ACTIVITY COEFFICIENT OF UNDISSOCIATED NITRIC ACID IN PURE NITRIC ACID

$$HNO_3 = H^+ + NO_3^- \qquad (4\text{-}10)$$

$$K_{(4\text{-}10)} = \frac{a_{H^+} a_{NO_3^-}}{a_{HNO_3}} = 23.5 \qquad (4\text{-}11)$$

Where the a's refer to the activities of the various species. If the activity is the product of the concentrations (C) and an activity coefficient (γ), the equilibrium constant can be rewritten as

$$K = \left(\frac{\gamma_{H^+}\gamma_{NO_3^-}}{\gamma_{HNO_3}}\right)\left(\frac{C_{H^+} C_{NO_3^-}}{C_{HNO_3}}\right) = 23.5 \qquad (4\text{-}12)$$

The dissociation constant (α) is defined such that

$$C_{H^+} = C_{NO_3^-} = \alpha C^s_{HNO_3} \qquad (4\text{-}13)$$

$$C_{HNO_3} = (1-\alpha)\, C^s_{HNO_3} \qquad (4\text{-}14)$$

Where $C^s_{HNO_3}$ is the nominal stoichiometric nitric acid concentration. By defining the activity coefficients term in (4-12) as R, the equilibrium constant can be rewritten as

$$K = R\left(\frac{\alpha^2}{1-\alpha}\right) C^S_{HNO_3} = 23.5 \qquad (4\text{-}15)$$

Rearrangement of (4-15) yields an expression for R.

$$R = \frac{23.5(1-\alpha)}{\alpha^2 C^s_{HNO_3}} \qquad (4\text{-}16)$$

Using Figure 4.30, it is possible to calculate R as a function of $C^s_{HNO_3}$ (Figure 4.32). Using Figures 4.30 and 4.31, it is possible to calculate the undissociated nitric acid activity as a function of $C^s_{HNO_3}$: (Figure 4.33)

$$a_{HNO_3} = \gamma_{HNO_3} C_{HNO_3} = \gamma_{HNO_3} (1-\alpha) C^s_{HNO_3} \qquad (4.17)$$

From Figure 4.33, the correlation between the organic phase unbound nitric acid concentration due to non-salted aqueous nitric acid solutions and aqueous phase undissociated nitric acid activity can be accomplished. The points in Figure 4.29 relating to non-salted aqueous nitric acid solutions were done in this manner.

The points relating to salted solutions involved some assumptions in their calculation. It was necessary to first calculate the dissociation constant α and from that calculate the concentration of the undissociated nitric acid in the aqueous phase

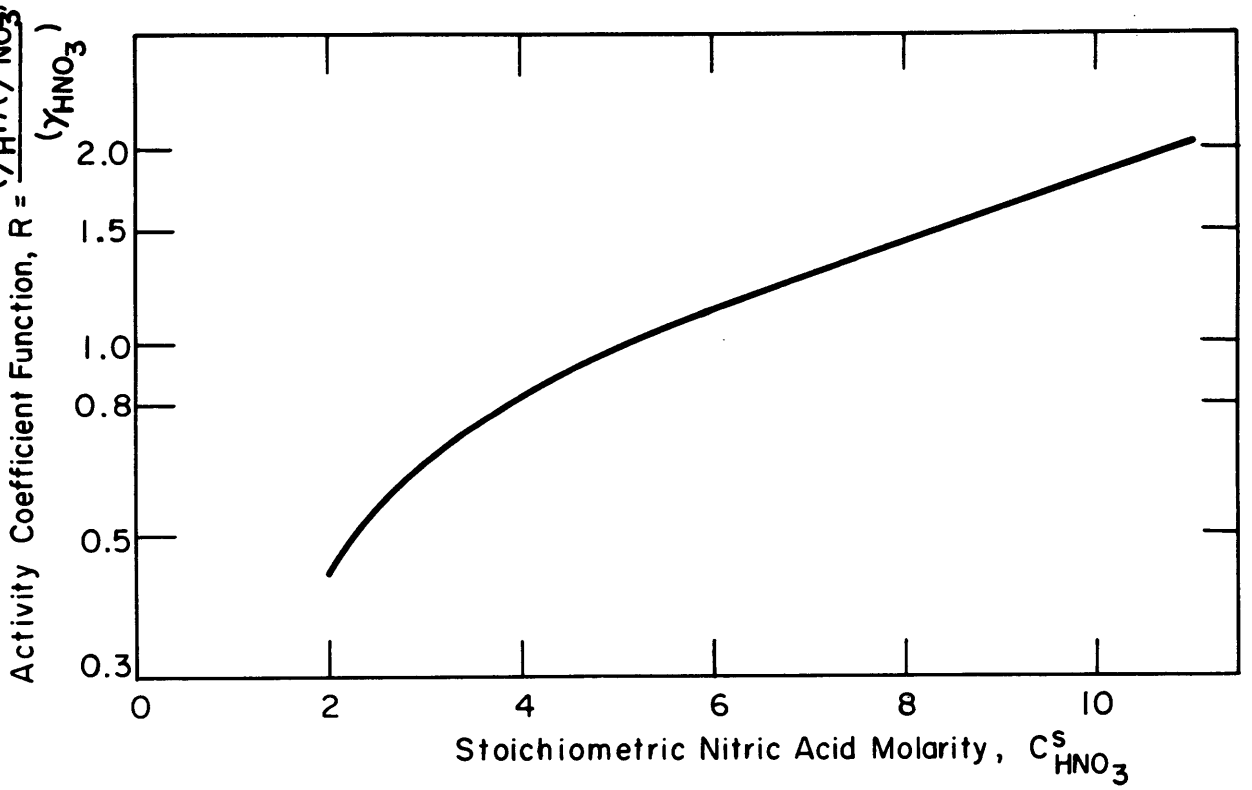

FIG. 4.32 ACTIVITY COEFFICIENT FUNCTION FOR PURE NITRIC ACID

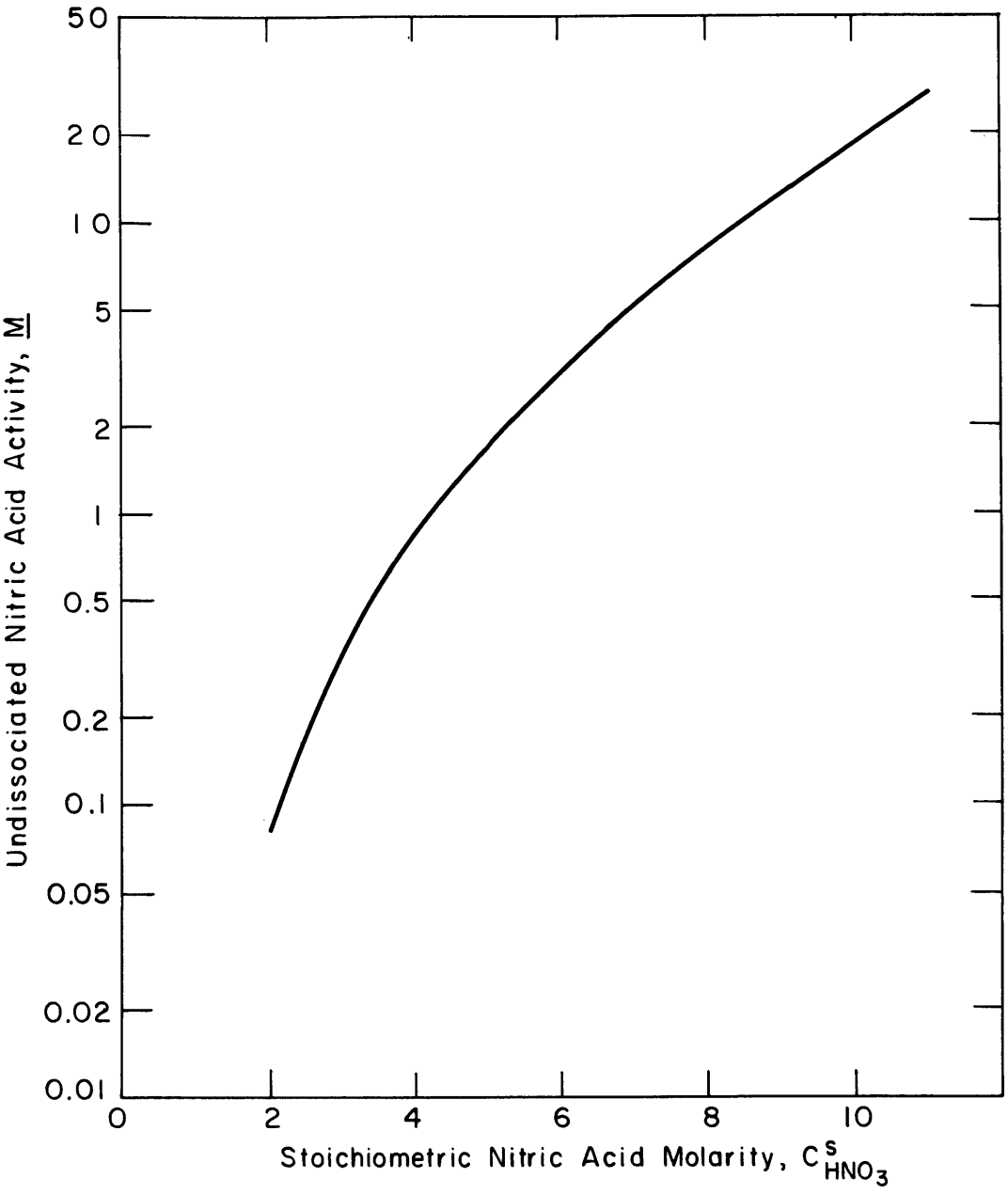

FIG. 4.33 ACTIVITY OF UNDISSOCIATED NITRIC ACID IN PURE NITRIC ACID

(C_{HNO_3}). The aqueous nitric acid activity was then calculated by multiplying the previous value of C_{HNO_3} by activity coefficient of the undissociated nitric acid activity. The question that had to be resolved was "what is the activity coefficient of the undissociated nitric acid in mixed nitric acid-sodium nitrate solutions?" Upon the suggestion of Prof. Scatchard (21), the values of γ_{HNO_3} in Figure 4.31 were assumed to be dependent upon the total stoichiometric nitrate concentration of the aqueous phase rather than upon the stoichiometric concentration of only the nitric acid in solution. For instance, in the case of a solution of 3M HNO_3 plus 3.1M $NaNO_3$, the value of γ_{HNO_3} would be taken from Figure 4.31 at the condition corresponding to $C^s_{HNO_3} = 3.0 + 3.1 = 6.1M$, not at $C^s_{HNO_3} = 3.0M$.

The calculation of α was accomplished as follows:

(1) Equation (4.15) was solved for α, yielding a quadratic equation

$$\alpha^2 + \left(\frac{23.5}{RC^s_{HNO_3}}\right)\alpha - \left(\frac{23.5}{RC^s_{HNO_3}}\right) = 0 \quad (4\text{-}18)$$

(2) The quadratic (4-18) was solved for α, using the value of R from Figure 4.32 at the value

corresponding to the total stoichiometric nitrate concentration. For the example mentioned above, R would be determined from Figure 4.32 at the value corresponding to $C^s_{HNO_3} = 6.1\underline{M}$, similar to γ_{HNO_3}. The value of $C^s_{HNO_3}$ in (4-18) is the actual stoichiometric nitric acid concentration existing in the salted solution. For the example above, the $C^s_{HNO_3}$ in (4-18) would be equal to $3.0\underline{M}$.

(3) The value of C_{HNO_3} was then determined by the relation of Equation (4-14). The value of α would be that just calculated and the value of $C^s_{HNO_3}$ would be that actually in solution and the same as Equation (4-18).

(4) The value of the activity (a_{HNO_3}) would be calculated by multiplying the above value of C_{HNO_3} by the activity coefficient γ_{HNO_3} determined at the total stoichiometric nitrate concentration.

As an example, consider the case of the solution containing $3.0\underline{M}$ HNO_3 and $3.1\underline{M}$ $NaNO_3$. The value of R in (4-18) would be equal to 1.12 (from Figure 4.32) and the value of $C^s_{HNO_3}$ in (4-18) would be equal to 3.0. Hence,

$$\alpha^2 + 7.0\alpha - 7.0 = 0 \qquad (4\text{-}19)$$

Solution of (4-19) yields $\alpha = 0.88$. The

undissociated nitric acid concentration would then be calculated as

$$C_{HNO_3} = (1-\alpha)C^s_{HNO_3} = (1-0.88)(3.0) = 0.36\underline{M} \quad (4\text{-}20)$$

The value of γ_{HNO_3}, from Figure 4.31, would be equal to 2.8. Therefore, the undissociated nitric acid activity would be calculated to be

$$a_{HNO_3} = \gamma_{HNO_3} C_{HNO_3} = (2.8)(0.36) = 1.01\underline{M} \quad (4\text{-}21)$$

The value of the organic phase unbound nitric acid concentration was observed (from Figure 4.8) to be 0.187$\underline{M}$. This point plotted in Figure 4.29 is seen to nearly coincide with that of the non-salted solution of 4.3$\underline{M}$ HNO_3.

4.4 Discussion of Results

4.4.1 Number and Forms of Species

As mentioned previously, the possible number of extractable species appears to be limited to five. Of the five nitrato complexes, the lower two (mono-and di-) do not seem to be likely prospects as extractable species for several reasons. First, it was shown that the more extractable species increase in proportion

as the stock solution nitric acid concentration is increased, which is quite the opposite of the mono- and di-nitrato complexes. Second, the possible forms of those species during extraction would necessarily have to be either cationic, which does not seem compatible with amine extraction; or else neutral with the possible ligands being either OH^- or NO_3^-. Ligand substitution by OH^- seems very unlikely due to hydrolysis and ligand substitution by NO_3^- would then change the complexes to higher nitrato complexes. Therefore, the possible extractable species seem to be limited to the tri-, tetra-, and penta-nitrato complexes. The correlation of the rapid dilution experiments, in conjunction with the organic phase titrations, appears to limit the extractable species to the tetra- and penta-nitrato complexes. However, the correlation was not performed for the case of three extractable species and so the extraction of a certain amount of the tri-nitrato complex cannot be summarily ruled out.

4.4.2 Mole Fractions and Partition Coefficients

The qualitative establishment of the more extractable species and the semi-quantitative estimations of their relative proportions and extractability seem to be fairly reliable. The

acceptance of the absolute values of the mole fractions and partition coefficients, of course, deserves some reservation, although, it is believed, not too much.

The large disagreement between the MIT values of the mole fractions and those of Fletcher (7) deserves an explanation. However, since neither of the investigations involved an actual separation and positive identification of each, or either, species, such an explanation is difficult to develop. Some possible reasons for the discrepancy are listed as follows and are meant only to be suggestions possibly worthy of investigation and are not intended to "resolve" the issue.

(1) The possibility that Fletcher's "Group D" is actually the sum of three complexes, the tri-, tetra-, and penta-nitrato complexes.

(2) The possibility that the tetra- and penta-nitrato acid complexes exist in equilibrium as both undissociated and dissociated acids, i.e.

$$H_2RuNO(NO_3)_5 \rightleftharpoons HRuNO(NO_3)_5^- + H^+ \qquad (4\text{-}22)$$

$$HRuNO(NO_3)_4(H_2O) \rightleftharpoons RuNO(NO_3)_4(H_2O)^- + H^+ \qquad (4\text{-}23)$$

and that the MIT mole fractions are for only the extractable undissociated forms while the Fletcher

Group D mole fractions are for the total sum of the two complexes.

(3) The possibility that the correction of unknown experimental and/or correlation error in either one or both of the studies could bring the two sets of data into closer agreement.

4.4.3 Disappearance Rate Constants

As mentioned previously, the absolute values of these parameters are questionable, due to the short length of delay times investigated. A second possible source of error exists in the form of temperature during extraction. The heat due to the extraction reaction and physical shaking could raise the temperature of the system a few degrees and consequently raise the values of the rate constants, which have been shown by Fletcher (7) to be very temperature dependent. The control of temperature was not possible due to the short times involved in the rapid dilution experiments.

Of considerable interest, however, is the indication of two values of the rate constants, one for each complex, and of the relative magnitude of each.

4.4.4 Extraction of Nitric Acid

The correlation performed utilizing nitric acid activity appears very promising. The possibility that the extraction mechanism may be more dependent upon organic phase unbound nitric acid concentration than upon aqueous phase nitric acid concentration seems firmly established. However, the effect of organic-phase unbound nitric acid concentration (or activity, since the concentrations in the organic phase were relatively small) and/or aqueous phase nitric acid activity upon the extraction mechanism appears to be inseparable. It seems possible, or even probable, that the two effects are actually one.

In any case, where activity data are available, the effect of activity (aqueous and/or organic phase) in solvent extraction processes in general should be considered.

V. EXTRACTION OF NITROSYL RUTHENIUM NITRO COMPLEXES BY TRILAURYLAMINE

5.0 General Discussion

5.0.1 Purpose

The purpose of the studies conducted on the RuNO-nitro complexes was twofold:

(1) To serve as a survey, or scouting, study on the nitro complexes and thereby obtain a general idea of their solution chemistry and solvent extraction characteristics.

(2) To serve as a comparison with the properties or the RuNO-nitrato complexes.

5.0.2 State of the Art

The state of the art of the RuNO-nitro complexes is not so well advanced as that for the RuNO-nitrato complexes. A general state of the art of the solution chemistry of the nitro complexes was presented in Chapter III.

The solvent extraction studies performed by a large percentage of the investigators of the nitro complexes were done in a manner such that the actual

species in solution were only assumed, or guessed at. For instance, Kraak (12) subjected a stock solution of the RuNO-nitrato complexes to NO-NO_2 gases bubbling through it for various selected lengths of time at various selected temperatures and assumed the result to be the formation (of unknown amount) of nitro complexes (of unknown composition). After comparing the extractability of the treated and untreated stock solution, Kraak concluded that the nitro complexes were less extractable than the nitrato complexes.

The above experiments were typical of a number of other experiments conducted on the nitro complexes in that the investigations did not include a controlled aqueous phase.

One of the few studies utilizing a controlled aqueous phase of nitro complexes was the previously mentioned work of Brown (1), and even then the extractions performed were for only a few selected points. However, Brown's extraction data appears to be diametrically opposed to Kraak's (12) conclusion, and the dinitro complex ($RuNO(NO_2)_2OH(H_2O)_2$) appears to be highly extractable at low acid concentrations.

5.0.3 Experimental Approach

The experimental approach differed from that of the RuNO-nitrato complexes in that limited-depth

studies only were conducted. The type of experiments performed on the nitro complexes were the parameter variation experiments similar to those conducted on the nitrato complexes. However, the more definitive rapid dilution experiments were not made, although it is strongly recommended that future work on the RuNO-nitro complexes include that type of experiment.

5.1 Parameter Variation Experiments

5.1.1 Effect of Solution Age

5.1.1.1 Freshly Prepared Solutions

Extractions of most of the fresh solutions (age after dissolution of the dinitro compound in DDW approximately 1-2 hours) were made for a two-minute contacting time. The data are shown plotted in Figure 5.1. Of interest are several observations:

(1) From Figure 5.1, it appears that sodium nitrate salting decreases the extractability of the freshly prepared nitro complexes. However, by plotting the values of E_A° against the final organic phase unbound nitric acid concentration rather than the final aqueous phase nitric acid concentration, it can be seen (Figure 5.2) that actually the salting has no observable effect. The organic phase unbound nitric acid concentration was not determined

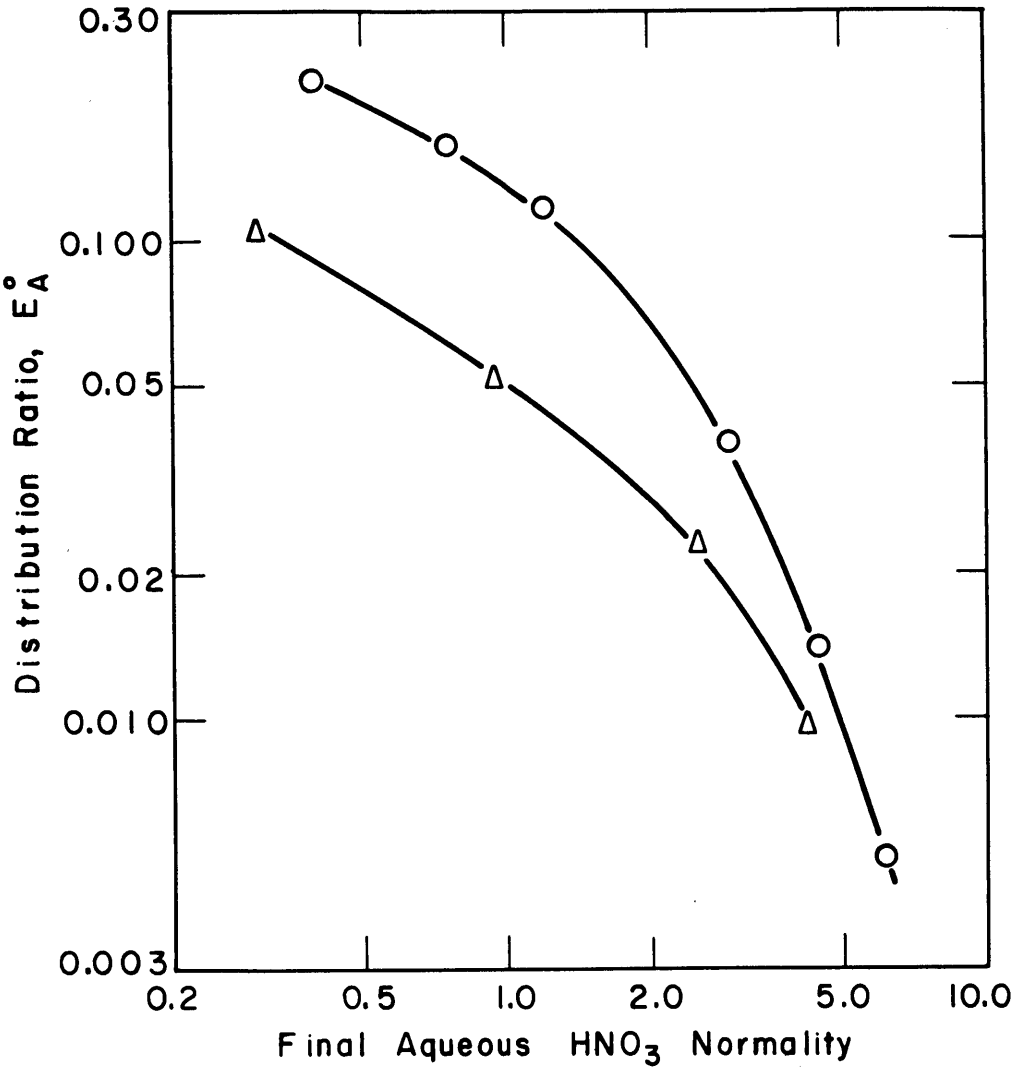

FIG. 5.1 EXTRACTION OF FRESHLY PREPARED RuNO-NITRO COMPLEXES
2-MINUTE CONTACTING AT 25°C WITH 0.26 M TLA IN TOLUENE
O = NITRIC ACID SYSTEM (NO SALTING)
Δ = NITRIC ACID–SODIUM NITRATE SYSTEM (TOTAL NITRATE = 6.3 M)

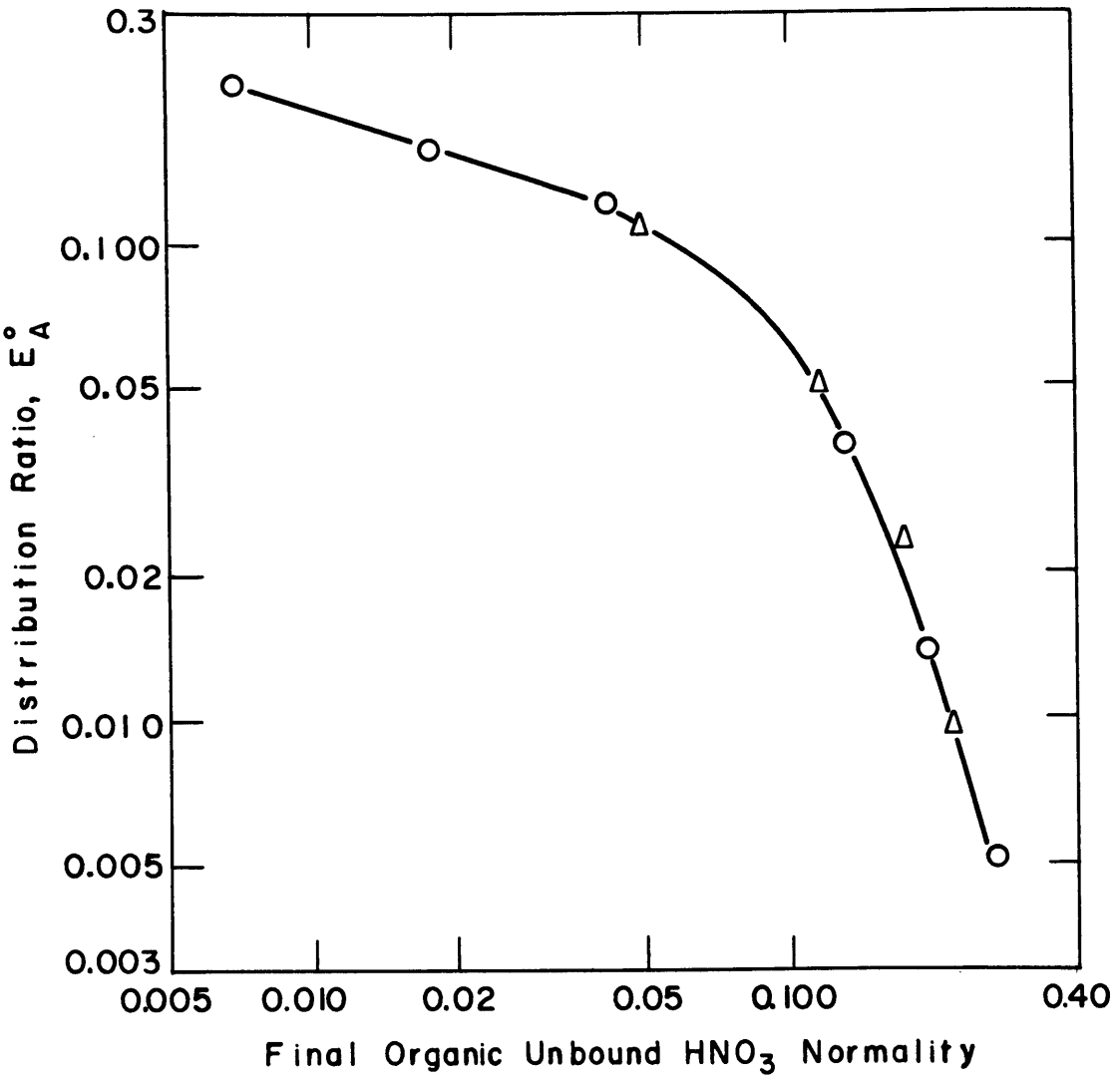

FIG. 5.2 EXTRACTION OF FRESHLY PREPARED RuNO-NITRO COMPLEXES
2-MINUTE CONTACTING AT 25°C WITH 0.26 M TLA IN TOLUENE
O = NITRIC ACID SYSTEM (NO SALTING)
Δ = NITRIC ACID - SODIUM NITRATE SYSTEM (TOTAL NITRATE = 6.3 M)

by organic phase titration of the samples but was obtained from Figure 4.8.

(2) The curve shows no maximum but decreases steadily with increasing aqueous nitric acid concentration. In fact, plotting the data on semi-log paper (Figure 5.3) yields a straight line that can be described empirically by $E_A^o = 0.25\ e^{-15N}$, where N is the organic phase unbound nitric acid normality.

(3) The freshly prepared RuNO-nitro complexes are more highly extractable as a whole than the freshly prepared RuNO-nitrato complexes, particularly at low acid concentration. Figure 5.4 shows the two systems plotted so as to enable comparison. At 0.5N HNO_3, the value of E_A^o for the nitro complexes is a factor of approximately 40 times that for the nitrato complexes.

There are two indications that only one species exists in the aqueous solutions at the freshly prepared solution age of 1-2 hours.

(1) The negligible effect of sodium nitrate salting indicates that no nitrate ligand substitution has taken place except for the possible immediate substitution for the hydroxyl ligand. This is consistant with the observed slow reaction rates of the nitro complexes described in Chapter III.

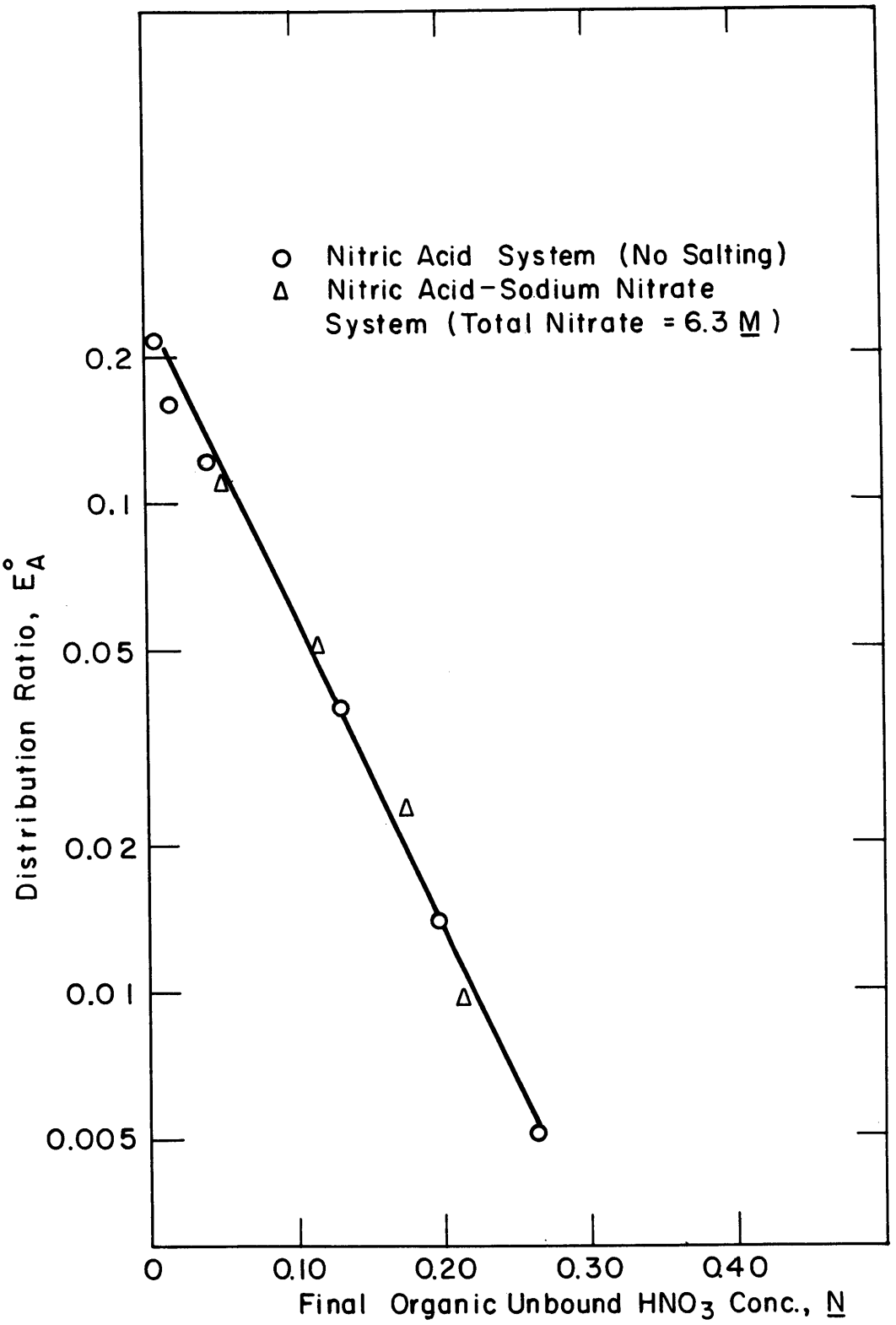

FIG. 5.3 EXTRACTION OF FRESHLY PREPARED RuNO-NITRO COMPLEXES 2-MINUTE CONTACTING AT 25° M TLA IN TOLUENE

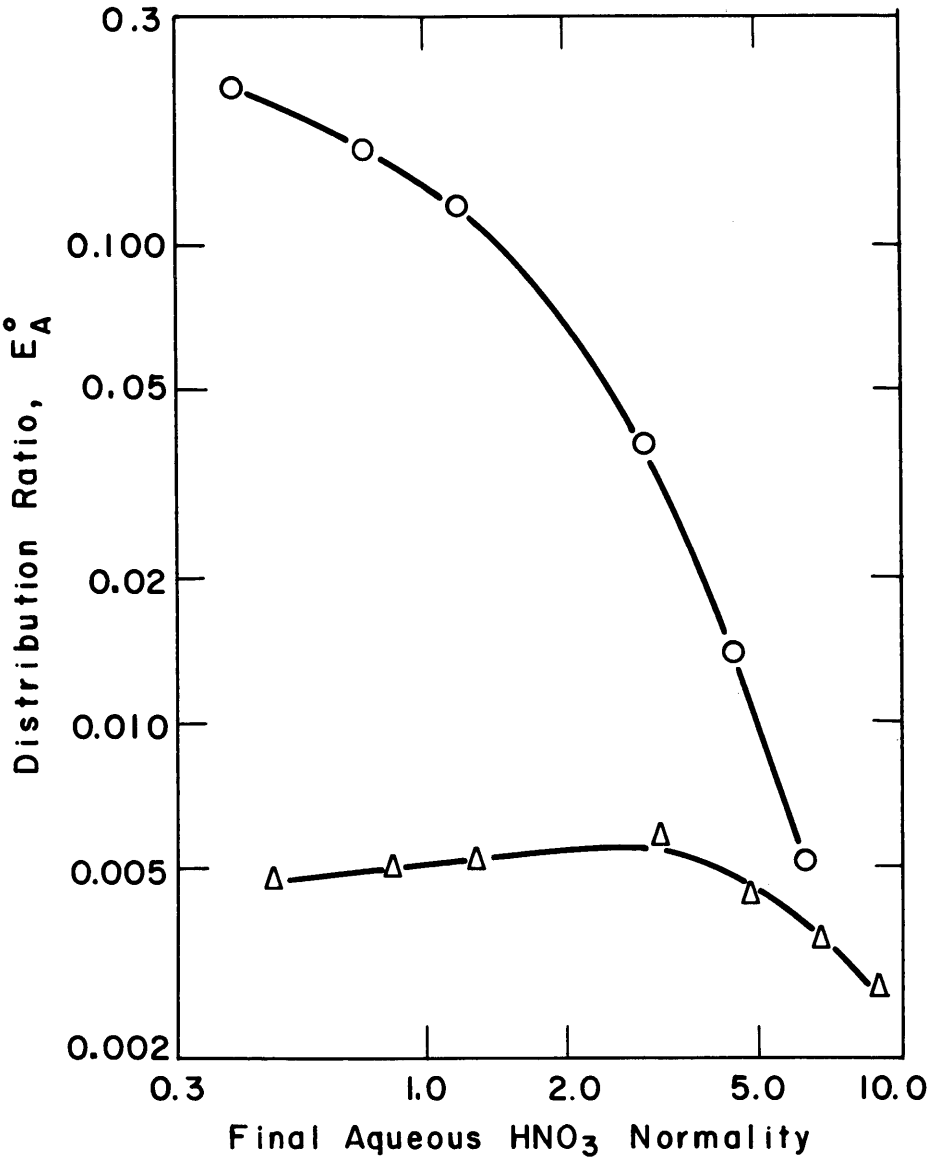

FIG. 5.4 EXTRACTION OF FRESHLY PREPARED RuNO-COMPLEXES
2-MINUTE CONTACTING AT 25°C WITH 0.26 M TLA IN TOLUENE
O = RuNO-NITRO COMPLEXES
Δ = RuNO-NITRATO COMPLEXES

(2) The straight-line dependence of E_A^o on acid concentration when plotted on semi-log paper (Figure 5.3) seems indicative of only one species since this type of behavior has the appearance displayed by the partition coefficients of Figure 4.23 and of the partition coefficients as calculated by Brown, et al (2). If there were more then one species and if the species had different partition coefficients, it would be unlikely that the observed values of E_A^o would display this straight line dependence since the values of E_A^o would be a function of the products of the mole fractions and partition coefficients. A more detailed discussion of the dependence of E_A^o on the number of species, the mole fractions of the species, and the partition coefficients of the species was presented in Section 4.1.2.

Of interest, also, is the data of Brown (1) for sodium nitrate salted solutions of the freshly prepared dinitro complex. Table 5.1 summarizes a portion of his data.

TABLE 5.1.

EXTRACTION OF FRESHLY PREPARED SOLUTIONS OF $RuNO(NO_2)_2OH(H_2O)_2$

Age of complex in solution approximately five minutes
Ru concentration 5×10^{-3}M, organic Phase = 30% TBP in kerosene
30-second equilibration at 20°C.

Aqueous Phase

HNO_3 Conc., N	$NaNO_3$ Conc., M	Distribution Ratio
1.0	---	1.70
1.0	4.5	1.20
3.0	----	0.506
3.0	2.5	0.215

Once again the apparent effect of nitrate salting is to reduce extractability. However, as a result of the work performed at MIT, it is suggested that if the above data were correlated as a function of organic phase unbound nitric acid concentration, the effect of sodium nitrate salting would be seen to be negligible, similar to Figure 5.3.

5.1.1.2 Aged Solutions

After aging at room temperature for one month, a set of extractions was made for two-minute

contacting of the aged solutions with the acid and nitrate concentrations in the samples the same as those for the freshly prepared solutions. The data are shown plotted as a function of final aqueous nitric acid concentration in Figure 5.5 and as a function of final organic unbound nitric acid concentration in Figure 5.6.

From Figure 5.6, it is seen that after aging for one month, the sodium nitrate salting has had the effect of increasing the extractability of the complexes. Although the rate of ligand substitution is very slow and after only one month of aging the amount of nitrato complexes existing in solution is probably very small, the formation of even a small amount of the relatively much more extractable tetra-and penta-nitrato complexes could account for the observed increase in extractability.

Of interest is the point (in Figure 5.6) at which the line of the salted sample merges with the line of the non-salted samples. The intersection is not at the organic phase excess acid concentration corresponding to 6.3N HNO_3 in the aqueous phase, but at a lower point. This is consistent with the previous discussion of the spectra of salted RuNO-nitrato complexes solutions in Chapter III and indicates again that nitrate in

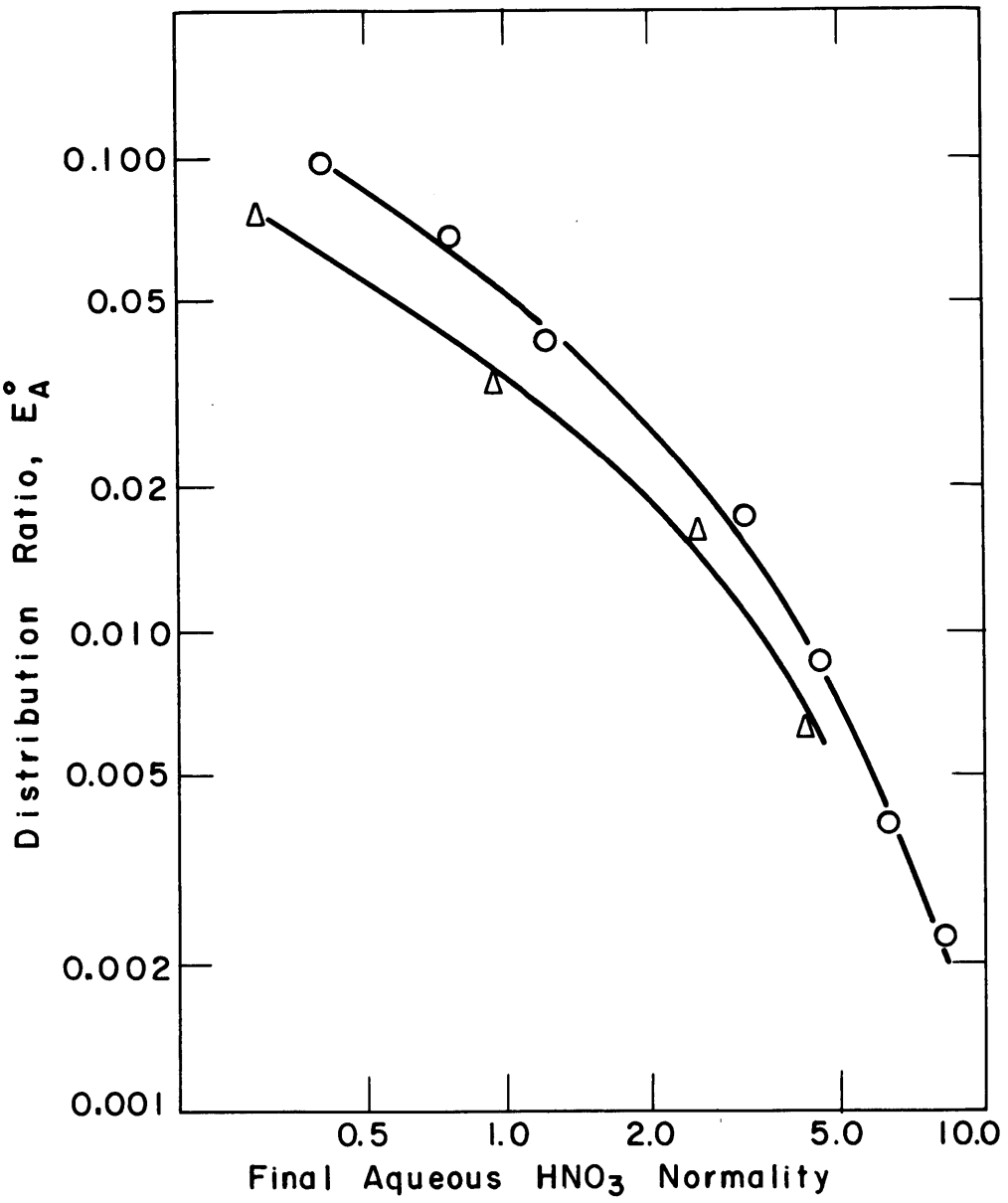

FIG. 5.5 EXTRACTION OF AGED RuNO-NITRO COMPLEXES
SOLUTIONS AGED FOR ONE MONTH AT ROOM TEMPERATURE
2-MINUTE CONTACTING AT 25°C WITH 0.26 M TLA IN TOLUENE
O = NITRIC ACID SYSTEM (NO SALTING)
Δ = NITRIC ACID–SODIUM NITRATE SYSTEM (TOTAL NITRATE = 6.3 M)

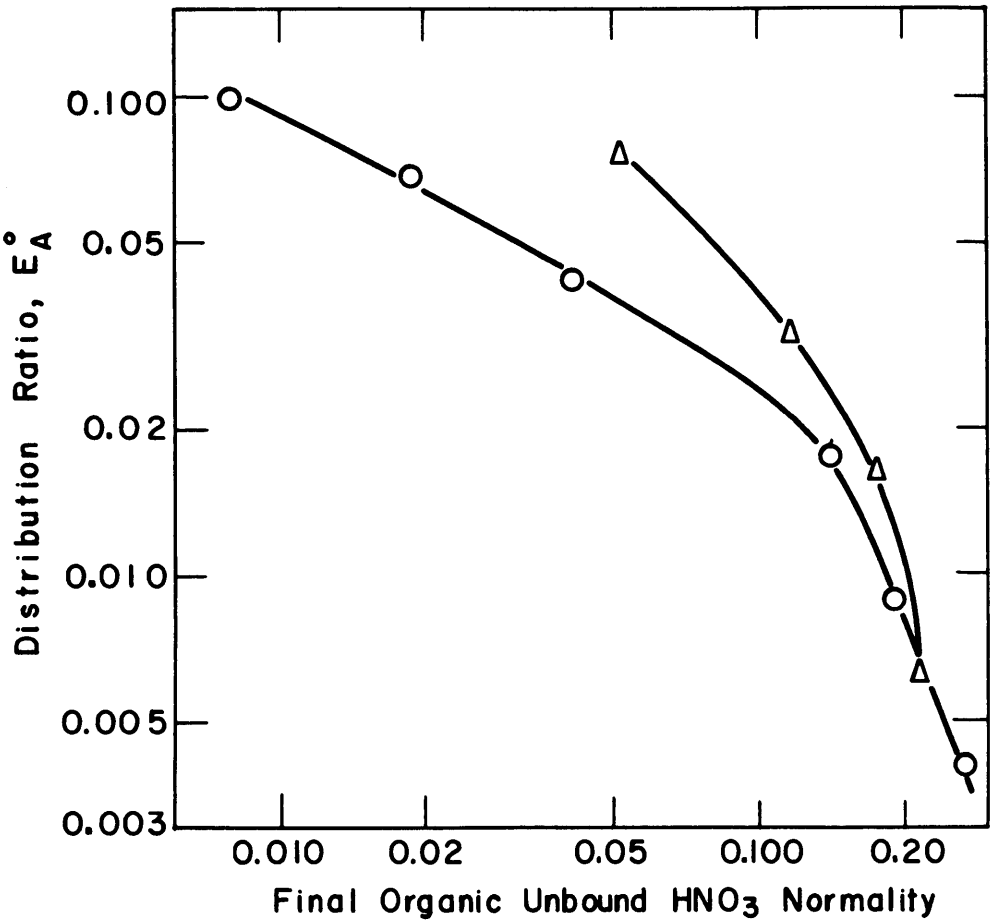

FIG. 5.6 EXTRACTION OF AGED RuNO-NITRO COMPLEXES
SOLUTIONS AGED FOR ONE MONTH AT ROOM TEMPERATURE
2-MINUTE CONTACTING AT 25°C WITH 0.26 M TLA IN TOLUENE
O = NITRIC ACID SYSTEM (NO SALTING)
Δ = NITRIC ACID SODIUM NITRATE SYSTEM (TOTAL NITRATE = 6.3 M)

the form of nitric acid is more effective with regard to nitrato complexing than is nitrate in the form of sodium nitrate. This indicates that the tetra- and penta-nitrato complexes exist in solution in the form of the acids of the species ($HRuNO(NO_3)_4(H_2O)$ and $H_2RuNO(NO_3)_5$) rather than as anions ($RuNO(NO_3)_4(H_2O)^-$ and $RuNO(NO_3)_5^=$). If the complexes existed in aqueous solution as the anionic species, then it would be expected that sodium nitrate would be a more effective complexing agent than nitric acid, since the sodium nitrate would be more highly dissociated then the nitric acid and would therefore yield a higher concentration of the nitrate complexing ligand. Since the reverse case is observed, and a lesser degree of dissociation appears to increase complexing, then it would indicate that the complexing ligand is the undissociated nitric acid molecule (HNO_3) rather than the dissociated nitrate ion (NO_3^-).

Comparison of the aged RuNO-nitro complexes with the freshly prepared RuNO-nitro complexes (Figure 5.7) shows that aging has resulted in decreasing the extractability of the complexes, although it appears that at an acid concentration of approximately 7N HNO_3 and higher that the extractability may be the same or may have been increased. The decrease in extractability is

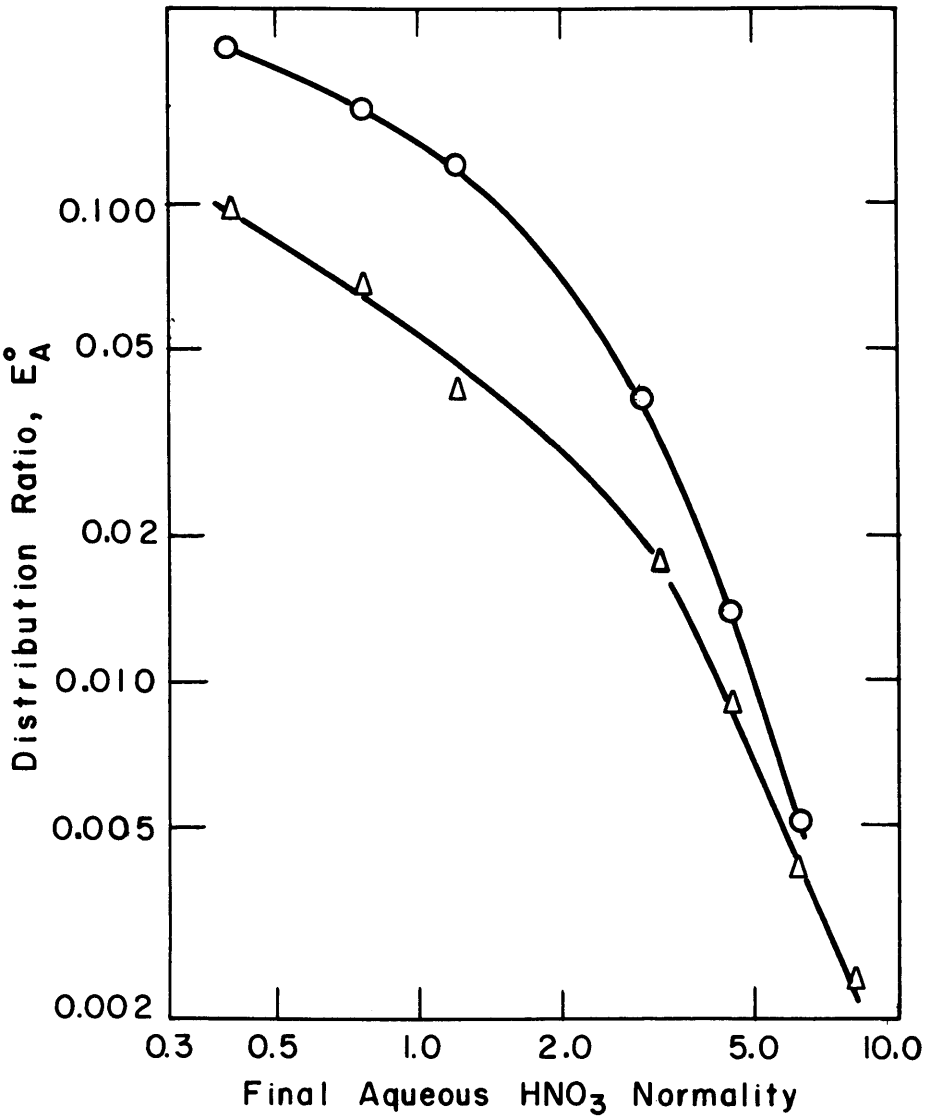

FIG. 5.7 THE EFFECT OF SOLUTION AGE ON EXTRACTION OF RuNO-NITRO COMPLEXES 2-MINUTE CONTACTING AT 25°C WITH 0.26 M TLA IN TOLUENE

O = FRESHLY PREPARED SOLUTIONS
Δ = SOLUTIONS AGED FOR ONE MONTH AT ROOM TEMPERATURE

thought to be due to the formation of nitro-nitrato complexes and/or lower (less than tetra-) nitrato complexes which are believed to be less extractable than either the higher nitrato complexes or the nitro species initially in solution.

In Figure 5.8 are plotted the values of E_A^o as a function of final organic nitric acid concentration for aged (one month) RuNO-nitro complexes for a 24-hour contacting time. By comparison with Figure 5.6 it can be seen that for the salted solutions the rate of increase of E_A^o with contacting time is greater than that of the non-salted solutions. For instance, at a final organic HNO_3 concentration of 0.060M, the values of E_A^o for the non-salted solutions are 0.035 and 0.095 for the two-minute contacting and 24-hour contacting respectively; a ratio of 2.71. The corresponding values for the salted solutions are 0.066 and 0.340, or a ratio of 5.15. This again is consistent with the previously mentioned difference of rates of reaction and redistribution between the RuNO-nitrato complexes and RuNO-nitro complexes. This difference is shown more clearly in Figures 5.9 and 5.10. Figure 5.9 shows the values of E_A^o for the non-salted aged RuNO-nitro complexes for the two-minute and 24-hour contacting times plotted so as to enable comparison. Figure 5.10 shows the value of the ratio

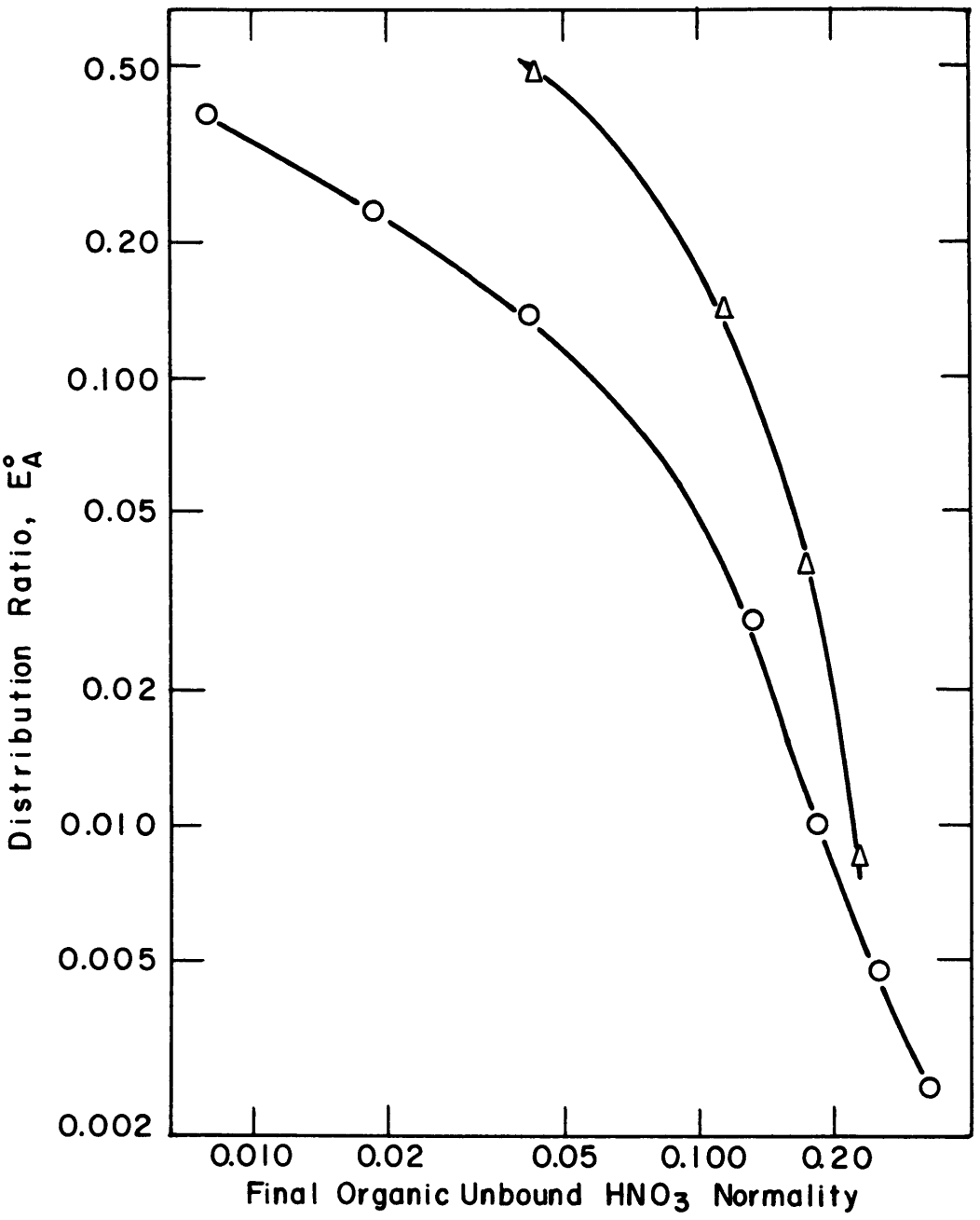

FIG. 5.8 EXTRACTION OF AGED RuNO-NITRO COMPLEXES SOLUTIONS AGED FOR ONE MONTH AT ROOM TEMPERATURE
24-HOUR CONTACTING AT 25°C WITH 0.26 M TLA IN TOLUENE
O = NITRIC ACID SYSTEM (NO SALTING)
Δ = NITRIC ACID-SODIUM NITRATE SYSTEM (TOTAL NITRATE = 6.3 M)

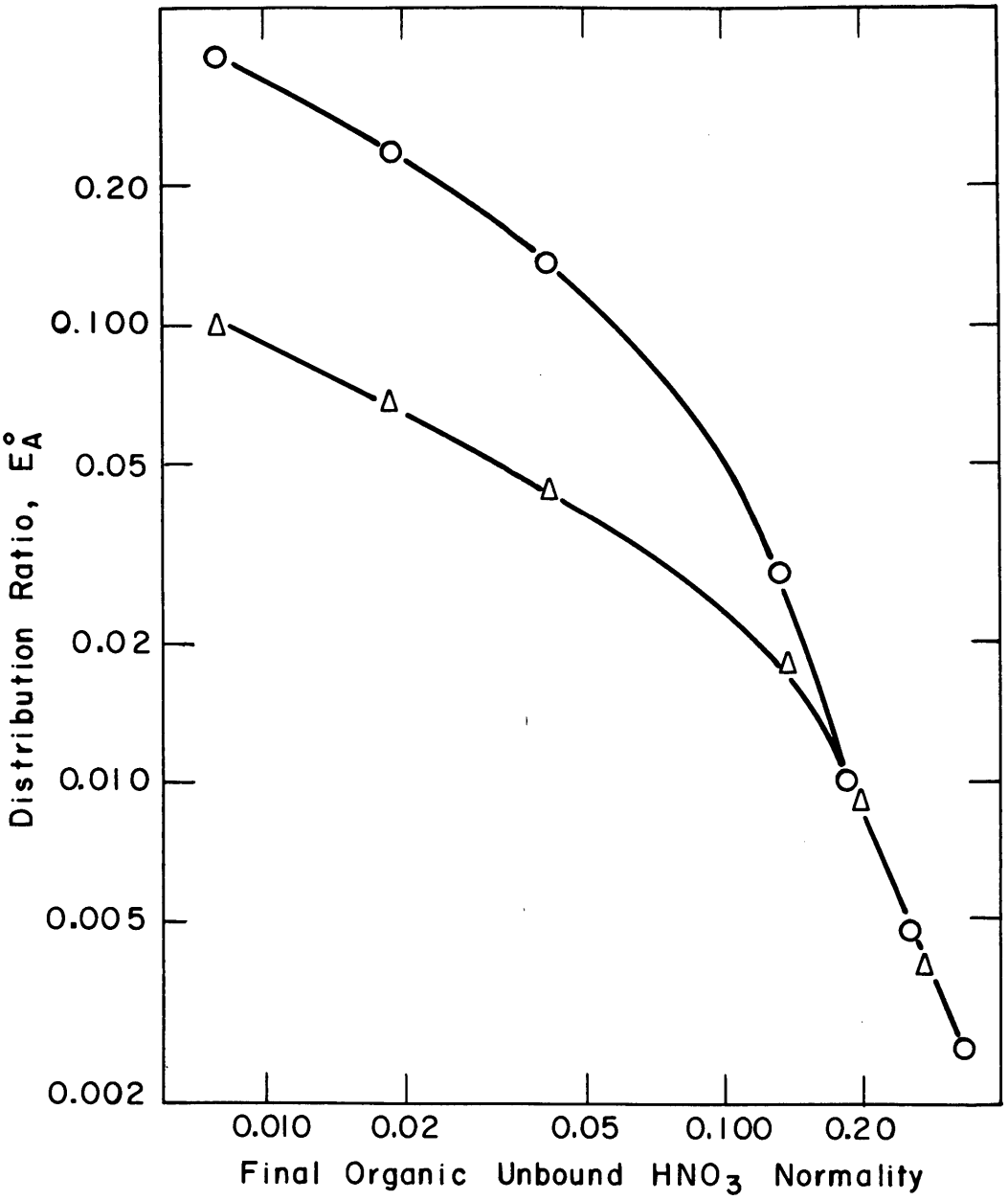

FIG. 5.9 THE EFFECT OF CONTACT TIME ON THE EXTRACTION OF RuNO-NITRO COMPLEXES
SOLUTIONS AGED FOR ONE MONTH AT ROOM TEMPERATURE 0.26 M TLA IN TOLUENE
Δ = 2 MINUTE CONTACTING AT 25°C
O = 24 HOUR CONTACTING AT 25°C

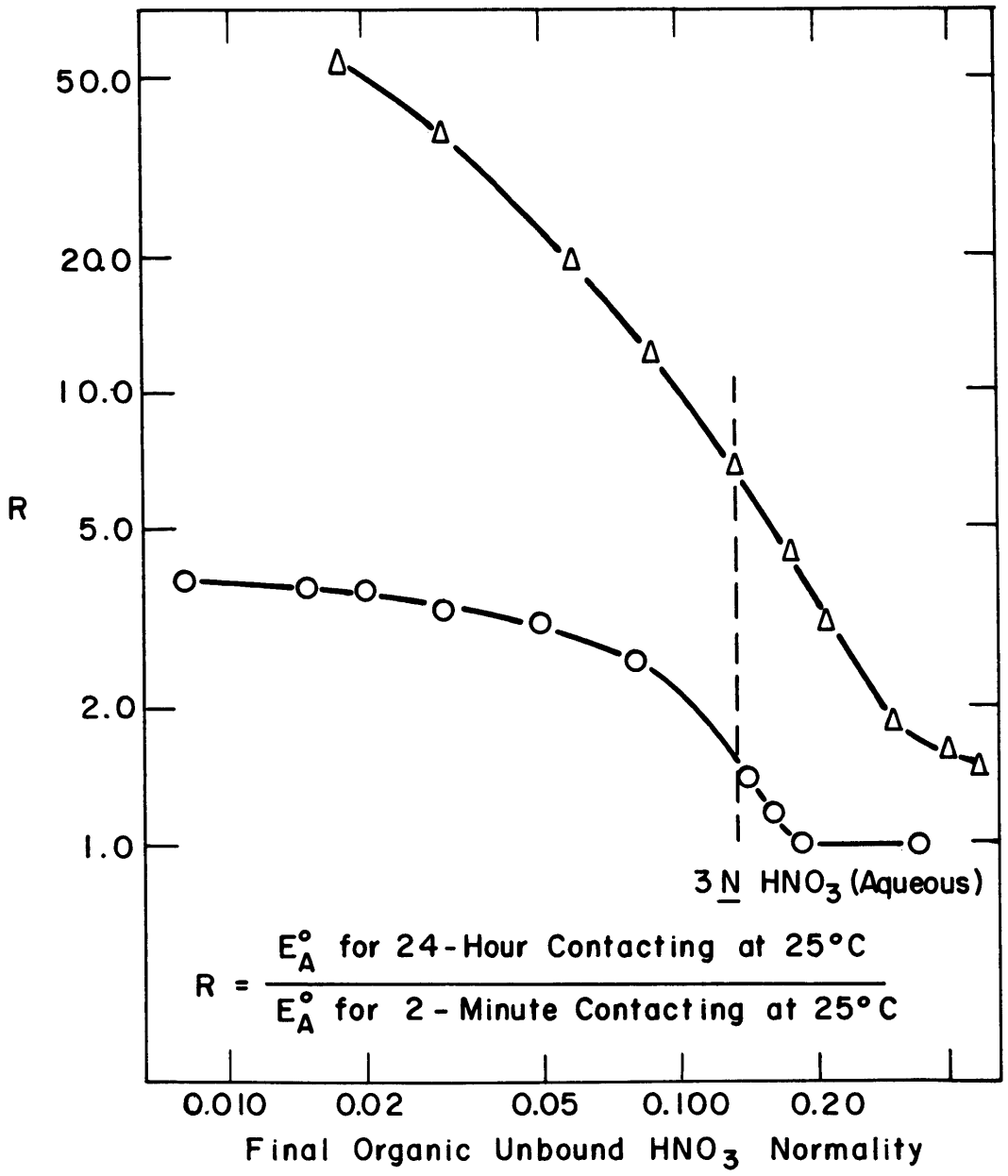

FIG. 5.10 THE EFFECT OF CONTACT TIME ON THE EXTRACTION OF RuNO-NITRO AND RuNO-NITRATO COMPLEXES

SOLUTIONS AGED FOR ONE MONTH AT ROOM TEMPERATURE 0.26 M TLA IN TOLUENE

O = RuNO-NITRO COMPLEXES

Δ = RuNO-NITRATO COMPLEXES

NO SALTING

(R) of the E_A^o values at 24 hour contacting to the E_A^o values at 2 minutes contacting as a function of final organic HNO_3 concentration for the aged (one month) RuNO-nitrato complexes and the aged (one month) RuNO-nitro complexes. The organic phase nitric acid concentration corresponding to an aqueous phase concentration of 3M HNO_3 is marked for reference purposes. It should be noted that since the RuNO-nitro complexes are very slow (compared to the RuNO-nitrato complexes) in approaching equilibrium in the aqueous phase, the aged RuNO-nitro solutions will be labelled as to the length of the aging time. Whereas for the RuNO-nitrato complexes there exists no appreciable difference in solution composition at ages of one month or six months, it has been shown (Figure 3.12) that the RuNO-nitro complexes are still in a process of change at an age of four months and possibly even at 5 1/2 months.

5.1.2 Effect of Nitrate Salting Concentration

Following the method employed in Chapter IV, the values of E_A^o for 24-hour contacting of the aged (one month) RuNO-nitro complexes are plotted in Figure 5.11 as a function of final organic unbound nitric acid concentration for constant total aqueous nitrate concentrations of 1.2M, 3M, 5M, and 6.3M.

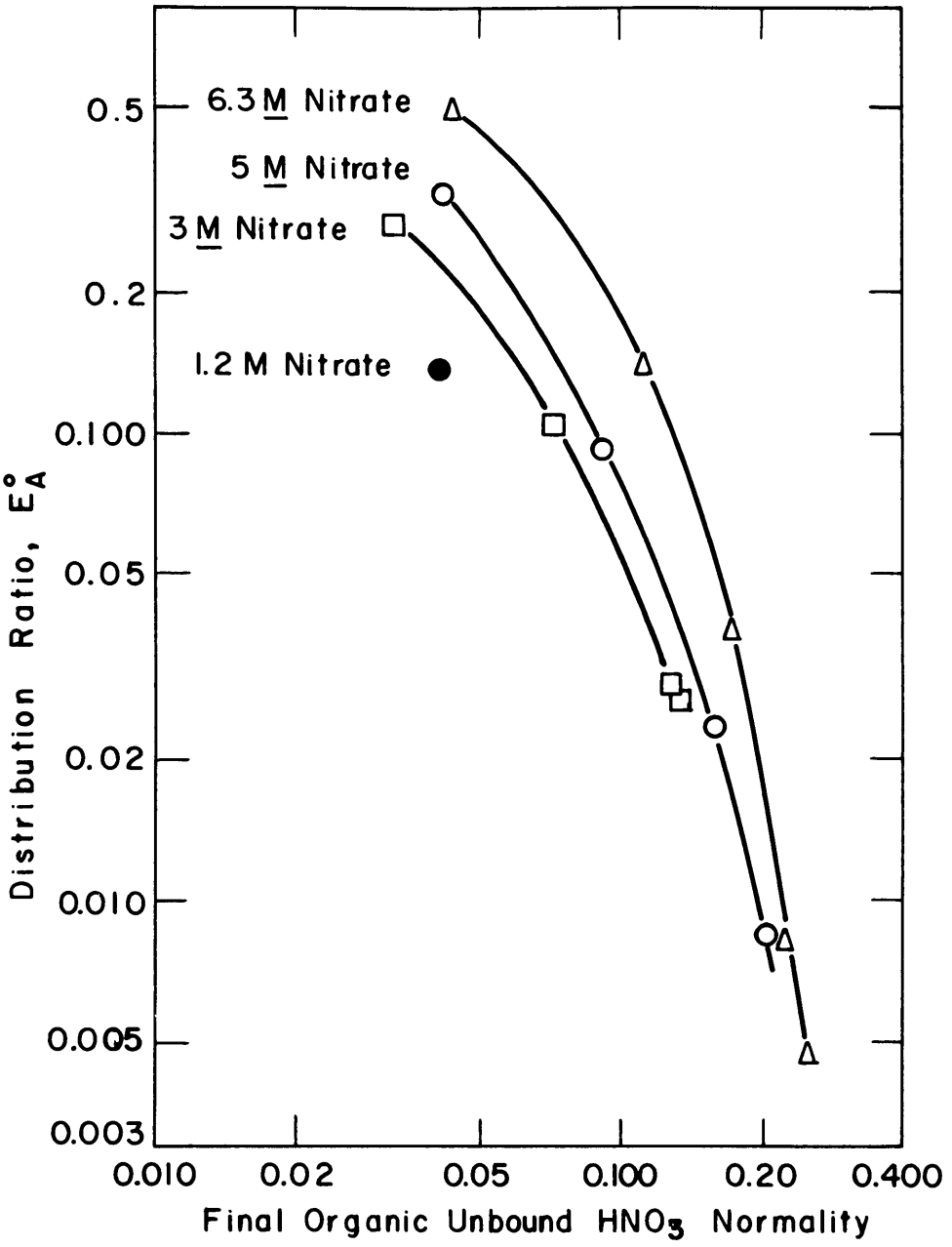

FIG. 5.11 THE EFFECT OF SODIUM NITRATE SALTING ON EXTRACTION OF RuNO-NITRO COMPLEXES
SOLUTIONS AGED FOR ONE MONTH AT ROOM TEMPERATURE
24-HOUR CONTACTING AT 25°C WITH 0.26 M TLA IN TOLUENE

Cross plotting from Figure 5.11 gives Figure 5.12, where the values of E_A^o are plotted as a function of total aqueous nitrate concentration for constant organic unbound nitric acid concentrations.

From Figure 5.12, it appears that the distribution ratio varies as the 0.8 to 4.7 power of the total aqueous nitrate concentration. A particularly strong function of total nitrate concentration seems to be apparent in the small range of 5M to 6.3M total nitrate. However, as was shown in Section 5.1.1.2, the rate of increase of E_A^o with contacting time is greater for the salted solutions (6.3M total nitrate) than for the non-salted solutions.

Therefore, in order to obtain a better idea of the dependence of E_A^o on total aqueous nitrate concentration, the dependence on contact time should be eliminated as much as possible. This can be accomplished by plotting the values of E_A^o for the two-minute contacting time. Cross plotting from Figure 5.6 yields Figure 5.13 which shows the values of E_A^o for two minute contacting of aged solution at the non-salted conditions and the salted condition of 6.3M total aqueous nitrate concentration. The values of E_A^o for the intermediate salted solutions are not plotted because those data points were taken only for the 24 hour contacting time and not for the two minute contacting time.

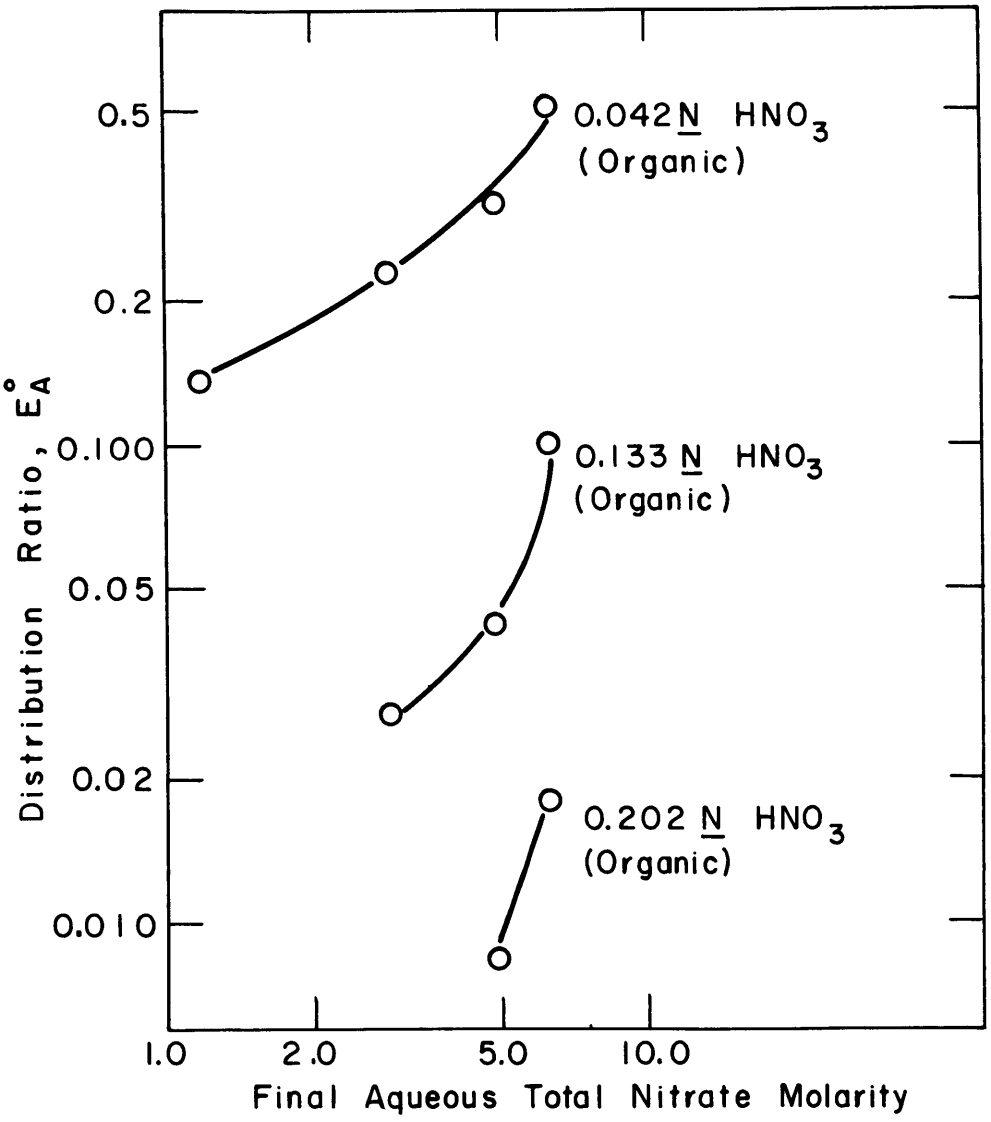

FIG. 5.12 THE EFFECT OF SODIUM NITRATE SALTING ON EXTRACTION OF RuNO-NITRO COMPLEXES SOLUTIONS AGED FOR ONE MONTH 24-HOUR CONTACTING AT 25°C WITH 0.26 M TLA IN TOLUENE

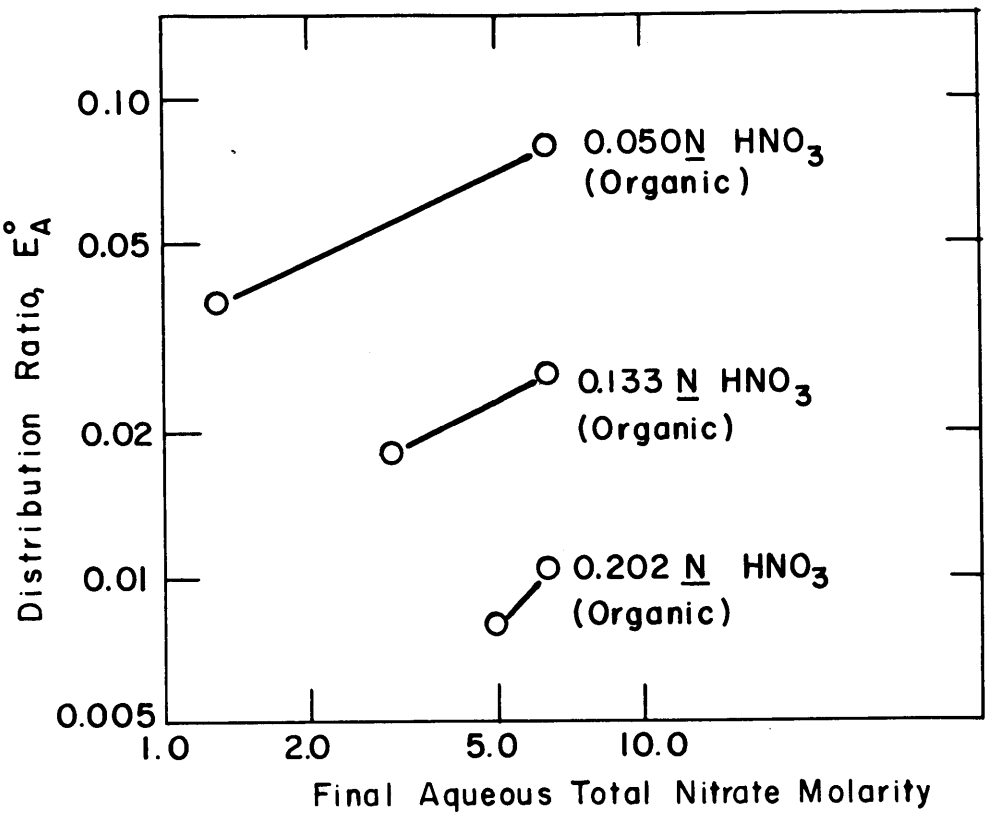

FIG. 5.13 THE EFFECT OF SODIUM NITRATE SALTING ON EXTRACTION OF RuNO-NITRO COMPLEXES 2-MINUTE CONTACTING OF ONE MONTH AGED SOLUTIONS AT 25°C WITH 0.26M TLA

From Figure 5.13, the value of E_A^o is seen to be dependent upon the 0.4 to 0.8 power of the total aqueous nitrate concentration. The actual exponent is probably closer to 0.4 than 0.8, since the slope of 0.8 is a result of two closely spaced points and a small error in their values could result in a large error in the slope of the line drawn through them.

5.1.3 Effect of Ruthenium Concentration

In Figure 5.14 are plotted the values of the final organic ruthenium concentration as a funtion of final aqueous ruthenium concentration for the RuNO-nitro complexes aged for two months. The aqueous ruthenium concentrations were varied at two different levels of acid concentrations. Both studies show the final organic ruthenium concentration to be dependent upon the 1.2 power of the final aqueous ruthenium concentration in the range of final aqueous ruthenium concentrations of from about 0.2 gm/liter to 5 gm/liter. This power dependence of greater than unity could possibly be due to polymeric species and in order to investigate this possibility, a series of spectra measurements was performed to determine if the spectra changed as a function of aqueous ruthenium concentration.

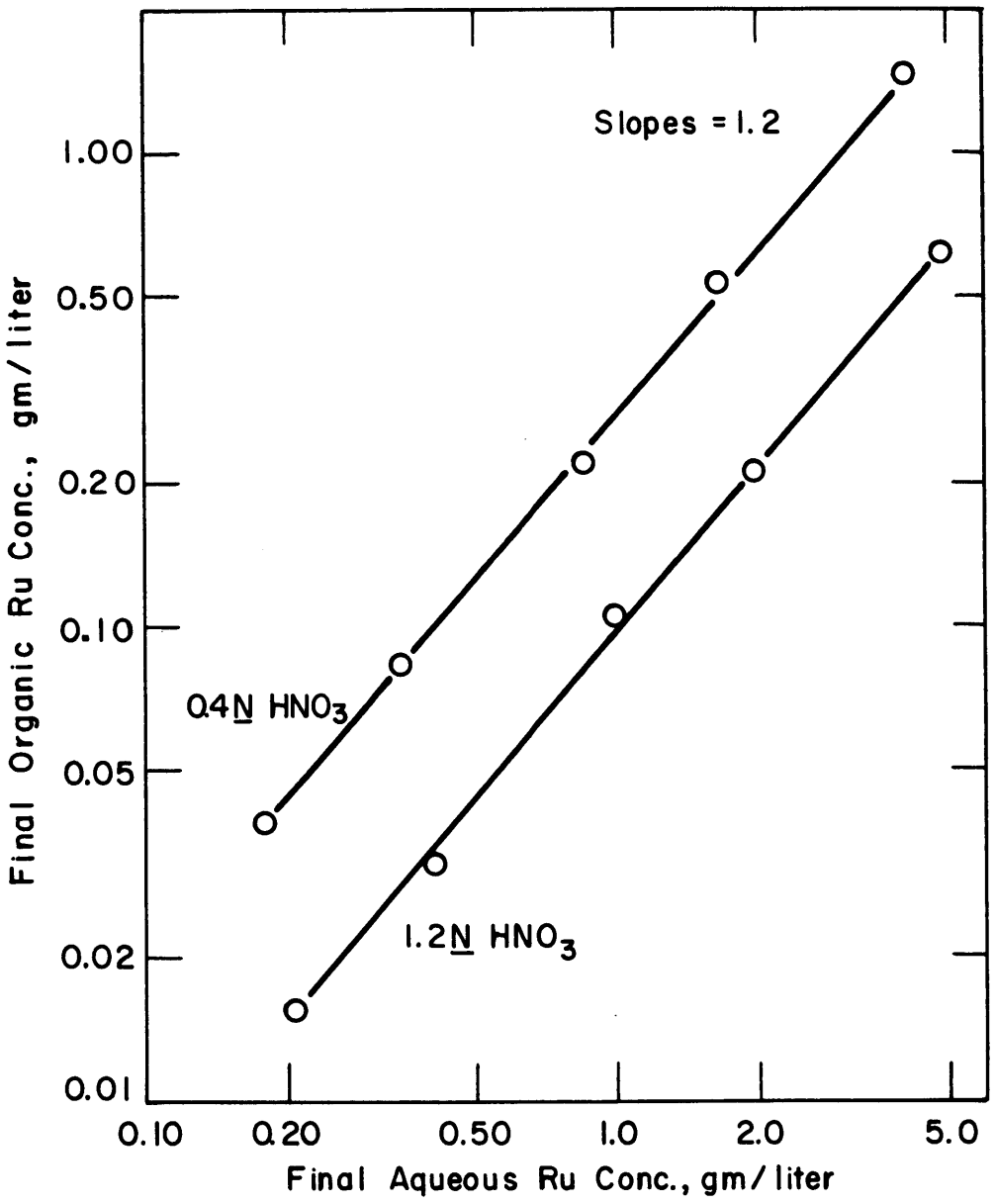

FIG. 5.14 THE EFFECT OF AQUEOUS RUTHENIUM CONCENTRATION ON EXTRACTION OF RuNO - NITRO COMPLEXES
SOLUTIONS AGED FOR TWO MONTHS AT ROOM TEMPERATURE
24 - HOUR CONTACTING AT 25°C WITH 0.26 M TLA IN TOLUENE

The measurements were made on 1.2N HNO_3 solutions of RuNO-nitro complexes. This solution was chosen for two reasons:

(1) The spectra of the 1.2N HNO_3 solution changes very little with solution age (see Figure 3.12).

(2) The value of 1.2N HNO_3 falls within the range of acid concentrations that displayed the dependence of the value of E_A^o on the 1.2 power of aqueous ruthenium concentration (see Figure 5.14).

Figure 5.15 shows the spectra for 1.2N HNO_3 solutions with aqueous ruthenium concentrations of 0.22, 0.44, 1.09, and 2.17 gm/liter. The solution had been diluted from the original stock solution concentration of 5.43 gm/liter with 1.2N HNO_3 after the stock solution had aged for two months. The diluted solutions were aged for two weeks before the extractions were made and the spectra taken. The spectra appear to be very regular with regard to one another and do not display any noticeable variations other than the expected decrease of absorbance with decreasing ruthenium concentration. In fact, the value of the absorbance at the maximum (480 mμ) varies linearly with concentration as shown by Figure 5.16. Visual inspection of Figure 5.15 shows that the linearity holds true at the lowest wave length measured (400 mμ), the highest wave length

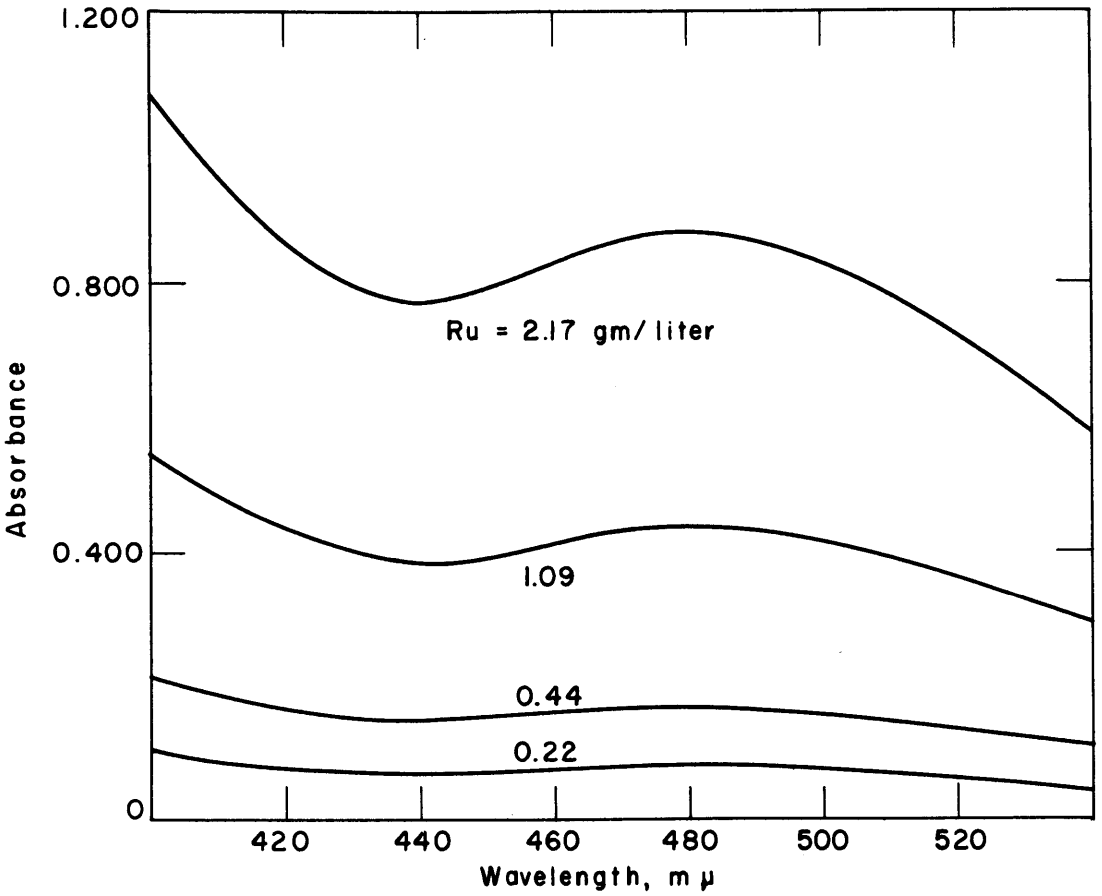

FIG. 5.15 THE EFFECT OF AQUEOUS RUTHENIUM CONCENTRATION ON ABSORPTION SPECTRA OF RuNO-NITRO COMPLEXES SOLUTIONS AGED FOR TWO MONTHS AT ROOM TEMPERATURE IN 1.2 N HNO_3 BECKMAN MODEL DU SPECTROPHOTOMETER, SLIT WIDTH = 0.30 mm

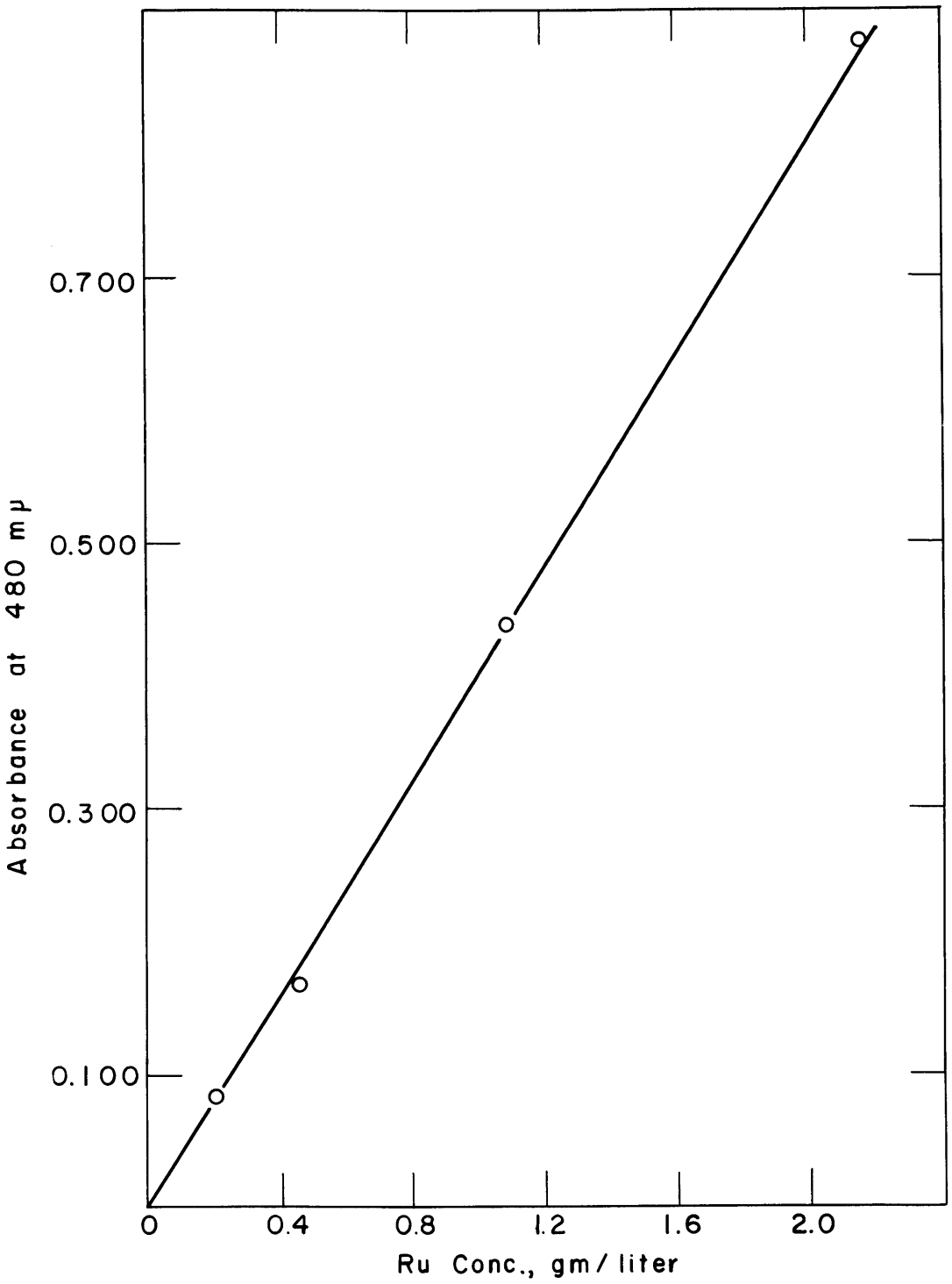

FIG. 5.16 THE EFFECT OF AQUEOUS RUTHENIUM CONCENTRATION ON ABSORPTION SPECTRA OF RuNO-NITRO COMPLEXES

SOLUTIONS AGED FOR TWO MONTHS AT ROOM TEMPERATURE IN 1.2N HNO_3 BECKMAN MODEL DU SPECTROPHOTOMETER, SLIT WIDTH = 0.30 mm

measured (540 mμ), and at the position of the minimum (440 mμ).

Although the regularity of the spectra cannot be considered proof of a lack of polymeric species, it is probable either that any polymeric species that exist do so in very small concentrations or that some other phenomenon, such as self-salting, is the cause of the observed 1.2 power dependence.

5.1.4 Effect of Amine Concentration

In a similar fashion to the aged nitrato complexes, the distribution ratio of aged (two months) RuNO-nitro complexes increases initially with the 1.2 power of the amine concentration and then tapers off to a lower power dependence above an amine concentration of about 0.13M, as shown by Figure 5.17.

5.2 Discussion of Results

The result of primary importance is the establishment of the stability and relatively high extractability of the dinitro complex. ($RuNO(NO_2)_2(OH)(H_2O)_2$). The latter two properties suggest that under actual process conditions, the nitro complexes in general, and perhaps the dinitro complex in particular, are the cause of the poor ruthenium decontamination.

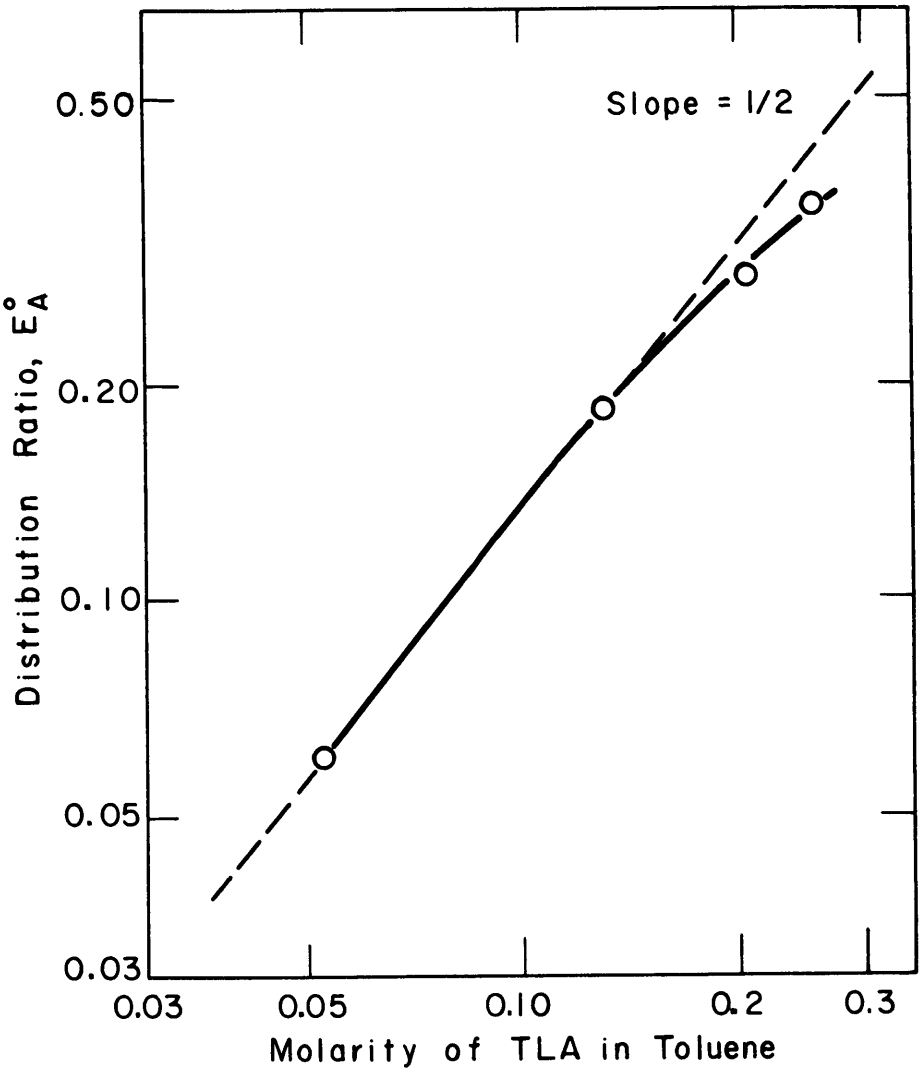

FIG. 5.17 THE EFFECT OF AMINE CONCENTRATION ON EXTRACTION OF RuNO-NITRO COMPLEXES
SOLUTION AGED FOR TWO MONTHS AT ROOM TEMPERATURE
24-HOUR CONTACTING AT 25°C WITH 0.4 N HNO_3 AQUEOUS
SOLUTION OF RuNO-NITRO COMPLEXES

The results of both the spectra studies and the extraction studies indicate that the nitro complexes slowly transform into the nitrato complexes. It was not determined, however, through what intermediate compounds and/or complexes the process proceeds.

VI CONCLUSIONS AND RECOMMENDATIONS

6.0 Nitrosyl Ruthenium Nitrato Complexes

6.0.1 Conclusions

The major conclusions derived as a result of the studies performed on the nitrato complexes are:

(1) The more extractable species are the tetra-nitrato and penta-nitrato complexes, the latter being the more highly extractable of the two.

(2) The species are extracted into the organic phase, and may exist, either wholly or in part, in the aqueous phase as the acids of the complexes rather than as the anions.

(3) The proportion of the extractable species in equilibrium in aqueous nitric acid solutions relative to the non-extractable species is very small at low acid concentrations and increases somewhat linearily with increasing nitric acid concentration.

(4) The species denitrate to lower nitrato complexes upon dilution of the acid concentration, the penta-nitrato acid complex doing so at a faster rate than the tetra-nitrato acid complex.

6.0.2 Recommendations

The major recommendations for future work on the RuNO-nitrato complexes are:

(1) An attempt should be made to try to resolve the difference between the values of Fletcher's Group D mole fractions and the sum of the values of the mole fractions of the tetra- and penta-nitrato complexes determined at MIT.

(2) Extractions should be made of the rapid dilution type using other organic phase extractants to see if the same type of correlation would yield supporting evidence for the amount of complexes in solution and the dependence of the amount on stock solution acid concentration. (Studies of this type are in progress at MIT using Primene JMT and Aliquat 336 as the extractants. The two amines are a primary and a quaternary, respectively).

(3) Other parameter variation experiments, such as the effect of temperature and the effect of impurities concentration and type, should be performed to more fully understand the solution chemistry and solvent extraction characteristics of the complexes.

6.1 Nitrosyl Ruthenium Nitro Complexes

6.1.1 Conclusions

The major conclusions derived as a result of the studies performed on the nitro complexes are:

(1) The rates of reaction for ligand substitution of the complexes are very slow compared to the nitrato complexes.

(2) The dinitro complex, in particular, is very stable and relatively highly extractable. It may possibly be the controlling agent in ruthenium decontamination of spent nuclear fuel processing.

(3) In nitrate solutions, the nitro complexes very slowly change to the nitrato complexes, changes in the spectra being observed even after 4-5 1/2 months of aging.

6.1.2 Recommendations

The major recommendations for future work on the RuNO-nitro complexes are:

(1) Experiments of the rapid dilution type, with the subsequent correlation, should be made to more fully investigate the number of extractable species and the amount and extractibility of species as functions of solution age and acid concentration.

(2) Other parameter variation experiments should also be performed in order to more fully understand the solution chemistry and extraction characteristics of the nitro complexes.

(3) Other nitro complexes should be investigated, as well as the dinitro complex.

(4) Other organic phase extractants should be investigated.

(5) To improve ruthenium decontamination of spent nuclear fuels, conditions leading to formation of $NO-NO_2$ gases and use of sodium nitrite should be minimized.

6.2 The Solvent Extraction Process In General

The importance of the concentration of organic phase unbound nitric acid and/or aqueous phase nitric acid activity has been indicated. It would be of interest to attempt to establish the limits of this field of importance regarding type of metal being extracted, organic phase extractant, aqueous phase acid, and other parameters of the solvent extraction process in general.

It should be established whether this phenomenon is fundamental to solvent extraction in general or whether it is peculiar to certain isolated systems.

VII APPENDIX

7.0 General Procedures

7.0.1 Preparation of the Organic Phase

The TLA was purchased as No. 7727 Tridodecylamine from Distillation Products Industries, Rochester, New York and was used in the "as received" condition.

The TLA was first dissolved in reagent grade toluene at a known volume per cent and the solution titrated with $HClO_4$ to determine the molarity. From the measured relationship between volume percent and molarity, the stock solution of 0.26M TLA was prepared. A concentration of 16% is equivalent to 0.26M. The amine stock solution was stored in an amber-colored glass bottle (one gallon size) with a screw cap lined with 0.002 inch Teflon film. All of the aqueous stock solutions, precontacted amine solutions, and both phases of all separated extraction samples were stored in dark amber bottles with screw caps lined with Teflon film.

The amine concentration was varied by volumetric dilution of the stock amine solution with reagent grade

toluene prior to precontacting with nitric acid.

Pretreatment of the amine was accomplished by contacting with an equal volume of nitric acid of a concentration of 0.3-0.4N greater than the desired final aqueous nitric acid concentration. After precontacting in a separatory funnel, the aqueous phase was drained off and the organic phase was centrifuged to complete phase separation. The organic phase was then decanted from the centrifuge tubes into amber bottles for storage. The precontacted amine solutions were used in extractions within one week subsequent to the precontacting.

7.0.2 Equilibration and Separation of Phases

The extractions were performed in round bottom 50 ml centrifuge tubes with screw caps, Corning No. 8422. The cap was lined with 0.002 inch Teflon film.

Twenty milliliters of the aqueous phase was placed carefully in the tube, following by an equal volume of organic phase. The organic phase was run down the wall of the tube to minimize pre-contacting of the phases. The tube was capped and placed in the constant temperature bath at an angle of 45° for a few minutes then submerged in the bath in an horizontal position and the shaking action started. After the requisite shaking time (one minute to 29 days, but

usually 24 hours) the shaker was stopped and the tube removed and put into the centrifuge for rapid and complete phase separation.

After centrifugation, the tube was placed vertically in a clamp, and the organic layer was withdrawn by suction through a narrow diameter glass probe directly into the sample bottle. (See Figure 7.1). The clamped tube was lowered on the ring stand to remove this probe and a second probe inserted by hand. The remaining droplets of organic phase were sought out and removed individually along with a few milliliters of aqueous phase solution and sent to the waste container. The organic sample bottle was removed and capped. The aqueous phase was either (1) removed by a probe similar to the organic phase sample, or (2) poured into the sample bottle directly and the scavenger probe used to remove any droplets of organic from the sample bottle.

7.0.3 Organic Phase Acid Determination

The organic phase titrations were performed directly by dissolving a small sample of the organic phase (about 1-5 ml) in approximately 400 ml of acetone, titrating against an aqueous NaOH solution (about 0.02-0.09N), and following the titration potentiometrically with a Beckman "Zeromatic" pH meter. The end point was

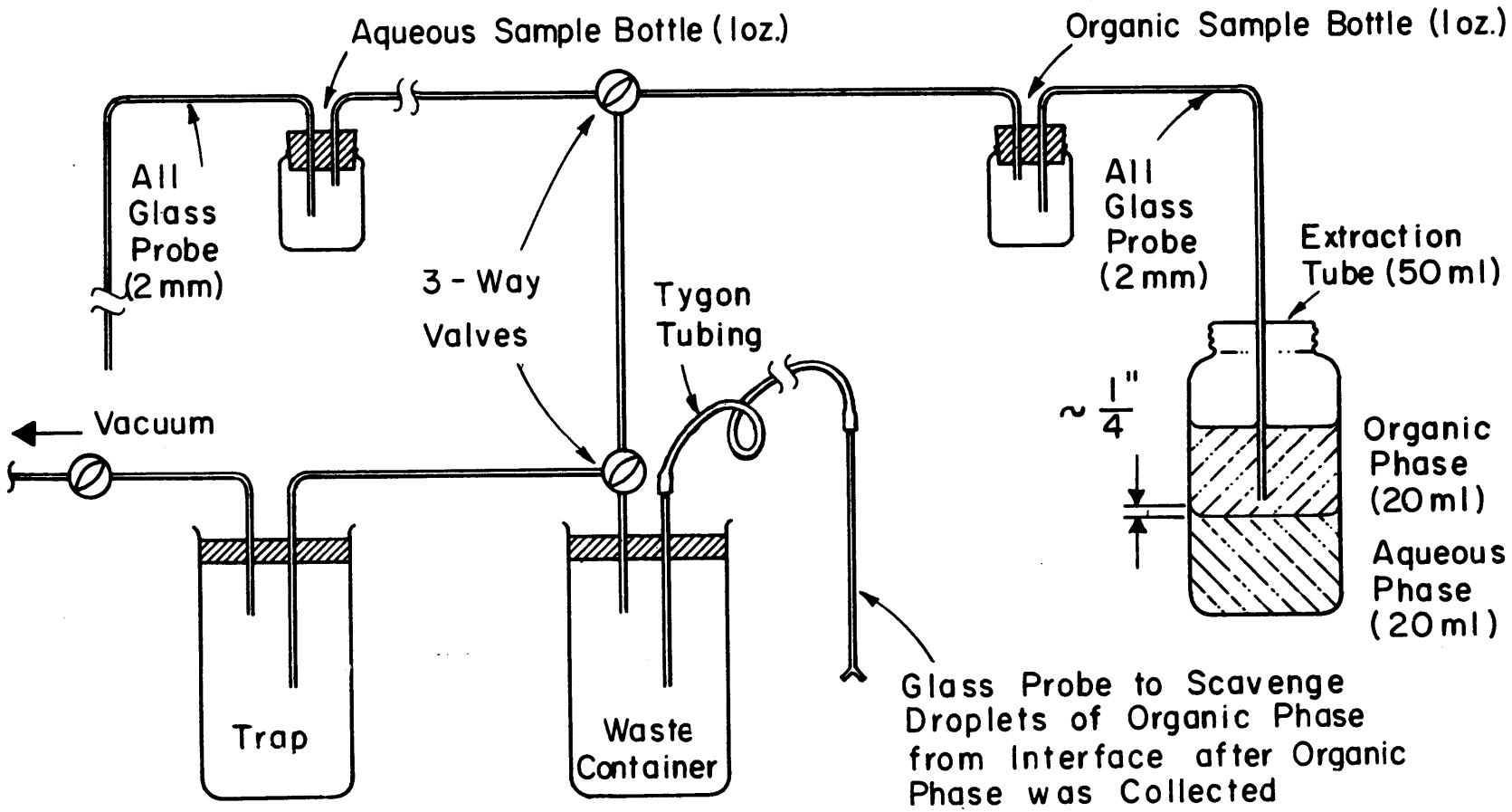

FIG. 7.1 VACUUM OPERATED PHASE SEPARATOR

determined graphically by plotting the potential versus ml of titre and the inflection points chosen by eye.

Neutralization curves of the nitric acid in the organic phase gave two end points indicating that the nitric acid in the organic phase exists in two degrees of availability. The lower the millivolt potential required to neutralize the acid, the more available is the acid. Since readily available nitric acid, i.e., physically dissolved in the amine phase, would be neutralized before the chemically bound nitric acid, the amount of physically dissolved nitric acid can be calculated from the first end point, whereas total nitric acid can be calculated from the second end point. It was noticed that the difference between the two end points was nearly constant, and that this difference was essentially equal to the amine concentration.

It was seen in the titrations of the ruthenium-bearing samples that the titratable ruthenium acids were neutralized after the unbound HNO_3 but before the amine nitrate HNO_3. Hence, the ruthenium acids are more tightly bound than the unbound HNO_3 but more available than the amine nitrate HNO_3, thus indicating that the extraction may proceed through a type of "sorption" reaction mechanism.

7.0.4 Determination of Amine Purity

Previous work here at MIT has been done with the use of TLA purchased from Archer-Daniels-Midland Co. and required the performance of a purification procedure before use in the extraction experiments. In order to bypass this purification step and upon the recommendation of Dr. C. Coleman of ORNL (19), TLA was purchased from the Distillation Products Division of Eastman Co. and was titrated for primary, secondary, and tertiary amine content, as received. The analysis was performed following the procedure of J.G. Moore, et al (18) and is as follows:

1. Total amine

Titrate 5 ml of amine solution against $HClO_4$. Record volume as V_1.

$$R_aNH_b + HClO_4 = R_aNH_{(b+1)}ClO_4$$

2. Primary amine

Take 5 ml of sample, add 2 ml of salicylaldehyde, and let stand at room temperature for 30 minutes. Titrate against $HClO_4$ and record volume as V_2.

$$R'\text{-}CHO + H_2NR'' \longrightarrow R'CH = NR'' + H_2O$$

The primary amine is inactivated and would not titrate. Therefore, the primary amine content would be equal to $(V_1-V_2)/V_1$.

3. Tertiary amine

Take 5 ml sample of amine solution, add 5 ml of acetic anhydride and 1 ml of glacial acetic acid and reflux gently for one hour. Cool and titrate against $HClO_4$. Record volume as V_3.

Primary: $CH_3\text{-}CO\text{-}O\text{-}CO\text{-}CH_3 + H_2NR' \longrightarrow CH_3\text{-}CO\text{-}NHR' + CH_3COOH$

Secondary: $CH_3\text{-}CO\text{-}O\text{-}CO\text{-}CH_3 + HNR_2 \longrightarrow CH_3\text{-}CO\text{-}NR_2 + CH_3COOH$

The primary and secondary amines are inactivated and will not titrate. Therefore, the tertiary amine content is equal to V_3/V_1, and subsequently, the secondary amine content is (1-primary-tertiary). =

$$1 - \left(\frac{V_1-V_2}{V_1}\right) - \left(\frac{V_3}{V_1}\right) = \left(\frac{V_2-V_3}{V_1}\right) .$$

The results of the differential titration of the Eastman TLA (as received) were:

Primary < 0.1%

Secondary = 2.7%

Tertiary = 97.3%

In reply to a request for their analysis of TLA the Distillation Products Division of Eastman Kodak Co. stated (20):

"Although we do not analyze specifically for the primary and secondary amines present in this product, we feel quite safe in stating that if such compounds are present they will be there in traces only. We base this statement upon the melting point of 15-16°C. and the refractive index $\left(\frac{20}{D}\right)$ of 1.4575. This latter value compares very closely with the value of 1.4567 given in the literature."

7.1 Summary of Ruthenium Extraction Data

See Table 7.1.

7.2 Summary of Organic Phase Titration Data

See Table 7.2.

7.3 Derivation of Rapid Dilution Distribution Ratio Equation (Eqn. 4-1)

Let; E_A^o = Gross ruthenium distribution ratio,

$$\frac{\text{conc. of gross Ru in organic phase}}{\text{conc. of gross Ru in aqueous phase}}$$

V_A = Volume of aqueous phase, liters

V_o = Volume of organic phase, liters

R = Concentration of ruthenium in aqueous phase after dilution but before extraction, grams per liter

P_x = Partition coefficient of species "X" at final acid concentration after extraction

TABLE 7.1

SUMMARY OF RUTHENIUM EXTRACTION DATA

Explanation of Symbols:

Complex: NO=RuNO-Nitro complexes; NA(X) = RuNO-Nitrate complexes, Batch "X".

Age of Solution: F = Freshly prepared, age about 1-2 hours after dissolution of solid compound.
A = Aged to equilibrium (at least 22 days), for RuNO-Nitrato complexes.
A(X)= Aged for "X" months, for RuNO-Nitro complexes.

Contact Time: s = seconds, m = minutes, h = hours, d = days.

*Samples 156-202; rapid dilution experiments; x-y = Phase volume ratio "x", $\frac{\text{aqueous}}{\text{organic}}$; delay time "y".

Temperature: RT = Room temperature, 20-25°C.

E_A^o: (B) = refers to back-extraction.

TABLE 7.1 (Continued)

SUMMARY OF RUTHENIUM EXTRACTION DATA

SAMPLE NO.	COMPLEX	AGE OF SOLU-TION	CONTACT TIME	TEMP, °C	AQUEOUS				ORGANIC		
					INITIAL HNO_3, N	FINAL HNO_3, N	$NaNO_3$, M	INITIAL Ru GM/L	TLA, M	FINAL Ru, GM/L	E_A^o
1	NA(A)	A	2m	25	0.32	0.34	-	9.10	0.26	-	-
2	"	"	"	"	1.21	1.22	-	8.63	"	0.034	0.0040
3	"	"	"	"	10.7	10.6	-	9.04	"	-	-
4	"	"	5M	"	0.32	0.36	-	9.10	"	0.0081	0.00088
5	"	"	"	"	1.21	1.28	-	8.63	"	0.049	0.0056
6	"	"	"	"	10.7	10.6	-	9.04	"	-	-
7	"	"	15m	"	0.32	0.36	-	9.10	"	0.020	0.0022
8	"	"	"	"	1.21	1.25	-	8.63	"	0.168	0.0199
9	"	"	"	"	10.7	10.6	-	9.04	"	0.039	0.0043
10	"	"	1h	"	0.32	0.32	-	9.10	"	0.058	0.0064
11	"	"	"	"	1.21	1.25	-	8.63	"	0.259	0.0310
12	"	"	"	"	10.7	10.4	-	9.04	"	0.042	0.0046
13	"	"	5h	"	0.32	0.36	-	9.10	"	0.096	0.0106
14	"	"	"	"	1.21	1.23	-	8.63	"	0.680	0.0855
15	"	"	"	"	10.7	10.5	-	9.04	"	-	-

SAMPLE NO.	COMPLEX	AGE OF SOLUTION	CONTACT TIME	TEMP, °C	AQUEOUS				ORGANIC		
					INITIAL HNO_3, N	FINAL HNO_3, N	$NaNO_3$ M	INITIAL Ru GM/L	TLA, M	FINAL Ru, GM/L	E_A^o
16	NA(A)	A	1m	25	0.32	0.38	-	9.10	0.26	-	-
17	"	"	"	"	1.21	1.28	-	8.63	"	0.019	0.0022
18	"	"	"	"	10.7	10.7	-	9.04	"	0.031	0.0034
19											
20	These Sample Numbers were not used										
21											
22	"	"	24h	"	0.32	0.34	-	9.10	0.26	0.193	0.0216
23	"	"	"	"	1.21	1.19	-	8.63	"	0.835	0.1072
24	"	"	"	"	10.7	10.4	-	9.04	"	0.047	0.0053
25	"	"	96h	"	0.32	0.34	-	9.10	"	0.292	0.0331
26	"	"	"	"	1.21	1.23	-	8.63	"	0.957	0.1248
27	"	"	"	"	10.7	10.3	-	9.04	"	-	-
28	"	"	2m	"	0.71	0.76	-	9.05	"	0.014	0.00154
29	"	"	"	"	3.13	3.22	-	8.79	"	0.103	0.0114
30	"	"	"	"	5.03	4.96	-	8.87	"	0.095	0.0109
31	"	"	"	"	7.09	7.19	-	8.86	"	0.072	0.0082
32	"	"	"	"	9.12	9.07	-	9.22	"	-	-
33	"	"	24h	"	0.71	0.75	-	9.05	"	0.715	0.086
34	"	"	"	"	3.13	3.21	-	8.79	"	0.610	0.074
35	"	"	"	"	5.03	5.02	-	8.87	"	0.281	0.033

SAMPLE NO.	COMPLEX	AGE OF SOLUTION	CONTACT TIME	TEMP, °C	AQUEOUS				ORGANIC		
					INITIAL HNO_3, N	FINAL HNO_3, N	$NaNO_3$ M	INITIAL Ru GM/L	TLA, M	FINAL Ru, GM/L	E_A^o
36	NA(A)	A	24h	25	7.09	7.16	-	8.86	0.26	0.127	0.0146
37	"	"	"	"	9.12	9.01	-	9.22	"	-	-
38	"	"	"	"	1.21	1.22	-	0.345	"	0.0348	0.112
39	"	"	"	"	1.21	1.23	-	0.863	"	0.0958	0.125
40	"	"	"	"	1.21	1.21	-	1.73	"	0.175	0.113
41	"	"	"	"	1.21	1.25	-	3.45	"	0.338	0.109
42	NO	F	2m	"	0.42	0.40	-	5.43	"	0.954	0.212
43	"	"	"	"	0.76	0.75	-	"	"	0.742	0.158
44	"	"	"	"	1.21	1.19	-	"	"	0.582	0.120
45	"	"	"	"	2.93	2.93	-	"	"	0.205	0.0382
46	"	"	"	"	4.51	4.48	-	"	"	0.075	0.0140
47	"	"	"	"	6.29	6.24	-	"	"	0.0276	0.0051
48	"	"	"	"	8.22	8.11	-	"	"	<0.02	<0.0037
49	"	"	"	"	9.60	9.56	-	"	"	<0.02	<0.0037
50	"	"	"	"	0.35	0.30	6.29	4.94	"	0.480	0.1076
51	"	"	"	"	1.00	0.94	6.20	"	"	0.240	0.0511
52	"	"	"	"	2.60	2.55	3.73	"	"	0.114	0.0236
53	"	"	"	"	4.31	4.26	2.27	"	"	0.048	0.0098
54	NA(B)	"	"	"	0.47	0.45	5.73	6.00	"	0.146	0.0249
55	"	"	"	"	1.27	1.21	4.92	"	"	0.0796	0.0134

SAMPLE NO.	COMPLEX	AGE OF SOLU-TION	CONTACT TIME	TEMP °C	AQUEOUS				ORGANIC		
					INITIAL HNO_3, N	FINAL HNO_3, N	$NaNO_3$ M	INITIAL Ru GM/L	TLA, M	FINAL Ru, GM/L	E^o_A
56	NA(B)	F	2m	25	3.10	3.05	3.07	6.00	0.26	0.0354	0.0060
57	"	"	"	"	5.05	4.98	1.30	"	"	0.0301	0.0050
58	"	"	"	"	0.52	0.49	-	6.45	"	0.0303	0.0047
59	"	"	"	"	0.89	0.87	-	"	"	0.0324	0.0050
60	"	"	"	"	1.32	1.31	-	"	"	0.0328	0.0051
61	"	"	"	"	3.10	3.07	-	"	"	0.0364	0.0057
62	"	"	"	"	4.91	4.92	-	"	"	0.0285	0.0044
63	"	"	"	"	6.85	6.86	-	"	"	0.0224	0.0035
64	"	"	"	"	8.74	8.84	-	"	"	0.0183	0.0028
65	"	"	"	"	10.08	10.19	-	"	"	0.018	0.0028
66	NO	A(1)	"	"	0.42	0.41	-	5.43	"	0.487	0.0986
67	"	"	"	"	0.77	0.77	-	"	"	0.345	0.0679
68	"	"	"	"	1.22	1.21	-	"	"	0.217	0.0417
69	"	"	"	"	2.94	3.20	-	"	"	0.0944	0.0177
70	"	"	"	"	4.51	4.59	-	"	"	0.0472	0.0088
71	"	"	"	"	6.29	6.42	-	"	"	0.0216	0.0040
72	"	"	"	"	8.22	8.16	-	"	"	0.0125	0.0023
73	"	"	"	"	9.60	9.81	-	"	"	0.0140	0.0026
74	"	"	"	"	0.36	0.31	5.98	4.94	"	0.345	0.0752
75	"	"	"	"	1.01	0.96	5.25	"	"	0.155	0.0324

SAMPLE NO.	COMPLEX	AGE OF SOLU-TION	CONTACT TIME	TEMP °C	AQUEOUS				ORGANIC		
					INITIAL HNO_3, N	FINAL HNO_3, N	$NaNO_3$ M	INITIAL Ru GM/L	TLA, M	FINAL Ru, GM/L	E_A^o
76	NO	A(1)	2m	25	2.60	2.59	3.73	4.94	0.26	0.0767	0.0160
77	"	"	"	"	4.31	4.38	2.27	"	"	0.0302	0.0061
78	"	"	24h	"	0.42	0.41	-	5.43	"	1.50	0.382
79	"	"	"	"	0.77	0.77	-	"	"	1.03	0.234
80	"	"	"	"	1.22	1.21	-	"	"	0.650	0.136
81	"	"	"	"	2.94	2.98	-	"	"	0.149	0.0282
82	"	"	"	"	4.51	4.34	-	"	"	0.0541	0.0101
83	"	"	"	"	6.29	5.98	-	"	"	0.0251	0.0041
84	"	"	"	"	8.22	8.21	-	"	"	0.0141	0.0026
85	"	"	"	"	9.60	9.74	-	"	"	0.0104	0.0019
86	"	"	"	"	0.42	0.41	0.58	"	"	1.23	0.293
87	"	"	"	"	0.41	0.36	2.58	"	"	1.19	0.281
88	"	"	"	"	0.38	0.33	4.58	"	"	1.33	0.324
89	"	"	"	"	0.36	0.26	5.98	4.94	"	1.62	0.488
90	"	"	"	"	1.16	1.13	1.78	5.43	"	0.515	0.105
91	"	"	"	"	1.07	0.95	3.78	"	"	0.449	0.0902
92	"	"	"	"	1.01	0.91	5.25	4.94	"	0.615	0.142
93	"	"	"	"	2.97	2.57	0.10	5.43	"	0.139	0.0263
94	"	"	"	"	2.76	2.77	2.10	"	"	0.123	0.0232
95	"	"	"	"	2.60	2.55	3.73	4.94	"	0.180	0.0378
96	"	"	"	"	4.60	4.65	0.50	5.43	"	0.045	0.0084
97	"	"	"	"	4.31	4.38	2.27	4.94	"	0.0406	0.0083
98	"	"	"	"	0.42	0.41	5.02	5.43	"	1.415	0.353
99	"	A(2)	"	"	0.42	0.41	-	2.17	"	0.525	0.320
100	"	"	"	"	0.42	0.40	-	1.09	"	0.235	0.277

SAMPLE NO.	COMPLEX	AGE OF SOLU-TION	CONTACT TIME	TEMP °C	AQUEOUS				ORGANIC		
					INITIAL HNO_3, N	FINAL HNO_3, N	$NaNO_3$ M	INITIAL Ru GM/L	TLA, M	FINAL Ru, GM/L	E_A^o
101	NO	A(2)	24h	25	0.42	0.40	-	0.435	0.26	0.0831	0.236
102	"	"	"	"	0.42	0.41	-	0.217	0.26	0.0386	0.217
103	"	"	"	"	0.42	0.41	-	5.43	0.21	1.195	0.282
104	"	"	"	"	0.42	0.42	-	"	0.13	0.847	0.185
105	"	"	"	"	0.42	0.44	-	"	0.053	0.313	0.0612
106	"	"	"	"	1.22	1.21	-	"	0.26	0.631	0.127
107	"	"	"	"	1.22	1.21	-	2.17	"	0.212	0.108
108	"	"	"	"	1.22	1.20	-	1.09	"	0.105	0.107
109	"	"	"	"	1.22	1.19	-	0.435	"	0.0323	0.080
110	"	"	"	"	1.22	1.19	-	0.217	"	0.0154	0.076
111	NA(B)	A	2m	"	0.47	0.44	5.73	6.00	"	0.154	0.0264
112	"	"	"	"	1.27	1.21	4.92	"	"	0.069	0.0116
113	"	"	"	"	3.10	3.02	3.07	"	"	0.040	0.0067
114	"	"	"	"	5.05	4.99	1.30	"	"	0.035	0.0059
115	"	"	24h	"	3.10	3.04	-	6.45	"	0.364	0.0600
116	"	"	"	"	4.91	4.90	-	"	"	0.164	0.0261
117	"	"	"	"	3.09	3.03	1.91	"	"	0.337	0.0552
118	"	"	"	"	3.10	3.02	3.07	6.00	"	0.307	0.0540
119	"	"	"	"	5.05	5.01	1.30	"	"	0.117	0.0200
120	"	"	"	"	1.32	1.31	-	6.45	"	0.502	0.0844

SAMPLE NO.	COMPLEX	AGE OF SOLUTION	CONTACT TIME	TEMP °C	AQUEOUS				ORGANIC		
					INITIAL HNO_3, N	FINAL HNO_3, N	$NaNO_3$ M	INITIAL Ru GM/L	TLA, M	FINAL Ru, GM/L	E_A^o
121	NA(B)	A	24h	25	1.27	1.21	1.89	6.45	0.26	0.848	0.151
122	"	"	"	"	1.29	1.18	3.89	"	"	0.969	0.177
123	"	"	"	"	1.27	1.16	4.92	6.00	"	0.987	0.197
124	"	"	"	"	0.52	0.49	-	6.45	"	0.266	0.043
125	"	"	"	"	0.50	0.48	0.72	"	"	0.709	0.124
126	"	"	"	"	0.48	0.40	2.80	"	"	1.70	0.358
127	"	"	"	"	0.46	0.35	4.91	"	"	2.51	0.637
128	"	"	"	"	0.47	0.37	5.73	6.00	"	2.38	0.657
129	"	"	"	"	1.32	1.31	-	6.45	0.21	0.430	0.0714
130	"	"	"	"	1.32	1.32	-	"	0.13	0.265	0.0428
131	"	"	"	"	1.32	1.32	-	"	0.053	0.074	0.0116
132	"	"	"	"	1.32	1.31	-	"	0.105	0.197	0.0315
133	"	"	"	"	1.32	1.33	-	"	0.084	0.143	0.0227
134	"	"	"	"	1.32	1.32	-	"	0.063	0.095	0.0150
135	"	"	2m	"	0.52	0.49	-	"	0.26	0.009	0.0014
136	"	"	"	"	0.89	0.82	-	"	"	0.019	0.0030
137	"	"	"	"	1.32	1.31	-	"	"	0.025	0.0039
138	"	"	"	"	3.10	3.02	-	"	"	0.049	0.0039
139	"	"	"	"	4.91	4.82	-	"	"	0.045	0.0070
140	"	"	"	"	6.85	6.71	-	"	"	0.035	0.0055

SAMPLE NO.	COMPLEX	AGE OF SOLUTION	CONTACT TIME	TEMP °C	AQUEOUS				ORGANIC		
					INITIAL HNO_3, N	FINAL HNO_3, N	$NaNO_3$ M	INITIAL Ru GM/L	TLA, M	FINAL Ru, GM/L	E^o_A
141	NA(B)	A	45s	RT	1.3	1.3	-	-	0.26	1.96	5.4 (B)
142	"	"	"	"	"	"	-	-	"	2.06	4.1 (B)
143	"	"	"	"	3.0	3.0	-	-	"	0.780	2.5 (B)
144	"	"	29d	25	3.10	3.1	-	6.45	"	0.452	0.0753
145	"	"	"	"	4.91	4.9	-	"	"	0.227	0.0365
146	"	"	"	"	6.85	6.8	-	"	"	0.112	0.0177
147	"	"	"	"	8.74	8.7	-	"	"	0.047	0.0073
148	"	"	"	"	10.1	10.1	-	"	"	Sample Lost-Cap Loosened in Bath.	
149	"	"	45s	RT	4.9	4.9	-	-	"	0.103	0.83 (B)
150	"	"	"	"	5.6	5.6	-	-	"	0.047	0.36 (B)
151	These Sample Numbers were not used.										
152											
153	NA(B)	A	29d	25	0.52	0.50	-	6.45	0.26	0.576	0.0981
154	"	"	"	"	0.89	0.90	-	"	"	0.591	0.1010
155	"	"	"	"	1.32	1.30	-	"	"	0.606	0.104
156	"	"	*1-30s	RT	4.9	3.0	-	3.93	"	0.127	0.0334
157	"	"	"	"	6.8	"	-	2.82	"	0.233	0.090
158	"	"	"	"	8.7	"	-	2.21	"	0.269	0.138
159	"	"	"	"	10.1	"	-	1.92	"	0.322	0.201
160	"	"	"	"	4.9	4.9	-	6.45	"	0.068	0.0107

SAMPLE NO.	COMPLEX	AGE OF SOLU-TION	CONTACT TIME	TEMP °C	AQUEOUS				ORGANIC		
					INITIAL HNO_3, N	FINAL HNO_3, N	$NaNO_3$ M	INITIAL Ru GM/L	TLA, M	FINAL Ru, GM/L	E_A^o
161	NA(B)	A	*1-30s	RT	6.8	4.9	-	4.61	0.26	0.111	0.0247
162	"	"	"	"	8.7	"	-	3.62	"	0.152	0.0438
163	"	"	"	"	10.1	"	-	3.14	"	0.180	0.0608
164	"	"	"	"	3.1	1.0	-	2.08	"	0.046	0.0227
165	"	"	"	"	4.9	"	-	1.32	"	0.108	0.0893
166	"	"	"	"	6.8	"	-	0.942	"	0.143	0.179
167	"	"	"	"	8.7	"	-	0.738	"	0.167	0.292
168	"	"	"	"	10.1	"	-	0.640	"	0.180	0.391
169	"	"	5-30s	"	10.1	1.0	-	0.645	"	0.623	1.20
170	"	"	1-30s	"	1.0	1.0	-	-	"	0.612	55.6(B)
171	"	"	5-30s	"	10.1	3.0	-	1.94	"	0.871	0.495
172	"	"	1-30s	"	3.0	3.0	-	-	"	0.694	3.92(B)
173	"	"	5-30s	"	10.1	4.9	-	3.23	"	0.225	0.071
174	"	"	1-30s	"	4.9	4.9	-	-	"	0.098	0.771(B)
175	"	"	5-30s	"	8.7	1.0	-	0.738	"	0.585	0.942
176	"	"	10-30s	"	"	"	-	"	"	0.990	1.55
177	"	"	25-30s	"	"	"	-	"	"	1.82	2.74
178	"	"	79-30s	"	"	"	-	"	"	3.58	5.17
179	"	"	5-30s	"	6.8	"	-	0.942	"	0.437	0.511
180	"	"	50-30s	"	6.8	"	-	"	"	2.01	2.23

SAMPLE NO.	COMPLEX	AGE OF SOLU-TION	CONTACT TIME	TEMP °C	AQUEOUS				ORGANIC		
					INITIAL HNO_3, N	FINAL HNO_3, N	$NaNO_3$ M	INITIAL Ru GM/L	TLA M	FINAL Ru, GM/L	E_A^o
181	NA(B)	A	5-30s	RT	4.9	1.0	-	1.32	0.26	0.269	0.212
182	"	"	33-30s	"	"	"	-	"	"	0.898	0.696
183	"	"	5-30s	"	3.1	"	-	2.08	"	0.123	0.0597
184	"	"	26-30s	"	"	"	-	"	"	0.328	0.158
185	"	"	1-30s	"	6.8	"	-	0.948	"	0.145	0.186
186	"	"	1-1m	"	"	"	-	"	"	0.136	0.168
187	"	"	1-1½m	"	"	"	-	"	"	0.133	0.163
188	"	"	1-2½m	"	"	"	-	"	"	0.122	0.148
189	"	"	1-5½m	"	"	"	-	"	"	0.100	0.118
190	"	"	1-30s	"	"	6.8	-	0.799	"	0.0059	0.0074
191	NA(C)	"	1-30s	"	9.7	1.0	-	0.828	"	0.217	0.355
192	"	"	1-1½m	"	"	"	-	"	"	0.190	0.298
193	"	"	1-2½m	"	"	"	-	"	"	0.176	0.270
194	"	"	1-5½m	"	"	"	-	"	"	0.145	0.212
195	"	"	1-30s	"	"	3.0	-	2.48	"	0.366	0.173
196	"	"	1-1½m	"	"	3.0	-	"	"	0.304	0.139
197	"	"	1-2½m	"	"	3.0	-	"	"	0.245	0.110
198	"	"	1-5½m	"	"	"	-	"	"	0.174	0.0753
199	"	"	1-30s	"	"	4.9	-	4.02	"	0.213	0.0559
200	"	"	1-1½m	"	"	"	-	"	"	0.180	0.0469
201	"	"	1-2½m	"	"	"	-	"	"	0.157	0.0407
202	"	"	1-5½m	"	"	"	-	"	"	0.124	0.0318

TABLE 7.2

SUMMARY OF ORGANIC PHASE TITRATION DATA

SAMPLE NUMBER	UNBOUND NITRIC ACID CONC., N.
64	0.375
82	0.186
115	0.136
116	0.207
117	0.168
118	0.187
119	0.236
120	0.049
121	0.077
122	0.107
123	0.127
124	0.008
125	0.020
126	0.035
127	0.046
128	0.059
129	0.037
130	0.022
131	0.0077
132	0.018
133	0.013
134	0.0096
140	0.283

M_x = Mole fraction of species "X" at initial (before) dilution) stock solution acid concentration.

$C_{x,A}$ = Concentration of species "X"; in aqueous phase after extraction, grams per liter as ruthenium

$C_{x,o}$ = Concentration of species "X" in organic phase after extraction, grams per liter as ruthenium

T = Phase volume ratio, $\frac{V_A}{V_o}$.

It is assumed that the contacting time of the two phases is long enough to ensure complete and equilibrium extraction of the extractable species present in the aqueous phase but short enough so that no redistribution of the complexes can take place.

Under those assumptions, the following derivation is possible. After extraction, and by definition

$$p_x = \frac{C_{x,o}}{C_{x,A}} \qquad (7.3\text{-}1)$$

By a material balance

$$V_A C_{x,A} + V_o C_{x,o} = V_A M_x R \qquad (7.3\text{-}2)$$

From (7.3-1),

$$C_{x,A} = \frac{C_{x,o}}{P_x} \qquad (7.3\text{-}3)$$

Substituting (7.3-3) into (7.3-2) yields,

$$V_A \left(\frac{C_{x,o}}{P_x}\right) + V_o C_{x,o} = V_A M_x R \qquad (7.3\text{-}4)$$

Solving (7.3-4) for $C_{x,o}$,

$$c_{x,o} = \frac{V_A M_x R}{\left(\frac{V_A}{P_x} + V_o\right)} = \frac{T M_x P_x R}{T+P_x} \qquad (7.3\text{-}5)$$

Equation (7.3-5) was used in the text as Equation (4-3). The total concentration of ruthenium in the organic phase is then equal to the sum of all the species, i.e.

$$C_o = \sum_x C_{x,o} = \sum_x \left(\frac{TRM_x P_x}{T+P_x}\right) = TR \sum_x \left(\frac{M_x P_x}{T+P_x}\right) \qquad (7.3\text{-}6)$$

Again, by a material balance,

$$V_o C_o + V_A C_A = V_A R \qquad (7.3\text{-}7)$$

Solving (7.3-7) for C_A yields,

$$C_A = \frac{V_A R - V_o C_o}{V_A} = R - \left(\frac{1}{T}\right) C_o = \frac{(TR-C_o)}{T} \qquad (7.3\text{-}8)$$

The distribution ratio would then be

$$E_A^o = \frac{C_o}{C_A} = \frac{TC_o}{TR-C_o} = \frac{T(TR)\sum_x\left(\frac{M_xP_x}{T+P_x}\right)}{TR-TR\sum_x\left(\frac{M_xP_x}{T+P_x}\right)} = T\left[\frac{\sum_x\left(\frac{M_xP_x}{T+P_x}\right)}{1-\sum_x\left(\frac{M_xP_x}{T+P_x}\right)}\right] \qquad (7.3\text{-}9)$$

Equation (7.3-9) was used in the text as Equation (4-1).

7.4 Derivation of Back-Extraction Distribution Ratio (Eqn. 4-4)

Let; T_F = Forward extraction phase volume ratio, $\frac{\text{aqueous}}{\text{organic}}$

T_B = Back-extraction phase volume ratio, $\frac{\text{aqueous}}{\text{organic}}$

$E_A^o(B)$ = Back-extraction distribution ratio

Other symbols as used in Section 7.3.

For the forward extraction, from Equation (7.3-5)

$$C_{x,o} = \frac{T_F R M_x P_x}{P_x + T_F} \qquad (7.4\text{-}1)$$

After back-extraction (denoted by "B"), and by definition

$$P_x = \frac{C^B_{x,o}}{C^B_{x,A}} \qquad (7.4\text{-}2)$$

By a material balance,

$$V_o^B C_{x,o}^B + V_A^B C_{x,A}^B = V_o^B C_{x,o} \qquad (7.4\text{-}3)$$

Solving (7.4-2) for $C_{x,A}^B$ and substituting in (7.4-3), an expression for $C_{x,o}^B$ can be derived.

$$C_{x,o}^B = \frac{T_B P_x C_{x,o}}{P_x + T_B} \qquad (7.4\text{-}4)$$

Substituting (7.4-1) into (7.4-4) gives

$$C_{x,o}^B = \frac{T_B T_F R M_x P_x^2}{\left(P_x+T_B\right)\left(P_x+T_F\right)} \qquad (7.4\text{-}5)$$

In a similar fashion

$$C_{x,A}^B = \frac{T_B T_F R M_x P_x}{\left(P_x+T_B\right)\left(P_x+T_F\right)} \qquad (7.4\text{-}6)$$

Hence

$$E_A^o(B) = \frac{\sum_x C_{x,o}^B}{\sum_x C_{x,A}^B} = \frac{T_B T_F R \sum_x \dfrac{M_x P_x^2}{\left(P_x+T_B\right)\left(P_x+T_F\right)}}{T_B T_F R \sum_x \dfrac{M_x P_x}{\left(P_x+T_B\right)\left(P_x+T_F\right)}} \qquad (7.4\text{-}7)$$

$$E_A^o(B) = \frac{\sum_x \left[\frac{M_x P_x^2}{(P_x+T_B)(P_x+T_F)} \right]}{\sum_x \left[\frac{M_x P_x}{(P_x+T_B)(P_x+T_F)} \right]} \qquad (7.4\text{-}8)$$

Equation (7.4-8) was used in the text as Equation (4-4), after expansion for x = 1 and 2.

7.5 Derivation of Time-Dependent Mole Fraction Equations

(Eqns. 4-8 and 4-9)

Assuming that upon dilution, the denitration reactions (4-6) and (4-7) take place with the indicated reaction rate constants,

$$H_2RuNO(NO_3)_5 + H_2O \xrightarrow{k_1} HRuNO(NO_3)_4(H_2O) + HNO_3 \qquad (4\text{-}6)$$

$$HRuNO(NO_3)_4(H_2O) + H_2O \xrightarrow{k_2} RuNO(NO_3)_3(H_2O)_2 + HNO_3 \qquad (4\text{-}7)$$

Assuming the reactions to be first order with respect to ruthenium, the rate of change of concentration of the pentanitrato acid complex can be expressed as

$$\frac{dM_1}{dt} = -k_1 (M_1 - M_1^*) \qquad (7.5\text{-}1)$$

Where M_1^* is the equilibrium stock solution mole fraction at the final acid concentration after dilution.

The rate of change of concentration of the tetranitrato acid complex can be expressed as

$$\frac{dM_2}{dt} = - k_2(M_2-M_2^*) + k_1(M_1-M_1^*) \qquad (7.5\text{-}2)$$

Where M_2^* is the equilibrium stock solution mole fraction at the final acid concentration after dilution. Using the LaPlace transformation with respect to time (t), one obtains,

$$p\bar{M}_1 - M_1^o = - k_1 \bar{M}_1 + \frac{k_1 M_1^*}{p} \qquad (7.5\text{-}3)$$

$$p\bar{M}_2 - M_2^o = - k_2\bar{M}_2 + \frac{k_2 M_2^*}{p} + k_1\bar{M}_1 - \frac{k_1 M_1^*}{p} \qquad (7.5\text{-}4)$$

Where M_1^o and M_2^o refer to the equilibrium stock solution mole fractions at the initial acid concentration before dilution.

Solving (7.5-3) for $\bar{M}_1$ yields,

$$\bar{M}_1 = \frac{k_1 M_1^*}{p(p+k_1)} + \frac{M_1^o}{(p+k_1)} \qquad (7.5\text{-}5)$$

Substituting (7.5-5) into (7.5-4) and solving for $\bar{M}_2$, one obtains

$$\bar{M}_2 = \frac{M_2^o}{(p+k_2)} + \frac{k_2 M_2^*}{p(p+k_2)} - \frac{k_1 M_1^*}{p(p+k_2)} + \frac{k_1^2 M_1^*}{(p+k_1)(p+k_2)} + \frac{k_1 M_1^o}{(p+k_1)(p+k_2)} \qquad (7.5\text{-}6)$$

By the use of partial fractions, the transforms can be inverted to yield

$$M_1 = M_1^* + \left(M_1^o - M_1^*\right) e^{-k_1 t} \qquad (7.5\text{-}7)$$

$$M_2 = M_2^* + \left(M_2^o - M_2^*\right) e^{-k_2 t} + \frac{k_1 \left(M_1^o - M_1^*\right)}{\left(k_1 - k_2\right)} \left[e^{-k_2 t} - e^{k_1 t}\right] \qquad (7.5\text{-}8)$$

Equations (7.5-7) and (7.5-8) were used in the text as Equations (4-8) and (4-9), respectively.

7.6 Summary of Material Balance Checks

The values of E_A^o reported are largely the result of the quantitative analysis of only the organic phase of the extraction samples. Since the initial aqueous ruthenium concentrations and final organic ruthenium concentrations were known, it was possible to calculate E_A^o by dividing the final organic concentration by the

difference of the initial aqueous concentration and final organic concentraion. Large errors would be possible in the values of E_A^o if the organic phase analysis was not reliable. Therefore, selected samples containing relatively large organic ruthenium concentrations were analyzed also for aqueous ruthenium concentration and the material balances showed that a reliable analysis is to be expected.

The material balance is reported in Table 7.3 as total final ruthenium divided by total initial ruthenium, on a percentage basis.

7.7 Apparatus

(1) Beckman Spectrophotometer Model DU, Serial No. 3236 with photomultiplier attachment and line operated power supply, Serial No. 179559.

(2) Beckman "Zeromatic" pH meter, Serial No. 166694.

(3) International Centrifuge Model CL, Serial No. 53220H, head 4-50ml.

(4) Constant temperature bath, homemade, 30"L x 18"Wx10"D, 25 $\pm$ 0.2°C.

(5) Horizontal shaker for constant temperature bath homemade, 30"L x 18"W, about 2"

excursion, frequency 89 cpm, capacity total of 20, 50 ml centrifuge tubes.

(6) Electronic Relay, Serial No. N-12, Precision Scientific Co., for temperature control.

(7) Phase separator, vacuum operated, homemade.

(8) Vacuum drying oven, Labline, Inc., Cat. No. 3610, Serial No. 1184.

(9) Vacuum pump for drying oven, Welch Duo-Seal Model 1400-B, Serial No. 42144-0.

(10) Standard laboratory equipment.

(11) Reagent Grade Chemicals, when available.

TABLE 7.3

SUMMARY OF MATERIAL BALANCE CHECKS

Sample Number	Initial Aq,Ru, gm/ℓ	Final Aq, Ru, gm/ℓ	Final Org. Ru, gm/ℓ	Material Balance
23	8.63	8.26	0.835	105.4
26	8.63	7.97	0.957	103.4
42	5.43	4.48	0.954	100.0
43	5.43	4.61	0.742	98.5
44	5.43	4.74	0.582	98.0
50	4.94	4.26	0.480	96.0
78	5.43	3.83	1.50	98.2
79	5.43	4.31	1.03	98.4
80	5.43	4.73	0.650	99.1
86	5.43	4.12	1.23	98.5
87	5.43	4.12	1.19	97.8
88	5.43	3.92	1.33	96.7
89	4.94	3.36	1.62	100.7
90	5.43	4.92	0.515	100.1
92	4.94	4.24	0.615	98.3
98	5.43	4.24	1.42	104.1
103	5.43	4.06	1.20	96.9
104	5.43	4.62	0.847	100.8

NOMENCLATURE

a = activity, moles per liter.

c = concentration, moles per liter, or grams per liter.

DDW = distilled deionized water.

E_A^o = distribution ratio, concentration of species in organic phase divided by concentration of species in aqueous phase.

gm/l = grams per liter.

k = rate constant, $minute^{-1}$

m = milli = $\times 10^{-3}$

M_x = mole fraction of species "x"

$\underline{M}$ = molarity, moles per liter

$\underline{N}$ = normality, equivalents per liter

ORNL = Oak Ridge National Laboratory, Oak Ridge, Tennessee

P_x = partition coefficient of species "x", concentration of species "x" in organic phase divided by concentration of species "x" in aqueous phase

RuNO = nitrosyl ruthenium

T_B = phase volume ratio, $\frac{\text{aqueous}}{\text{organic}}$, for back--extraction.

T_F, T = phase volume ratio, $\frac{\text{aqueous}}{\text{organic}}$, for forward extraction

TBP = tri butyl phosphate

TLA = tri lauryl amine (nitrate form)

Greek Letters

α = dissociation constant for nitric acid

γ = activity coefficient

μ = micro = x 10^{-6}

Subscripts, Superscripts, and Prefixes

A,aq = aqueous phase

B = back-extraction

f = at final condition

F = for forward extraction

i = at initial condition

O,org = organic phase

s = stoichiometric

+ = positive charge on ion or radical

- = negative charge on ion or radical

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