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Considerations on the distribution of ions between an
organic solution of alkyl ammonium salts and an aqueous solution
of inorganic salts in the presence of homopolymers and heteropolymers in
the organic phase.

by

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ABSTRACT

The distribution of a monovalent simple anion, Y^- , or of a monovalent metal complex anion, $MX_{n,1}^-$, between an aqueous solution of the supporting electrolyte CX and a water immiscible solution of an alkyl ammonium salt $\overline{RX}$ has been described considering the presence in the organic phase of the homopolymers $(\overline{RX})_1$, $(\overline{RY})_j$ and of the heteropolymers $[(\overline{RX})_a(\overline{RY})_b]$. A set of equations has been derived that show the dependence of the experimental distribution data on the concentration of the alkyl ammonium salt and the extracted anion.

A successful reinterpretation of the data existing in the literature on the distribution of $UO_2(NO_3)_2$ between aqueous nitrate solution and alkyl ammonium nitrate solutions has been carried out. The presence of a mixed tetramer and of a monomer terms seems to fit the experimental data.

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The distribution of the anion Y^- between an organic solution (water immiscible) of an alkyl ammonium salt, $\overline{RX}$, and an aqueous solution of the salt MY in the presence of the supporting electrolyte MX has been described by the following exchange reaction (1-3):

with the bar indicating the organic salt.

The equilibrium constant of reaction (1) in terms of the concentration, $\bar{m}$, and of the activity coefficient, γ , of each species is given by the following equation

$$K = \frac{\bar{m}_{RY} \bar{\gamma}_{RY} m_X \gamma_X}{\bar{m}_{RX} \bar{\gamma}_{RX} m_Y \gamma_Y} \quad (2)$$

Introducing the mean activity coefficients for the aqueous phase the equation (2) reduces to

$$K = \frac{\bar{m}_{RY} \bar{\gamma}_{RY} m_{MX} \gamma_{MX}^2}{\bar{m}_{RX} \bar{\gamma}_{RX} m_{MY} \gamma_{MY}^2} \quad (3)$$

with γ_{MX}^2 and γ_{MY}^2 mean activity coefficients of MX and MY in presence of MY and MX respectively.

Equations (1), (2), and (3) are based on the assumptions that only monomeric species, RX and RY , are involved in the exchange and that the ratio of the organic activity coefficients, Γ , takes into account the non-ideality of the organic phase.

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The validity of these assumptions can be established only by reference to experimental facts. At very low concentrations of alkyl ammonium salt the existence of only monomeric species can be accepted and equation (1) probably describes the exchange reaction. Experimental results indicate that the monomer is the predominant specie in 10^{-4} M solutions of tertiary ammonium chloride, nitrate, and perchlorate salts in an organic solvent of low dielectric constant.⁽⁴⁻⁶⁾ However, it seems unlikely that reaction (1) can describe the distribution of anions between phases if the concentration of ammonium salt is in the range where dimers, trimers, and higher polymers are known to exist. A more suitable reaction would take into account all species existing in the organic phase since the number and type of species in the initial and equilibrium phase can be different.

It should be pointed out that equation (2) accounts for structural changes of the organic phase with the activity coefficient ratio Γ . However, it is a more realistic approach to consider all of the species participating in the distribution process and to account for a part of the solute-solute interactions in terms of n-mer existing in the organic phase. If, in addition, an inert diluent is chosen to give a minimum of specific solvent-solute interactions, the activity coefficient of each specie in the organic solution approaches the unity.

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- 5) J. I. Bucher and R. M. Diamond, J. Phys. Chem. 69, 1565, (1965).
- 6) E. Hogfeldt, Svensk Kemisk Tidskrift 76, 4, (1964) and references therein.

In the presence of species in addition to monomers the exchange process can be described by the following equilibrium:

with i, j, a and b integer numbers $1, 2, 3, \dots, n$. I, J, A, B indicate the maximum polymerization in the system. The term with the double sum, $\sum \sum$, accounts for the presence of mixed aggregates that can be formed between RX and RY .

An equilibrium constant for the equilibrium (4) is given by the following equations

$$K^* = K_T \Gamma = \frac{\prod_{j=1}^J (\overline{RY})_j}{\prod_{i=1}^I (\overline{RX})_i} \frac{\prod_{a=1}^A \prod_{b=1}^B [(\overline{RX})_a (\overline{RY})_b]}{1} / \frac{\prod_{i=1}^I (\overline{RX})_i}{1} \times (X/Y)^t \times F^t \quad (5)$$

where $\prod()$ indicates the product of the concentrations of the species $(\overline{RY})_j$, $(\overline{RX})_i$ and $(\overline{RX})_a (\overline{RY})_b$, Γ is the ratio of the products of the organic activity coefficients, $F = \frac{\gamma_{MX}^2}{\gamma_{MY}^2} / \frac{\gamma_{MX}^2}{\gamma_{MY}^2}$ is the ratio of the mean aqueous activity coefficients, and (X) and (Y) the concentrations of MX and MY . $\gamma_{MX}^{\pm}(MY)$ and $\gamma_{MY}^{\pm}(MX)$ are the mean activity coefficients of the species MX and MY in the presence of MY and MX respectively.

The evaluation of K^* requires the determination of the concentration of each specie participating in the equilibrium (4).

In order to give a physical picture of the exchange process and to describe equilibrium (4) in terms of measurable quantities we can imagine the following mechanism. Of all the $(\overline{RX})_i$ species in equilibrium, only the monomeric specie RX exchanges with Y to form RY . RY is itself in equilibrium

with the $(\overline{RY})_i$ species and with the heteropolymers $[(\overline{RX})_a(\overline{RY})_b]$.

The following equations and their relative equilibrium constants are then to be considered

The $K_{(1,X,Y)}$ is the equilibrium constant for the exchange between the monomers. Equilibrium(7) and (8) account for the formation of i- and j-mers. Equilibrium(9) deals with the heteropolymer formation.

By using equations (6), (7), (8), (9) equilibrium (4) reduces to

$$\sum_{i=1}^I K_{(i,X)} (\overline{RX})^i + t(Y^-) \rightleftharpoons \sum_{j=1}^J K_{(1,X,Y)}^j K_{(j,Y)} (\overline{RX})^j (Y)^j (X)^{-j} F^{-j} +$$

$$+ \sum_{a=1}^A \sum_{b=1}^B K_{(1,X,Y)} K_{(a,b)} (\overline{RX})^{a+b} + t(X^-) \quad (10)$$

$(\overline{RX})$ is the equilibrium monomer concentration of the salt RX in the organic phase.

When $i = j = 1$ it is $K_{(1,X)} = K_{(1,Y)} = 1$

The equation (5) reduces to

$$K^* = K_T \Gamma = K^t_{(1,X,Y)} \left[\prod_{a=1}^A \prod_{b=1}^B (K_{(a,b)}) \right] \left[\prod_{i=1}^J (K_{(i,X)}) \right]^{-1} \quad (11)$$

where K_T is the true thermodynamic constant.

The validity of equations (10) and (11) depends on the assumption that all the reactions are fast and simultaneous reactions, and that there is no appreciable dissociation of the salt into ions.

Equilibrium (4) interprets the deviations of the exchange process from the simple mass-action law, expressed by reaction (1), in terms of solute-solute interactions. Thus if an inert diluent is used, so that the absence of solvent-solute interactions can be assumed, the value of the activity coefficient of every specie approaches unity and we can approximate Γ to 1 and K^* to K_T .

Other mechanisms can be imagined to describe the exchange process but they are thermodynamically indistinguishable from the mechanism pictured by equations (6), (7), (8), (9). The difference between them is only mechanistic in nature and is based on the interpretation of the process.

The following is a brief review of the work of the author in this field. It is intended to be a summary of the work done in this field and is not intended to be a comprehensive review of the literature.

Distribution coefficient of simple monovalent anion. In the equilibrium distribution experiments of the anion Y^- between an organic solution of the salt $\overline{RX}$ and an aqueous solution of the salt MY in mixture with the electrolyte CX the distribution coefficient of Y^- is given by the following expression

$$D = (Y)_{\text{org}} / (Y)_{\text{aq}} \quad (12)$$

where $(Y)_{\text{org}}$ and $(Y)_{\text{aq}}$ are the concentrations of Y^- in the organic and aqueous medium respectively.

Considering equilibrium (4) the concentration of (Y^-) in the organic phase will be given by

$$(Y)_{\text{org}} = \sum_1^J j(\overline{RY})_j + \sum_1^A \sum_1^B b[(\overline{RX})_a (\overline{RY})_b] \quad (13)$$

Using equations (6), (7), (8), (9) the (13) reduces to

$$(Y)_{org} = \sum_1^J j K_{(1,X,Y)}^j K_{(j,Y)} (\overline{RX})^j (Y)^j (X)^{-j} F^{-j} +$$

$$+ \sum_1^A \sum_1^B b K_{(1,X,Y)}^b K_{(a,b)} (\overline{RX})^{a+b} (Y)^b (X)^{-b} F^{-b} \quad (14)$$

From equations (12) and (14) we have

$$D = K_{(1,X,Y)} (\overline{RX}) (X)^{-1} F^{-1} + \left[\sum_2^J j K_{(1,X,Y)}^j K_{(j,Y)} (\overline{RX})^j (Y)^{j-1} (X)^{-j} F^{-j} + \right.$$

$$\left. + \sum_1^A \sum_1^B b K_{(1,X,Y)}^b K_{(a,b)} (\overline{RX})^{a+b} (Y)^{b-1} (X)^{-b} F^{-b} \right] \quad (15)$$

The first term on the right part of equation (15) is the distribution coefficient when the simple mass action law is followed.

The terms in square brackets account for the presence of $(\overline{RY})_j$ species and for the formation of heteropolymer $[(\overline{RX})_a (\overline{RY})_b]$. The use of the monomer concentration (RX) accounts for the aggregation of the salt RX .

From equation (15) the difference $\Delta D = D - (K_{(1,X,Y)} (\overline{RX}) X^{-1} F^{-1})$ can be calculated if experimental values for D are available in the low concentration range where the monomer predominates. In this condition the ΔD is given by the term in square brackets

$$\Delta D = \left[\sum_2^J j K_{(1,X,Y)}^j K_{(j,Y)} (\overline{RX})^j (Y)^{j-1} (X)^{-j} F^{-j} + \right.$$

$$\left. + \sum_1^A \sum_1^B b K_{(1,X,Y)}^b K_{(a,b)} (\overline{RX})^{a+b} (Y)^{b-1} (X)^{-b} F^{-b} \right] \quad (16)$$

On a logarithmic plot of D vs. $(\overline{RX})$, ΔD is represented by the difference between the experimental D values and the line with slope 1. To draw the line with slope 1 it is assumed that the D values of the lowest

ammonium salt concentration used in the experiment matches the assumption that simple mass action law is followed. The definition of a concentration range where the plot of $\log D$ vs. $\log(\overline{RX})$ follows a straight line with slope 1 is sometime experimentally difficult. It is then more suitable to obtain an expression connected with D that allows a limit operation to zero $(\overline{RX})$ values.

A new function, Q , is obtained by multiplying equation (15) by $(\overline{RX})^{-1} (X)(F)$

$$Q = K_{(1,X,Y)} + \sum_{j=1}^J j K_{(1,X,Y)}^j K_{(j,Y)} (\overline{RX})^{j-1} (Y)^{j-1} (X)^{-(j-1)} F^{-(j-1)} +$$

$$+ \sum_{a=1}^A \sum_{b=1}^B b K_{(1,X,Y)}^b K_{(a,b)} (\overline{RX})^{(a+b-1)} (Y)^{b-1} (X)^{-(b-1)} F^{-(b-1)} \quad (17)$$

From equation (17) the values of $K_{(1,X,Y)}$ can be obtained as the limit of the function $Q = f(\overline{RX})$

$$\lim_{(\overline{RX}) \rightarrow 0} Q = K_{(1,X,Y)} \quad (18)$$

It must also be noted that $K_{(1,X,Y)}$ can be obtained using the total ammonium concentration as the variable in calculating the limit by the extrapolation method even if the presence of i-mers have been detected.

From equations (17) and (18) it is possible to calculate a new function ΔQ ,

$$\Delta Q = Q \cdot K_{(1,X,Y)} = \sum_2^J j K_{(1,X,Y)}^j K_{(j,Y)} (\overline{RX})^{j-1} (Y)^{j-1} (X)^{-(j-1)} F^{-(j-1)} +$$

$$+ \sum_{l=1}^A \sum_{l=1}^B b K_{(1,X,Y)}^b K_{(a,b)} (\overline{RX})^{(a+b-1)} (Y)^{b-1} X^{-(b-1)} F^{-(b-1)} \quad (19)$$

The function $\Delta Q = f(\overline{RX})$, as well as $\Delta D = f(\overline{RX})$, can be used to analyze the presence of $(\overline{RY})_j$ species in the organic phase. If different $(\overline{RX})_i$ species are present, the free monomer concentration $(\overline{RX})$ at equilibrium must be used for this analysis. Equations (15) and (17) show that D and K depend on both $(\overline{RX})$ and (Y).

Distribution coefficient of anionic metal-complex. The simple case of a monovalent anionic metal complexes will be considered. In the case of a metal ion, M^{n+} , of valence n forming anionic complex with the ligand X^- (anion of the supporting electrolyte CX) the distribution coefficient is given by the ratio of the metal concentration in the organic and in the aqueous phases

$$D = (M)_{\text{org}} / (M)_{\text{aq}} \quad (20)$$

Considering the equilibrium formation of the specie MX_i with $i = 0, 1, \dots, n+1$

its equilibrium constant $K_{(i,aq)}$ is given by the expression

$$K_{(i,aq)} = (MX_i^{n-i}) / (X^-)^i (M^{n+}) \times F_i' \quad (22)$$

where () indicates concentrations and F_i' is an activity coefficient function that take into account the activity coefficient of each species

in the equilibrium (21). When $i = 0$ it is $K_{(1,aq)} = 1$.

The total aqueous concentration of the metal is then given by the expression

$$(M)_{aq} = (M^{n+}) \sum_i K_{(i,aq)} (X^-)^i (F_i')^{-1} \quad (23)$$

It will be convenient to the following discussion to express

the activity function F' in terms of mean activity coefficients when $i = (n+1)$. The equation (22) for $i = (n+1)$ reduces to

$$K_{(n+1,aq)} = (MX_{n+1}^-) / (M^{n+})(X^-)^{n+1} \times \gamma_{MX_{n+1}}^{+} (CX) / \gamma_{MX_n}^{n+1} (CX) \gamma_{CX(0)}^{+} \quad (24)$$

where $\gamma_{MX_{n+1}}^{+} (CX)$ is the mean activity coefficient of the electrolyte $C^+MX_{n+1}^-$ (with C^+ the monovalent cation of the supporting electrolyte CX) in the presence of CX, $\gamma_{MX_n}^{+} (CX)$ is the mean activity coefficient of the electrolyte MX_n in the presence of CX, and $\gamma_{CX(0)}^{+}$ is the mean activity coefficient of the supporting electrolyte in the presence of the other species. If $CX \gg MX_n$ it justifies the use of the mean activity coefficient of CX, γ_{CX}^{+} , in place of $\gamma_{CX(0)}^{+}$.

The distribution of the metal complexes can be described by means of a set of equations equivalent to equations (6), (7), (8), and (9), considering the anionic complex MX_{n+1}^- in place of Y^- . Of course all the considerations concerning these equations are still valid.

Considering equilibrium (4) and the equations (6), (7), (8), (9), and (24), the total metal concentration in the organic phase is given by the expression

$$\begin{aligned}
M_{(\text{org})} = & K_{(1,X,Y)} K_{(n+1,aq)} (M^{n+}) (\overline{RX}) (X^-)^n \gamma + \\
& + \sum_2^J j K_{(1,X,Y)}^j K_{(n+1,aq)}^j K_{(1,X)} (M^{n+})^j (\overline{RX})^j (X^-)^{nj} (\gamma)^j + \\
& + \sum_1^A \sum_1^B b K_{(1,X,Y)}^b K_{(n+1,aq)}^b K_{(a,b)} (\overline{RX})^{a+b} (M^{n+}) (X^-)^{nb} (\gamma)^b
\end{aligned} \tag{25}$$

$$\text{with } \gamma = \frac{n+1}{\gamma_{\pm}^{MX(CX)}}.$$

From equations (20), (23), and (25) the distribution coefficient is given by the expression

$$\begin{aligned}
D = & [K_F (\overline{RX}) (X^-)^n (\gamma)] + \sum_2^J j K_F^j K_{(j,X)} (M^{n+})^{j-1} (\overline{RX})^j (X^-) (\gamma)^j + \\
& + \sum_1^A \sum_1^B b K_F^b K_{(a,b)} (\overline{RX})^{a+b} (M^{n+})^{b-1} (X^-)^{nb} (\gamma)^b \left[\sum_i K_{(i,aq)} (X^-)^i (F_i')^{-1} \right]^{-1}
\end{aligned} \tag{26}$$

$$\text{with } K_F = K_{(1,X,Y)} K_{(n+1,aq)}.$$

At fixed aqueous ionic strength a logarithmic plot of D vs. $(\overline{RX})$ must give a straight line with slope 1 if only monomers are present in the organic phase. In presence of other species a positive deviation from the line of slope 1 is expected and the function $\Delta D = f(\overline{RX})$ can be calculated as well as has been done in equation (16).

$$\Delta D = \left[\sum_2^j K_F^j K_{(j,X)} (M^{n+})^{j-1} (\overline{RX})^j (X^-)^{nj} (\gamma)^j + \sum_1^A \sum_1^B b K_F^b K_{(a,b)} (\overline{RX})^{a+b} \right. \\ \left. \times (M^{n+})^{b-1} (Y^-)^{nb} (\gamma)^b \right] \left[\sum_i K_{(i,aq)} (X^-)^i (F_i')^{-1} \right]^{-1} \quad (27)$$

Let us now define the following function, $(Z)^{-1} (o)$

$$(Z)^{-1} = K_{(n+1,aq)} (X^-)^n \gamma / \sum_i K_{(i,aq)} (X^-)^i (F_i')^{-1} \quad (28)$$

Multiplying equation (26) by Z and $(\overline{RX})^{-1}$ the following expression is obtained

$$Q = K_{(1,X,Y)} + \left[\sum_2^j K_{(1,X,Y)}^j K_{(j,X)} (M^{n+})^{j-1} (\overline{RX})^{j-1} (X^-)^{(nj-n)} (\gamma)^{j-1} + \right. \\ \left. + \sum_1^A \sum_1^B b K_{(1,X,Y)}^b K_{(a,b)} (\overline{RX})^{(a+b-1)} (M^{n+})^{b-1} (X^-)^{nb-n} (\gamma)^{b-1} \right] \quad (29)$$

Equation (29) is the twin of equation (17) for the case of monovalent metal-anionic complex. The value of $K_{(1,X,Y)}$ can be obtained by calculating the limit for $RX \rightarrow 0$ of the function $K = f(\overline{RX})$. The eventual partition of the specie MX_n at the place of MX_{n+1} will require the use of $K_{(n,aq)}$ instead of $K_{(n+1,aq)}$ in equations (26), (28) and (29).

From equation (29) the function $\Delta Q = f(\overline{RX})$, can be obtained

$$\Delta Q = Q - K_{(1,X,Y)} = \left[\sum_2^j K_{(1,X,Y)}^j K_{(j,X)} (M^{n+})^{j-1} (\overline{RX})^{j-1} (X^-)^{(nj-n)} (\gamma)^{j-1} + \right. \\ \left. + \sum_1^A \sum_1^B b K_{(1,X,Y)}^b K_{(a,b)} (\overline{RX})^{(a+b-1)} (M^{n+})^{b-1} (X^-)^{nb-n} (\gamma)^{b-1} \right] \quad (30)$$

In reference (7) the distribution data of ReO_4^- ion between aqueous electrolyte solutions and tertiary ammonium salt in organic solvent have been analyzed using equation (17). The analysis has been successful and

(c) It must be noted that we can obtain the molar fraction of the complex MX_{n+1} multiplying $(Z)^{-1}$ by $(X^-)^2 \gamma_{CX(o)}^2 Y_{MX_{n+1}}^{-2} (CX)$.

the formation constant of the mixed dimer $[(\overline{RX})_1 (\overline{RY})_1]$ with $X = Cl, NO_3, Br$, and $Y = ReO_4$ has been calculated.

An application of the approach here developed for the distribution of metal ion forming complexes with ligands will be made using the data of reference (8).

In reference (8) the extraction of $UO_2(NO_3)_2$ by tridodecylammonium nitrate in benzene has been studied over a rather large set of experimental conditions. The following model has been suggested by the authors to fit the experimental results.

To avoid a long explanation of the model, assumptions, and conditions, a careful reading of the quoted reference is suggested. Briefly it can be said that the authors describe the extraction of $UO_2(NO_3)_2$ as involving equilibria between amine nitrate monomer and dimer species, extraction of uranium by both of these species, and extraction of HNO_3 by amine nitrate. The final macroscopic result is that on an average in the organic phase one molecule of $UO_2(NO_3)_2$ interacts with three amine nitrate molecules.

(7) G. Scibona, R. A. Nathan, A. S. Kertes and J. W. Irvine, Jr. J. Phys. Chem.

(8) P. J. Lloyd and E. A. Mason, J. Phys. Chem. 68, 3120 (1964).

Now it is interesting to handle the data of Tables 1 and 11 of reference 7 using equations (29) and (30) and forgetting the model suggested in the quoted reference.

Since equations (29) and (30) ask for the use of the monomer concentration, $(\overline{RX})$, and these data are not available for toluene solutions of the salt RNO_3 , we have used the monomer concentration values of benzene solutions of tridodecylammonium nitrate salt (4).

It seems reasonable to us that the use of toluene in place of benzene doesn't affect the values of the monomer concentration appreciably.

The extraction of UO_2^{2+} from nitrate media by monomeric RNO_3 can be represented by either of the following reactions, which are thermodynamically indistinguishable.

The equilibrium constant of the equilibrium (35) is given by equation (24); the experimental distribution coefficient is described by equation (26). Tables 1 and 2 give the values of Q' obtained by dividing the distribution coefficient by the concentration of monomeric alkylammonium nitrate.

In the experimental conditions of reference 8 the equilibrium nitrate concentration in the aqueous solution is 2.85 ± 0.15 . The aqueous ionic strength, therefore the term $(X)^\gamma$ in equations (26) and (29), can be considered constant. Although Z is nearly constant under these conditions, it cannot be evaluated since $K_{(i, aq)}$ and F_i' are not known. Consequently, we will not multiply D by Z , with the result that all the terms of equation (29) are multiplied by the

constant term $(X)^{n_7}$ and that the values in Table 1 and 2 are $Q' = Q(X)^{n_7}$.

A very rough estimation of Z from equation (28), using the $K_{(i,aq)}$ at 35°C of reference (9) and neglecting F'_i , gives $Z = 1.2$.

The data in Table 2 refer to D values obtained using the same initial ammonium salt concentration and different aqueous uranium concentrations. The two different sets of data in Table 2 refer to different H^+ concentrations.

The D values in Table 1 obtained at H^+ 0.01 M have been obtained at such conditions as to make negligible both the uranium loading of the organic phase and the extraction of HNO_3 in excess with respect to the stoichiometry of the salt.

The monomer concentration of the salt corresponding to each amine concentration have been obtained from reference (4) and are reported in Table 1 (a) and (b).

A plot of Q' vs $(\overline{RNO_3})$ is in fig. 1. Using equations (29) and (30) the values of $\Delta Q'$ have been calculated. In fig. 2 the logarithmic plot of $\Delta Q'$ vs. $(\overline{RNO_3})$ shows a straight line with slope 3 suggesting the presence of the heteropolymer $[(\overline{RNO_3})_4(\overline{RUO_2(NO_3)_3})_1]$. Equation (29) then reduces to

$$Q' = K'_{(1,X,Y)} + K''(\overline{RX})^3 \quad (37)$$

with $K'' = K'_{(1,X,Y)} K_{(3,1)}$ and $K'_{(1,X,Y)} = K_{(1,X,Y)} (X)^{n_7}$

In Table 1 the values of $\Delta Q' / (\overline{RNO_3})^3 = K''$ and $\Delta Q'$ are reported. Since it is $K'_{(1,X,Y)} \approx 0.3$, the $K_{(3,1)}$ value is $K_{(3,1)} \approx K'' / K'_{(1,X,Y)} = \sim 3 \times 10^6$.

Considering both the monomer, $\text{RUO}_2(\text{NO}_3)_3$, and the heteropolymer, the average number of alkylammonium nitrate molecules per uranium atom is 2.5. If the D values are obtained at conditions that give excess HNO_3 in the organic phase and significant loading of the organic phase with uranium, it is necessary to know the nature of the salts in the organic phase in order to calculate the concentration of monomer. This information is not available at this time. However, an approximation can be tried. Assuming that the average aggregation number of the free ammonium salt is not affected by the presence of the heteropolymers and $\text{HNO}_3\text{-RNO}_3$ complexes, the free ammonium salt concentration, B, can be calculated by using the following expression

$$B = C_i - C_{\text{HNO}_3} - 2.5 C_U \quad (38)$$

C_i , C_{HNO_3} , and C_U are the initial amine concentration, the excess HNO_3 concentration in the organic phase, and the organic uranium concentration respectively. Values of B are reported in tables 1 (b) and 2 (a), (b). From reference (4) the monomer concentration for each B value is obtained, except for the highest B values, and are reported in tables 1 (b) and 2 (a), (b).

In fig. 3 the values of D vs. the monomer concentration ($\overline{\text{RNO}_3}$) are reported for the four sets of data of Tables 1 and 2. All the D values are reasonably well distributed around a straight line of slope 3.3 except for the last two points of Table 2 (b). The D values for the highest ammonium salt concentrations are not reported as a consequence of the uncertainty of the monomer values obtained by extrapolation.

Of course all the points on the straight line are satisfied by the same parameters. This means that all four sets of data fit the model of

a monomer and a 3 - 1 heteropolymer in the organic phase. $\Delta Q / (\overline{RNO_3})^3 = K''$ values are reported in Table 1 (b). K'' values are not calculated in Table 2 since there are not K values available at low (RNO_3) concentrations.

The two points far from the straight line are obtained at high loading conditions of the organic phase. The assumptions involved in equation (38) could not be satisfied in this condition. This analysis does not exclude the presence of other species that cannot be ^{detected} as a consequence of the precision of the distribution data.

From this discussion it seems that the approach here developed is able to carry out a satisfactory explanation of the data. The existence of a mixed tetramer in the organic phase does not disagree with the observation that the U.V. spectra show the pattern of trinitrato uranyl ion $UO_2(NO_3)_3^-$ (8). Dipole-dipole interactions are in fact possible in the organic phase.

It must be also pointed out that equation (26) gives a satisfactory explanation for non-integer slope found by different authors in the extraction of uranyl nitrate by amine nitrate (9 - 11). Furthermore it suggests that the use of a semiempirical equation of the form $D = K(C_1 - mC_U)^n$ used in the literature (12, 13) must be carefully considered. In fact these equations do not use the monomer concentrations necessary for the correct interpretation of the distribution process.

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Table 1.(a)

Amine Conc. M	$(\overline{\text{RNO}_3})$ Monomer M	D	Q'	$\Delta Q'$	$\Delta Q' / (\overline{\text{RNO}_3})^3$
0.346 ^a		2.91			
0.210 ^a	0.052	1.04	32.7	32.3	1.0×10^6
0.109 ^a	0.023	0.254	11	10.7	8.5×10^5
0.0501 ^a	0.015	0.0624	4	3.7	1.0×10^6
0.0210 ^a	0.0086	0.0141	1.6	1.3	2.0×10^6
0.0101 ^a	0.0057	0.0030	0.5	0.2	1.0×10^6

(b)

	B					
0.339 ^b	0.246	0.035	1.45	41.4	41	9.6×10^5
0.204 ^b	0.153	0.028	0.706	25.4	25	1.1×10^6
0.103 ^b	0.079	0.020	0.169	8.5	8	1.0×10^6
0.0515 ^b	0.039	0.0137	0.060	4.3	4	1.6×10^6
0.0208 ^b	0.016	0.0074	0.0084	1.1	0.8	2.0×10^6
0.0105 ^b	0.0081	0.0048	0.0006	0.4	0.1	1.0×10^6

^aFrom reference (8). Amine in equilibrium with 2.75 M NO_3^- , 0.010 M H^+ .

^bFrom reference (8). Amine in equilibrium with 2.95 M NO_3^- , 0.93 M H^+ .

Table 2 (a)

Amine Conc. M	B	$\overline{(\text{RNO}_3)}$ Monomer M	D
0.346	0.318	0.044 ^(o)	3.27
0.346	0.282	0.040 ^(o)	2.37
0.346	0.225	0.033	1.18
0.346	0.175	0.029	0.59
0.346	0.116	0.023	0.32

(b)

0.339	0.196	0.031	1.18
0.339	0.165	0.029	0.775
0.339	0.127	0.025	0.503
0.339	0.056	0.0165	0.305
0.339	0.048	0.015	0.281

^aFrom reference (8). Amine in equilibrium with 2.72 M NO_3^- , 0.0047 M H^+ .

^bFrom reference (8). Amine in equilibrium with 2.92 M NO_3^- , 0.940 M H^+ .

^(o)The monomer concentration has been arbitrarily extrapolated from the experimental data of reference (4).

Figures

Fig. 1 Plot of Q' against $\overline{(RNO_3)}$. The solid points refer to data of table 1 (a) the empty circles refer to data of table 1 (b).

Fig. 2 Logarithmic plot of $\Delta Q'$ against $\overline{(RNO_3)}$. The solid points refers to data of table 1 (a). The empty circles refer to data of table 1 (b).

Fig. 3 Logarithmic plot of D against $\overline{(RNO_3)}$. The solid points refer to data of table 1 (a). The empty circles refer to data of table 1 (b). The square ($\square$) refers to table 2 (a). The cross (x) refers to the data of table 2 (b).

Figure 1

Figure 2

Figure 3