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Thermodynamics of extraction by solutions of amines and salts of substituted ammonium bases

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ABSTRACT. Extraction systems containing amines and their salts are widely used to concentrate and separate metals. From the theoretical viewpoint, these systems are among the most complex, because of the variety of intermolecular interactions in the organic phase. The explanation and quantitative description of the observed regularities of extraction became possible only as a result of progress in the study of the thermodynamics of binary and multicomponent solutions of salts of substituted ammonium bases in non-polar organic solvents, which make it possible to distinguish the contribution of each type of interaction to the non-ideal character of the solutions. All known "anomalous" features are due to the influence of the hydration of the salts of the substituted ammonium bases on their activity.

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I. Introduction

The extraction of acids and metal salts by solutions of substituted ammonium bases is widely used in the processing of irradiated nuclear fuel, in hydrometallurgy, and in the analytical chemistry of various elements. The extensive published experimental material on extraction equilibria in various systems has been summarised in monographs,[1–7] reviews,[8–21] and reference works.[22,23] At the same time, systems containing the salts of substituted ammonium bases are very complex, and until recently for a number of systems there was even lack of agreement about the composition of the compounds extracted; contradictory data have been published on the state of the retracting agents in organic solvents, obtained from inter-phase distribution data and from independent physicochemical measurements.

An examination of the results of a large number of studies of the extraction properties of amines and their salts, and also the properties of solutions of salts of substituted ammonium bases in organic solvents, shows that the principal reason for these discrepancies is the lack of data on the influence of various factors on the activity of the salts.

The present review examines the thermodynamics of solutions of salts of substituted ammonium bases in organic solvents, the influence of various factors (molecular association, hydration, and solvation) on the activity coefficients of the salts, and the use of the observed regularities for the explanation and quantitative description of the extraction equilibrium. The review does not deal with molecular-statistical models of the solutions, except for models of an ideal associated solution (IAS), which can be regarded as one of the methods for describing deviations from ideal behaviour, so long as no physical significance is assigned to the calculated values of the association constants.

The thermodynamic methods for describing the deviations from ideal behaviour in solutions of substituted ammonium bases are general, and make it possible to predict the equilibrium in extraction systems containing reagents of different classes. The material in the present review is useful for explaining the properties of ion-selective electrodes with liquid and solidified membranes based on the salts of completely substituted onium bases, and also for describing the kinetics of the reactions taking place in the synthesis of organic compounds in two-phase systems containing inter-phase transfer catalysts.

II. Regularities of the extraction of acids and metal salts

The extraction of acids and metal salts by solutions of amines in organic solvents usually involves chemical reactions between molecules of the extracting agent and the substance being extracted. A knowledge of the stoichiometry of the reaction involved in the formation of the compound being extracted is a necessary condition for an understanding of the regularities of the extraction and the description of the extraction equilibrium.

The extraction of monobasic inorganic acids from their sufficiently dilute aqueous solutions by solutions of amines in non-polar solvents, when the electrolytic dissociation of the salt formed in the process can be neglected, is usually described by the reaction

$$R_3N(org) + H^+ + X^- \rightleftarrows R_3NHX(org), \qquad (1)$$

where R represents an organic group or a hydrogen atom, and X^- an anion. In the extraction of polybasic acids H_mX, normal $(R_3NH)_mX$ and acid R_3NH_mX salts are formed, the concentration of which depends on the equilibrium acidity, the nature of the organic solvent, and the strength of the acid and the base. For example, in the extraction of phosphoric acid by solutions of primary amines, normal phosphates are formed, whereas in extraction by tertiary amines, normal phosphates are not formed.[4] In the extraction of sulphuric acid by solutions of N,N-dioctylaniline, only the hydrogen sulphate $R_3NH_2SO_4$ is formed,[24] whereas in the extraction of sulphuric acid by the more basic tri-n-octylamine (TOA), various physicochemical methods have detected not only TOA sulphate and hydrogen sulphate

but also a compound with the intermediate composition $(R_3N)_3.(H_2SO_4)_2$.[25] Compounds with complex compositions are also formed in various other cases. Micro-quantities of peroxomolybdates are extracted by a trialkylmethylammonium sulphate as R_4NHMoO_6. The composition of the complex extracted at high molybdenum concentrations corresponds to the formula $(R_4NHMoO_6)_2H_2MoO_6$.[26]

The kinetics of the extraction of hydrochloric, perchloric, and sulphuric acids by solutions of TOA, tri-n-decylamine, and tri-n-laurylamine have been studied using a diffusion cell with stirring and with brief contact between the phases.[27] Since the rate of extraction is independent of the pH of the aqueous solutions and the concentration of the anion of the acid, it was concluded that the reversible protonation of the amine takes place at the inter-phase boundary.

The extent of the extraction of acids according to reaction (1) increases in the order $HCl < HBr < HI < HClO_4$, that is with decrease in the proton affinity and the hydration energy of their anions in aqueous solution. When different amines are used, the extraction of the acids decreases with increase in the degree of substitution: primary > secondary > tertiary amine.[28] Since the electronegativity of the hydrogen atom is lower than that of alkyl groups, the observed order of extractability is the opposite of that expected.[29] This contradication is apparently due to association of the amine salts as a result of the formation of hydrogen bonds between the non-substituted hydrogen atoms of the bases and the anions of the other salts. The existence of these interactions in solution has not yet been confirmed experimentally, but X-ray diffraction studies of crystals of the salts showed that they contain intermolecular hydrogen bonds.[29] Moreover, it has been established spectrophotometrically that hydrogen bonds are formed between the N–H groups of primary amines and the anions of the salts of quaternary ammonium bases R_4NX.[30]

The extraction of acids is influenced considerably by the nature of the organic diluent used and by the presence in the systems of a modifier (usually an alcohol or tri-n-butyl phosphate) added to prevent the formation of a second organic phase in the extraction. The distribution coefficients of acids usually increase with increase in the polarity of the organic solvents. Alcohols and other protogenic solvents generally facilitate the extraction of acids when normal salts are formed, and lower the distribution coefficients slightly when acid salts are formed.

The description of the extraction equilibrium is complicated considerably by the extraction of super-stoichiometric quantities of acid by the amine salts according to the equation

$$R_3NHX(org) + lH^+ + lX^- \rightleftarrows R_3NHX.lHX(org). \quad (2)$$

In the extraction of weak acids, for example hydrofluoric acid, the ratio of the concentrations of the acid and the amine in the organic phase increases continuously with increase in the concentration of the acid in the aqueous phase. A similar phenomenon is observed in the extraction of strong acids from their concentrated solutions. In this case, however, the extraction isotherm usually shows a clearly defined inflection corresponding to the point of complete neutralisation of the mine according to reaction (1). The extraction of super-stoichiometric quantities of the acid increases with decrease in the radius of the anion of the acid in the order perchlorate < iodide < bromide < chloride, and also on going from the salts of secondary amines to the salts of quaternary ammonium bases. Similar regularities are characteristic of the extraction of water by solutions of ammonium salts.

In the extraction of mineral acids by salts of onium bases, containing the anions of organic acids (HA), according to the reaction

$$R_4NA(org) + H^+ + X \rightleftarrows R_4NX(org) + HA(org) \quad (3)$$

the organic acid and the salt R_4NX are formed.[31,32] There is a close analogy between the regularities of the distribution of mineral acids in systems containing R_4NA and the regularities of extraction by neutral reagents with dissociation of the compound extracted in the organic phase.[33] By changing the nature of the components and the composition of the organic phase, it is possible to control the values of the distribution coefficients of inorganic acids and metal salts over a wide range at the stages of extraction and re-extraction. In particular, mixtures of TOA chloride with various acids (*p*-t-butylphenol, octanoic acid, di-2-ethylhexyl hydrogen phosphate, 5-t-butyl-2-hexadecylbenzenesulphuric acid) effectively extract H_2PtCl_6 and H_2PdCl_4. Conditions under which platinum and palladium in these systems can be re-extracted with water have been found.[34]

When aqueous solutions containing the anions of a mineral acid HY are treated with solutions of ammonium salts, anion exchange takes place:

$$R_4NX(org) + Y^- \rightleftarrows R_4NY(org) + X^-. \quad (4)$$

The degree of extraction of the ions of monobasic acids decreases in the order $ClO_4^- > I^- > NO_3^- > C_6H_5COO^- > Br^- > Cl^- > HSO_4^- > HCO_3^- > CH_3COO^- > F^- > OH^-$.[10] A similar lyophilic series is observed for liquid and solidified ion-selective electrodes based on quaternary ammonium salts.

Reaction (1) usually precedes the extraction of metal salts by ammonium salts, which may involve addition

$$qR_3NHX(org) + M^{z+} + zX^- \rightleftarrows (R_3NH)_qMX_{z+q}(org), \quad (5)$$

or anion exchange

$$qR_3NHX(org) + MX_{z+q}^{q-} \rightleftarrows (R_3NH)_qMX_{z+q}(org) + qX^-. \quad (6)$$

The final equilibrium products of reactions (5) and (6) are identical, that is these reactions are thermodynamically indistinguishable. Studies of the kinetics of extraction showed that it takes place according to reaction (6) when acido-complexes of the metals predominate in the aqueous phase, and according to reaction (5) in their absence.[13,17] From an analysis of data on the extraction of uranyl chloride by solutions of trioctylmethylammonium chloride it was suggested that metals may be extracted by a cation-exchange mechanism by molecules of the extracting agent combined with super-equivalent acid.[35]

Equilibria (5) and (6) are influenced considerably by the nature of the organic diluent. The influence of the diluent on the distribution coefficient of the metal salt depends markedly on the nature of the cation and anion of the onium salt.

Metal salts may also be extracted by other mechanisms. Thus in the extraction of the platinum metals, the amines are coordinated to the metal atoms.[2] The formation of bonds between the nitrogen atoms of the amines and the metal being extracted is most characteristic of primary amines. In particular, it has been established by different methods that in the extraction of divalent zinc from thiocyanate solutions by primary amines, the amine complexes $(RNH_2)_2Zn(SCN)_2$ are formed.[36] Long-chain primary aliphatic amines, unlike tertiary and secondary amines, effectively extract hydrolysed forms of aluminium sulphate.[37] In the systems formed by R_3NHX and R_4NX with platinum metals, the extraction equilibrium is often displaced towards the formation of polynuclear complexes, whose concentration increases with decrease in the concentration of the extracting agent.[38] The extraction of alkali metal carbonates by solutions of quaternary ammonium carbonates is accompanied by appreciable inter-phase distribution of water, and this has been attributed to the extraction of the salts by a hydrate–solvate mechanism.[39]

A characteristic feature of extraction systems containing salts of substituted ammonium bases is the marked positive deviations of the organic phase from ideal behaviour, due to molecular association and solvation of the salts. Until recently there was no method for taking account of the influence of various interactions on the activity of the components of the organic phase, so that extraction isotherms had been described only for various simple systems, and many observed phenomena could not be explained even qualitatively.

The extraction constant for the extraction of acids according to Eqn. (1) is given by the expression

$$K = \frac{\overline{C}_s \overline{y}_s}{\overline{C}_a \overline{y}_a a_{HX}} = \frac{\overline{y}_s}{\overline{y}_a}, \qquad (7)$$

where C represents the molar concentrations of the components, K and $\tilde{K}$ the thermodynamic and effective extraction constants respectively, y the activity coefficient, a_{HX} the activity of the acid in the aqueous solution, the subscripts s and a denote the amine salt and the amine respectively, and the bar above the symbols denotes the concentrations and activities of the components of the organic phase. Data on the activity of water (a_w) and the activity coefficients of electrolytes in aqueous solution are given, for example, by Mikulin.[40] The characteristics of the calculation of the activity of the components in mixed electrolyte solutions have been examined by a number of authors.[40–43]

The extraction constant for the extraction of metals according to reaction (5) can also be written as

$$K = \frac{\overline{C}_c y_c}{\overline{C}_s^q \overline{y}_s^q a_{MX_z}} = \tilde{K} \frac{\overline{y}_c}{\overline{y}_s^q} = \overline{K} \frac{\overline{y}}{\overline{y}_s^q \gamma_\pm^{z+1}}, \qquad (8)$$

where $\overline{K}$ is the apparent constant calculated without allowance for the mean ionic activity coefficients in the aqueous phase $\gamma_\pm$, a_{MX_z} the activity of the metal salt in the aqueous phase, and the subscript c denotes the metal complex extracted.

The stoichiometric coefficient q is often determined by studying the extraction of micro-quantities of the metal at a constant composition of the aqueous phase and varying concentration of the extracting agent $\overline{C}_s$. Eqn. (8) then becomes

$$\lg D = \text{const} + q \lg \overline{C}_s + \lg(\overline{y}_s^q / \overline{y}_c), \qquad (9)$$

where D is the distribution coefficient of the metal, and const $= \lg(K[X^-]^z \gamma_\pm^{z+1})$. The plot of $\lg D$ against $\lg \overline{C}_s$ will obviously be linear, with slope q, only if the ratio of the activity coefficients $\overline{y}_s^q/\overline{y}_c$ remains constant in the range of concentrations $\overline{C}_s$ studied.

To understand the influence of macro-components on the extraction of micro-quantities of substances by solutions of quatarnary ammonium salts, it is of fundamental importance to take account of the electrolytic dissociation of the salts and the complexes formed in the organic phase.[44] The dissociation constants of simple and complex high-molecular-weight ammonium salts in benzene and nitrobenzene have been determined and tabulated.

Experimental data on the extraction of mineral acids by amine solutions show that the effective extraction constants depend markedly on the concentration $\overline{C}_s$.[20] It is usually assumed that the values of $\overline{y}_a$ are close to 1, and the increase in $\tilde{K}$ with increase in the concentration of the amine salt is attributed to the decrease in $\overline{y}_s$ as a result of association of the salts:

$$n R_3NHX(org) \rightleftarrows (R_3NHX)_n(org). \qquad (10)$$

The association constant is

$$\beta_n = \overline{C}_s(n)/[\overline{C}_s(1)]^n, \qquad (11)$$

where $\overline{C}_s(1)$ and $\overline{C}_s(n)$ are respectively the concentrations of the monomer and the n-mer of the amine salt. The association constants have been determined either from independent data (cryoscopic, ebullioscopic, etc.) or from distribution data (two-phase potentiometric titration). In the last case, the following equilibrium was studied[16]

$$n R_3N(org) + n H^+ + n X^- \rightleftarrows (R_3NHX)_n(org), \qquad (12)$$

with equilibrium constant

$$K_n = \overline{C}_s(n)/\overline{C}_a^n a_{HX}^n = K^n \beta_n. \qquad (13)$$

The concentration of the amine salt is

$$\overline{C}_s = \sum_n \beta_n [\overline{C}_s(1)]^n = \sum_n K^n \beta_n \overline{C}_a^n a_{HX}^n. \qquad (14)$$

The extraction of sulphuric acid has been studied in most detail. The earliest study of the extraction of sulphuric acid by benzene solutions of TOA[45] established that the effective extraction constant remains constant only as far as a TOA sulphate concentration of 0.02 M, after which it increases. The deviations from ideal behaviour were attributed to the "polymerisation" of TOA sulphate in benzene.

The use of the equilibrium-displacement method to determine the composition of the compound formed in the extraction of uranyl sulphate by amine sulphates[13,14] established that the distribution coefficient of uranium is proportional to the concentration of "free" amine sulphate to the approximate power 0.5. At the same time, according to saturation data, one molecule of uranyl sulphate reacts with two molecules of TOA sulphate.[18,46] This discrepancy was also attributed to the formation of associates, present in a stable colloidally dispersed state. Independent physicochemical studies showed, however, that in anhydrous benzene solutions, TOA sulphate is monomeric[25,47] and undergoes association to only a slight extent when water is added to the organic phase.[48,49] This weak association can explain only a small fraction of the deviation from ideal behaviour in the organic phase of the extraction systems studied.

The effective extraction constants for the extraction of monobasic inorganic acids by amine solutions also depend markedly on the concentration of the ammonium salts formed. The experimental data are often represented on coordinates $\lg \overline{C}_s$–$\lg(\overline{C}_a a_{HX})$. If it is then assumed that the deviations from ideal behaviour are due only to the association of the amine salt in the organic phase and that Eqns. (10) to (14) are applicable, then for the slope of the tangent to the curve on these coordinates it is possible to write

$$\frac{\partial \lg \overline{C}_s}{\partial \lg(\overline{C}_a a_{HX})} = \frac{\sum_n n K^n \beta_n \overline{C}_a^n a_{HX}^n}{\sum_n K^n \beta_n \overline{C}_a^n a_{HX}^n} = \overline{n}, \qquad (15)$$

where $\overline{n}$ is the average degree of association of the amine salt in the organic phase.

Experimental data[8,20] show that at low concentrations of the ammonium salt, the slope is close to 1 (linear section), that is there is no association. With further increase in $\overline{C}_s$, the slope gradually begins to increase, and at a certain concentration the tangent becomes perpendicular to the abscissa. From this it was concluded that the average degree of association had become infinite, and this was interpreted as corresponding to the formation of a colloidal solution. With further increase in $\lg(\overline{C}_a a_{HX})$, however, the curve deviates to an even greater extent towards the ordinate, and the slope becomes negative, indicating that Eqn. (15) and the entire concept developed cannot be used to describe the extraction in this range. According to

independent data,[20] at concentrations corresponding to the vertical position of the tangent the average degree of association is not even close to infinity.

For a long time there was no accepted explanation for this phenomenon. For example, Diamond[8] suggested that the "anomalous" relationships are due to a change in the properties of the pure solvent resulting from the presence of a large number of ions, so that the solvent acquires the properties of a completely new substance with better extraction characteristics. Later,[50] he concluded that the "anomalous" relationship is due entirely to the behaviour of the "free" amine, and that increase in the concentration of the salt leads to an increase in the activity coefficient of the amine and a marked decrease in the ratio of the activity coefficients of the components of the organic phase. Others[51] suggested that "the increase in the dielectric constant of the solution with increase in the concentration of the ammonium salt leads to a decrease in the association and an increase in the extraction constant. The superposition of these effects gives different curves, including the anomalous curve".

Similarly, no unambiguous explanation was found for the nature of the dependence of the extraction of metal salts on the structure of the cations of the substituted ammonium salts. The extraction of metal salts from nitric acid solutions increases in the order primary < secondary < tertiary < quaternary alkylammonium.[5] In sulphuric acid solutions, at least for the actinides(IV) and (VI), the opposite relationship is observed, and was described as "curious".[19]

The influence of modifiers on the extraction equilibrium is often examined using the model of an ideal associated solution. According to this model, the deviations of the solutions from ideal behaviour are due to the formation of associates or solvates, whose solution behaves as an ideal solution, and the equilibria between them obey the law of mass action. Thus it is assumed that in the presence of alcohols or other solvating additives (B), mixed associate–solvates are formed

$$n\mathrm{R_3NHX(org)} + p\overline{\mathrm{B}} \rightleftarrows (\mathrm{R_3NHX})_n\mathrm{B}_p\mathrm{(org)}. \qquad (16)$$

and the equilibrium constant is written as

$$\beta_{np} = \frac{[(\mathrm{R_3NHX})_n\mathrm{B}_p]}{[\overline{C}_s(1)]^n[\overline{C}_B(1)]^p}. \qquad (17)$$

Eqns. (16) and (17) are more general than Eqns. (10) and (11). Similar equations can be written for the extraction of metals. This approach has not yet been used systematically to describe the influence of modifiers on extraction by amines. Eqns. (16) and (17) are most frequently used when $n = 1$.[14,15] These equations, however, can hardly explain various "anomalous" features of extraction, for example the fact that the distribution coefficient of the metal passes through a maximum with increase in the alcohol concentration.[52]

An explanation of these and various other "anomalous" features became possible after the development of methods for taking systematic account of the influence of various interactions on the activity of the salts of substituted ammonium bases.

III. Determination of the activity of the components in ammonium salt solutions

The organic phase of amine extraction systems is a multicomponent solution, which in the general case contains a diluent, an amine, neutral and acidic amine salts, water, a modifier, and the metal complexes extracted. A characteristic of these solutions is that the amines and the ammonium salts formed in the extraction are non-volatile substances, sparingly soluble in water. There are at present no direct methods for determining the thermodynamic activity of substances of this kind. The activity of the ammonium salts is therefore usually determined by indirect methods from the activity of the other components of the solution.

1. Experimental methods

Most frequently, in solutions of ammonium salts, the activity of the solvent is determined. Since existing methods are not of equal value, it is necessary to consider them briefly. The direct method involving measurement of the vapour pressure of the solvent is rarely used,[53,54] since it requires extremely complex apparatus and does not make it possible to study sufficiently dilute solutions in which the mole fraction of the solute $x_2 < 0.01$. The most accurate and sensitive method for determining the activity of the solvent is apparently the cryoscopic method. It has been used to study solutions in benzene with a molality down to 0.0003.[55–57] The chief disadvantage of the cryoscopic method is the need to carry out the studies at the freezing point of the solvent. It is thus practically impossible to determine the influence of the nature of the solvent and temperature on the activity of the components of the solution. Of the diluents usually employed in extraction, only benzene is widely used for cryoscopic measurements. Isolated studies have been carried out using cyclohexane and *p*-xylene.[58]

The ebulliometric method using a manostat has the advantage over the cryoscopic method that it makes it possible to carry out studies with a large number of volatile solvents at different temperatures. Ebulliometry is widely used to study solutions of polymers. The instruments developed for these purposes make it possible to carry out measurements in solutions with solute concentrations down to 0.0003 mol kg^{-1} and even lower.[59–61]

Isothermal distillation, and the isopiestic method, are applicable only to solutions with concentrations not lower than 0.01 mol kg^{-1}. Studies by these methods were previously carried out at temperatures close to room temperature (25–50 °C) using the solvents benzene, tetrachloromethane, cyclohexane, and chloroform.[20,62–64] Methods of measurement were subsequently developed for studying solutions in less volatile solvents (toluene, chlorobenzene, butylbenzene, and chloronaphthalene) at temperatures up to 130 °C.[65]

The above methods make it possible to determine directly only the activity of the solvent a_1. Nevertheless, in many papers, the experimental data are given as the average degrees of association of the solute $\bar{n}$:

$$\bar{n} = \ln x_1/\ln a_1 = 1/\varphi, \qquad (18)$$

where x_1 is the mole fraction of the solvent, and φ the osmotic coefficient. The values of $\bar{n}$ give a clear picture of the deviations from ideal behaviour in solution, and are widely used in the theory of IAS. This theory has been justifiably criticised for the insufficient clarity of the physical ideas on which it is based. However, so long as a physical significance is not given to the association (solvation) constants calculated from Eqns. (11), (13), and (17), then the theory of IAS can be regarded as a method for describing deviations from ideal behaviour, where the activity of the solute is equal to the concentration of its monomer.

Another component of the organic phase of amine extraction systems whose activity can easily be determined is water. In practice, however, the opposite approach is used; the dependence of the concentration of water in the organic phase on its activity a_w is determined. Titration with the Karl Fischer reagent is usually employed for this purpose, although other methods are also known. The saturation of the organic phase with water at a definite water activity is often carried out by the isopiestic method with

thermostatting.[12] The previously popular method involving the equilibration of the organic phase with an aqueous salt solution with known a_w has a number of unsatisfactory features, and is now seldom used.

The activity of the other components of the organic phase of amine extraction systems has not yet been determined experimentally. The determination of the activity of a number of susbstances used as modifiers is possible in principle.

2. Methods for calculating the activity of the components

The activity of the components of the solution is most frequently calculated from the activity of the solvent using the Gibbs–Duhem equation in the form

$$\frac{10^3}{M_1} d\ln a_1 + \sum_{i=2}^{n} m_i d\ln a_i = 0 \qquad (19)$$

or

$$\frac{10^3}{M_1} d\ln f_1 + \sum_{i=2}^{n} m_i d\ln f_i = 0, \qquad (20)$$

where m_i, a_i, and f_i represent respectively the molality, activity, and molar activity coefficient of the ith component of the solution, the subscript 1 refers to the solvent, and M_1 is the molecular mass of the solvent.

For binary solutions, integration of Eqn. (20) gives the expression

$$\ln f_2/f_2^0 = -\frac{10^3}{M_1}\int_0^{m_2} \frac{1}{m_2}\frac{\partial \ln f_1}{\partial m_2} dm_2, \qquad (21)$$

where f_2^0 is the activity coefficient in the infinitely dilute solution. The absolute activity coefficients (standard state the pure substance) of the solute cannot be determined using the Gibbs–Duhem equation, so that the concentration activity coefficients are generally determined using $f_2^0 = 1$.

Eqn. (21) is practically never used to calculate activity coefficients, since as $m_2 \to 0$, the right-hand side becomes indeterminate. To avoid this difficulty, the concept of osmotic coefficient is used. Substituting Eqn. (18) in Eqn. (20) and integrating gives the following equation for the concentration activity coefficient:

$$\ln f_2 = \varphi - 1 - \int_0^{m_2} \frac{1-\varphi}{m_2} dm_2. \qquad (22)$$

The calculation of the activity coefficients from Eqn. (22) is usually carried out by graphical integration of the function $(1 - \varphi)/m_2$, extrapolating it to $m_2 = 0$.

The use of cross relationships has been proposed[66] for calculating the activities of the components in muiltcomponent solutions. Thus for solutions with components i, j, and k it is possible to write

$$\left(\frac{\partial \ln a_i}{\partial r_{kj}}\right) r_{ij} = \left(\frac{\partial \ln a_k}{\partial r_{ij}}\right) r_{kj} \qquad (23)$$

and

$$\left(\frac{\partial \ln f_i}{\partial r_{kj}}\right) r_{ij} = \left(\frac{\partial \ln f_k}{\partial r_{ij}}\right) r_{kj}, \qquad (24)$$

where $r_{ij} = x_i/x_j$ is the relative concentration. A particular case of r_{ij} is the molal concentrations

$$m_i = \frac{10^3}{M_1} r_{i1} = \frac{10^3}{M_1}\frac{x_i}{x_1}.$$

The method involving the calculation of the Gibbs free energy of the solution from the partial molar Gibbs free energy of one of the components,[67] and various other methods,[68–70] have been used in the calculation of the activities of the components of metallic alloys, but have not yet been used to interpret the results of the study of an extraction equilibrium.

It should be emphasised that different methods of calculation should theoretically give the same results. In practice, however, errors which are different for different methods are unavoidably introduced in the calculations. The well-founded selection of a method of calculation applicable to the systems being discussed in order to achieve the smallest uncertainty is as yet impossible, because of the lack of accurate experimental data.

3. Binary solutions

A knowledge of the activities in binary solutions is necessary for calculating the activities in more complex systems. Of the large number of binary solutions which may be formed with the participation of the components of the organic phase of amine extraction systems, only solutions of the amine salt (or amine)–non-polar solvent type have as yet been studied.

Only slight deviations from ideal behaviour have been observed in solutions of water[71] and amines[20,62] in non-polar organic solvents, so that the concentration activity coefficients of these substances in the binary solutions can be taken as 1.

Appreciable association takes place in solutions of alcohols in non-polar organic solvents. The activity coefficients of alcohols in binary solutions can be readily calculated from experimental data using Eqn. (22). A large number of studies have been devoted to binary solutions of substituted ammonium salts, whose degree of association varies over a wide range. Analysis of the experimental data[15] has shown that the association of ammonium salts increases in the following cases: 1) with increase in the radius of the anion (for a given cation) in the order fluoride < chloride < bromide < thiocyanate < nitrate < iodide < perchlorate; 2) with decrease in the length of the group of the ammonium cation; 3) with decrease in temperature; 4) with decrease in the dielectric constant of the solvent in the order of nitrobenzene > chloroform > benzene > xylene > tetrachloromethane > cyclohexane > alkanes; and 5) with decrease in the degree of replacement at the nitrogen atom for salts with a given anion in the order tertiary < secondary < primary amines. The salts of quaternary ammonium bases occupy an intermediate position between the salts of tertiary and secondary amines. Since the publication of the review cited,[15] a large number of new studies[1,3,5] of the association of ammonium salts have been published, confirming the above features.

It is assumed that the formation of intermolecular hydrogen bonds generally facilitates the association of salts of primary and secondary amines. The main factor responsible for the association of the salts of tertiary amines and quaternary ammonium bases, which have extremely high dipole moments,[1] is the electrostatic attraction between the molecules (chiefly dipole–dipole interaction), although in some cases (acid salts) intermolecular hydrogen bonds are also probably formed. Thus the dipole moments of the molecules of the hydrogen sulphates of tertiary amines are lower than those of the molecules of the chlorides or bromides of the same amines, although the latter are associated to a smaller extent than the hydrogen sulphates.[1,72]

There are comparatively few published data on the association of complex ammonium salts with metal salts in binary solutions. This is partly due to the insufficient stability of many complex salts, as a consequence of which it is necessary to introduce simple ammonium salts to displace the equilibrium in the solution. For stable complex

salts, the degree of association varies over a wide range, from 1 for the complex of uranyl sulphate with trioctylammonium sulphate in benzene[72] to 10 or more for tetraheptylammonium tetrachloro- and tetrabromoferrates.[62] NMR[73] has established that the association of the acido-complexes of lanthanide nitrates with the nitrates of tertiary amines increases with decrease in the length of the n-alkyl groups in the cations of the salts, and also on going from symmetrical to unsymmetrical cations.

A high degree of association makes it difficult to calculate the activity coefficients of ammonium salts from Eqn. (22). Thus in solutions of tridodecylammonium bromide in cyclohexane at a minimum concentration of 0.0077 M, the average degree of association $\bar{n} = 1.83$,[62] which corresponds to $\varphi = 0.546$. At the same time, for reliable extrapolation to infinite dilution in the calculation using Eqn. (22), it is necessary that the values of φ be close to 1 or at least greater than 0.9 at the minimum concentration of the solute. In the study of binary solutions of ammonium salts, this condition can be satisfied extremely rarely (the measurements have to be carried out in the concentration range 10^{-4}–10^{-3} M). Attempts have therefore been made to approximate the dependence of $\ln f_1$ or φ on the concentration of the solute by various functions, and then to carry out the integration of Eqns. (21) and (22).

For this purpose, the following polynomial expansion has been used[62]

$$\lg f_2 = A + Bm_2 + Cm_2^2 + Dm_2^3, \qquad (25)$$

where the subscript 2 refers to the ammonium salt, and the coefficients A, B, C, and D are non-zero. Since it follows from the definition of the concentration activity coefficient that $\lg f_2 = 0$ for $m_2 = 0$, Eqn. (25) can be regarded as an interpolation equation, applicable only in the range of concentrations studied in the work cited.[62] As noted by the authors cited,[62] the values of $\lg f_2$ calculated from Eqn. (25) may differ from the true values by a certain constant amount as a consequence of the inaccuracy of the extrapolation to infinite dilution in the integration of the Gibbs–Duhem equation. The value of $\Delta \lg f_2$ may reach about 0.15.[74]

A different approach was used by Gal and co-workers,[63] who represented the function under the integral sign in Eqn. (22) in the form of the polynomial

$$\frac{1-\varphi}{m_2} = A + Bm_2 + Cm_2^2 + Dm_2^3 + Em_2^4. \qquad (26)$$

This expansion is obviously preferable to that in Eqn. (25), since substituting Eqn. (26) in Eqn. (22) and integrating gives for $\lg f_2$ a polynomial which becomes zero for $m_2 = 0$. The dependence of $(1-\varphi)/m_2$ on m_2, however, is given by a curve resembling a hyperbola. For these relationships, the approximation by the polynomial is not effective, and the values of the coefficients of the polynomial are extremely sensitive to change in the range of the approximation. An extensive verification of the applicability of Eqn. (26) has not yet been carried out. It may be noted that the inverse function $m_2/(1-\varphi)$ is close to linear.

The following equation has been proposed[75] for solutions of ammonium salts in non-polar solvents

$$m_2^2/\ln f_1 = b_0 + b_1 m_2. \qquad (27)$$

This equation is useful for extrapolating data to infinitely dilute solutions, since significant deviations from linearity are observed only at high concentrations. Substituting Eqn. (27) in Eqn. (21) and integrating gives the equation

$$\ln f_2 = -\frac{10^3}{M_1 b_1}\left[\ln\left(1 + \frac{b_1}{b_0} m_2\right) + \frac{b_1 m_2}{b_0 + b_1 m_2}\right]. \qquad (28)$$

Thus the calculation of the activity coefficients in binary solutions of ammonium salts reduces to the determination of two empirical parameters, b_0 and b_1. This makes Eqns. (27) and (28) preferable to other equations used to describe the thermodynamic functions in these solutions. The values of the parameters b_0 and b_1 for a number of solutions have been published.[1] When $m_2 \ll 10^3/M_1$, Eqn. (27) becomes

$$\frac{m_2}{1-\varphi} = \frac{M_1}{10^3}(b_0 + b_1 m_2). \qquad (29)$$

Many authors use the theory of IAS to describe the deviations from ideal behaviour in binary solutions of ammonium salts. The calculation of the association constants for the same solutions using this theory leads to ambiguous results, however. For example, two alternative descriptions of the tridodecylammonium chloride–*o*-xylene system have been published.[76,77]

The activity coefficients (or the association constants, which to some extent are equivalent) in binary solutions are often used to describe the extraction equilibrium. This approach has been successful in a number of cases.[78] To avoid errors, however, before using the activity coefficients found in binary solutions, it should be established that the introduction of other components into the solution does not influence the values of the activity coefficients. For this it is necessary to develop methods for calculating the activity coefficients in multicomponent solutions of ammonium salts.

4. Calculation of the activities of solutes from the activities of the solvent in multicomponent solutions

The most complex problem is the calculation of the activities of substances in multicomponent solutions from the activities of the solvent. This problem can be simplified and reduced to the calculation of the change in the activity of a solute when another substance is added to the solution. The two most important cases may be noted. To explain the "anomalous" dependence of $\lg \bar{C}_s$ on $\lg(\bar{C}_a a_{HX})$ it has been suggested that the activity coefficient of the amine $\bar{y}_a$ increases when an amine salt is added to the solution.[50] Experimental data also indicate that the metal complex extracted may react with the amine salt in the organic phase. This interaction must be taken into account in the determination of q by the equilibrium-displacement method.

In the extraction of iron(III) chloride, only tetrachloroferrate ions $FeCl_4^-$ are present in the organic phase.[79] The values of q found by the equilibrium-displacement method, however, depending on the conditions of the experiment, lie in the range 1–2, due to the formation of $FeCl_5^{2-}$ ions or to the reaction of the tetrachloroferrate and the amine chloride.

In the extraction of lanthanide nitrates by amine nitrates, the dependence of $\lg D$ on $\lg \bar{C}_s$ is not linear,[80] and the deviation from linearity cannot be attributed entirely to the change in the activity coefficients of the salt $\bar{y}_s$. Finally, in some cases, reaction between the extracted complexes of different metals is possible.

The following equation was obtained[81] for calculating the activity coefficients in these systems by transforming the Gibbs–Duhen equation and the cross relationship (23)

$$\ln \gamma_2 = -\frac{10^3}{M_1}\int_0^{m_3}\frac{1}{m_3}\left[\frac{M_1}{10^3} + \left(\frac{\partial \ln a_1}{\partial m_2}\right)_{m_2=0;m_3}\right] dm_3, \qquad (30)$$

where γ is the activity coefficient when the concentration is expressed as the molality, and the subscript $m_2 = 0$ indicates that the derivative is taken as the concentration $m_2 \to 0$. Eqn. (30) can be used to calculate the change in the activity coefficients of micro-quantities of a solute when a third component is introduced.

Eqn. (30) has been used to determine the influence of an amine salt on the activity of an amine.[82] Three-component tetrachloromethane–tridodecylamine–tridodecylammonium bromide solutions were chosen as model systems; for these solutions, the slope of the plot of $\lg \overline{C}_s$–$\lg(\overline{C}_a a_{HX})$ becomes equal to infinity at $0.05\ M < \overline{C}_s < 0.1\ M$.[20]

Ebulliometric measurements showed that at a concentration $m_s = m_3 = 0.0482$ mol kg^{-1}, the expression in square brackets under the integral sign in Eqn. (30) is practically equal to zero, and the activity coefficients $\gamma_2 = \gamma_a$ do not differ significantly from 1. Thus the suggestion by Diamond and Bucher[50] that γ_a depends significantly on the concentration of the amine salt is not confirmed in this system, and it is necessary to look for another explanation of the anomalous dependence of $\lg \overline{C}_s$ on $\lg(\overline{C}_a a_{HX})$.

The ebulliometric method has been used to study the chloroform–tridodecylammonium chloride–tridodecylammonium tetrachloroferrate system.[83] The binary solutions based on these components are close to ideal, but in the ternary solutions, strong interaction between the solutes is observed. Thus the activity coefficients of micro-quantities of the amine tetrachloroferrate γ_c, calculated from Eqn. (30), decrease rapidly with increase in the concentration m_s, and at $m_s = 6 \times 10^{-3}$ mol kg^{-1}, $\gamma_c = 0.49$.

The systems formed by a solvent (tetrachloromethane or benzene) with tridodecylammonium nitrate and the complex of cerium or europium nitrate with tridodecylammonium nitrate have been studied in most detail.[85] Eqn. (30) was used to calculate the dependence of the activity coefficients of micro-quantities of the complex salts γ_c on the concentration of the amine nitrate, and it was shown that γ_c is smaller for the europium salts than for the cerium salts.[84] The values of γ_c were then used to describe the dependence of the distribution coefficient of micro-quantities of cerium and europium on the tridodecylammonium concentration at a constant composition of the aqueous phase. The extraction constants (more accurately, the products $K\gamma_{\pm}^4$) remained practically constant with change in the concentration of the extracting agent by a factor of 20, whereas neglect of γ_c led to a systematic drift of the constants (for example, in the extraction of europium, the apparent extraction constant changed by a factor of 2–3 in the concentration range studied).

Eqn. (30) can be used to calculate the activity coefficients of a solute only when its concentration is very low (micro-component). An equation has been derived,[85] making it possible to calculate the change in the activity coefficients of a solute when another substance is introduced into the solution over a wide range of concentrations For this purpose, the cross relationship (24) was intregated with replacement of the variables r_{12} and r_{13} by m_2 and m_3 respectively:

$$\ln f_2 = -\frac{10^3}{M_1}\int_0^{m_s}\left(\frac{\partial \ln f_1}{\partial m_2}\right)_{m_s}\frac{dm_3}{m_3}. \qquad (31)$$

It can be shown that as $m_2 \to 0$, Eqn. (31) becomes Eqn. (30). The calculation using Eqn. (31) is difficult, since the dependence of $\ln f_1$ on m_2 in solutions of amine salts is not linear. To eliminate this difficulty, Eqn. (31) was transformed to the equation[85]

$$\ln f_2 = \ln f_2^0 - \frac{10^3}{M_1}\int_0^{m_s}\left[\frac{\partial \ln (f_1/f_1^0 f_1^*)}{\partial m_2}\right]_{m_s}\frac{dm_3}{m_3}, \qquad (32)$$

where the superscripts 0 and * indicate that the activity coefficients were determined for binary solutions with $m_3 = 0$ or $m_2 = 0$. Eqn. (32) has been used to calculate the activity coefficients γ_c of the complexes of cerium and europium nitrates with tridodecylammonium nitrate. When the amine salt is added in the concentration range studied, γ_c is independent of the metal concentration.[85]

Allowance for the intermolecular association of the amine salts in the IAS model made it possible to develop mathematical models for the extraction of lanthanides from nitric acid solutions containing a salting-out agent by solutions of the nitrates of tertiary amines[86] and quaternary ammonium bases.[87]

IV. The influence of solvation of the extraction equilibrium

The solvation of ammonium salts by protogenic solvents in non-polar media has been studied in sufficient detail,[1,5,12,15] For example, infrared spectroscopy has shown that the reaction of the molecules of alcohols or water with the anions of the salts increases with increase in the degree of replacement at the nitrogen atom of the bases, and also with increase in the proton affinity of the anions.[88,89] Allowance for the influence of solvation on the extraction equilibrium using IAS theory does not explain the "anomalous" extraction relationships. The concepts of non-stoichiometric hydration and solvation of the salts[1] have proved to be more fruitful for describing the extraction equilibrium and understanding the essential features of the inter-particle interactions accompanying the extraction of acids and metal salts in systems containing solutions of amines and ammonium salts.

1. The hydration of ammonium salts

For many systems containing ammonium salts, in which the solubility of water (m_w) is relatively high, the distribution of water is described by the equation[90]

$$m_w = m_w^0 a_w (1 + k_r m_2), \qquad (33)$$

where m_w^0 is the solubility of water in the pure solvent at an equilibrium activity of water $a_w = 1$, and k_r the hydration parameter, related to the degree of hydration h by the expression

$$h = k_r m_w^0 a_w. \qquad (34)$$

An equation describing the activity of a solute in a ternary solution[1] was obtained from Eqn. (34) using cross relationships of the type (23) and (24):

$$\ln a_2 = \ln a_{20} - k_r m_w^0 a_w = \ln a_{20} - h, \qquad (35)$$

where a_{20} is the activity of the solute in the binary ammonium salt–solvent solution not containing water. Eqn. (35) was previously obtained by other methods.[91–93] Eqns. (33) and (35) were generalised to the case of multicomponent solutions.[94]

Thus the degree of hydration is a quantitative measure of the influence of the hydration of a solute on its activity on going from the binary solutions to solutions saturated with water at an equilibrium a_w. For the case being considered, where the distribution of water in the pure solvent and in the solution of the extracting agent obeys Henry's law, it is possible to write:

$$\Delta\mu_{2,hydr} = -RTh, \qquad (36)$$

that is the degree of hydration reflects the change in the partial molar Gibbs free energy of the ammonium salt when the solute is transferred from its dry solution to a solution containing water. Eqn. (35) can be transformed to the equation

$$\gamma_{hydr} = \exp(-h). \qquad (37)$$

It follows from Eqn. (37) that hydration lowers the activity coefficient of solutes if solutions of unit molality with the properties of infinitely

dilute solutions in the dry solvent are taken as the standard state. For the case being considered, the degree of hydration h is equal to the number of water molecules combined with a molecule of the solute in the organic solvent.[95] Thus for given values of m_w^0, hydration leads to lower values of γ_{hydr}, the higher the solubility of water in the organic phase of the extraction system.

In a number of cases it is more convenient to take as standard state a solution with the properties of an infinitely dilute solution, saturated with water at $a_w = 1$. The dependence on a_w of the activity coefficient γ_{21}, determined relative to this standard state, then has the form

$$\gamma_{21} = \gamma_2 \exp[h_\infty(1 - a_w)], \quad (38)$$

where h_∞ is the degree of hydration in the infinitely dilute solution at $a_w = 1$. In other words, the concentration activity coefficients in solutions saturated with water at $a_w = 1$ are equal to the concentration activity coefficients in the binary dry solutions. The equality of the activity coefficients determined in this way was established experimentally in a study of the extraction of hydrochloric and hydrobromic acids by trilaurylamine solutions.[78] This equality is observed in a relatively narrow range of change in the concentration of the trilaurylammonium salt, in which the distribution of water obeys Henry's law satisfactorily. The applicability of Eqns. (35)–(38) to ammonium salt solutions was confirmed by determining the activity of the salts in ternary solutions.[12,91] The range of change in h for the salts studied is fairly large. The greatest decrease in activity (by five orders of magnitude) was observed when water was added to solutions of methyltrioctylammonium sulphate.

Published data on the hydration of ammonium salts have been summarised.[1] The molar ratio of the concentrations of water and the salt in the solutions saturated with water depends on many factors. For quaternary ammonium salts it varies from 2 to 15, increasing with decrease in the molecular mass and symmetry of the cation.[96] In solutions of TOA sulphate and the salts of unsymmetrical ammonium bases, in which the solubility of water is high, the distribution of water shows appreciable deviations from Henry's law. These deviations are also observed in solutions of weakly hydrated amine salts, but at high concentrations of these salts. The deviations increase with decrease in the polarity of the organic solvents used.[90,91]

When there are deviations from Henry's law, the isotherm for the distribution of water can be described by the equation

$$m_w = \sum_{n_1,n_2} b_{n_1,n_2} a_w^{n_1} m_2^{n_2}, \quad (39)$$

where b_{n_1,n_2} is an empirical coefficient.

Substituting Eqn. (39) in the cross relationship (23)

$$(\partial \ln a_2/\partial \ln a_w) = -(\partial m_w/\partial m_2)_{a_w} \quad (40)$$

and integrating gives the expression

$$\ln a_2 = \ln a_{20} - \sum_{n_2,n_2} \frac{n_2}{n_1} b_{n_1,n_2} a_w^{n_1} m_2^{n_2-1}. \quad (41)$$

If all the terms with $n_1 \gg 2$ and $n_2 \gg 2$ are neglected, Eqn. (41) becomes Eqn. (35). For practical calculations, in the description of the influence of "non-linear" hydration, the following semi-empirical equation[97] is used instead of Eqn. (41)

$$\gamma_2 = \gamma_{20} \exp(-h_{int}), \quad (42)$$

and the integral degree of hydration h_{int}, reflecting the actual contribution of hydration to the decrease in the activity of the solute, is calculated from the isotherms for the distribution of water into the solution of the salt and into the pure solvent. With allowance for Eqn. (42), Eqn. (38) becomes

$$\gamma_{21} = \gamma_2 \exp(h_\infty - h_{int}). \quad (43)$$

Thus by using the values of h_{int} and h_∞ it is possible to change from the activities determined relative to solutions in the dry solvent to the activities determined relative to solutions saturated with water at a water activity a_w. In general, $h_{int} \geqslant h_\infty$, and the value of γ_{hydr} decreases with increase in the concentration of the salt.

Eqns. (35)–(43) make it possible to determine the regularities of the influence of hydration on the extraction equilibrium. Thus hydration is revealed most strongly in systems which include polybasic acids, and also ammonium salts containing methyl substituents. The contribution of hydration to the non-ideal behaviour of the organic phase of extraction systems decreases with decrease in the concentration of the salts and the proton affinity of their anions and with increase in the polarity of the solvents used.

As noted in section II, the most familiar "anomalous" relationship in extraction by amines is the discrepancy between the data on the degree of association of the ammonium salts obtained by analysing the distribution on the one hand, and independent physicochemical measurements on the other. The anomalies found[20] in the analysis of data on the extraction of monobasic acids by solutions of trilaurylamine on coordinates $\lg \overline{C}_s$–$\lg(\overline{C}_a a_{HX})$ are observed to an even greater extent[91] for the sulphuric acid–water–benzene–TOA system, that is the anomalies increase with increase in the solubility of water in the extracts. The solubility of water in solutions of TOA sulphate does not obey Henry's law even for dilute solutions, and the integral degree of hydration increases with increase in the salt concentratrion. For this system over a wide range of change in the salt concentration, $\gamma_{20} \simeq 1$. The activity coefficient of TOA sulphate in the ternary solutions was determined by two methods: from the combined results of cryoscopic and isopiestic measurements, and also by calculation using Eqn. (42) and the isotherms for the distribution of water in salt solutions with different concentrations.[12] The extraction constants for the extraction of sulphuric acid by benzene solutions of TOA, calculated with allowance for the values of γ_2, are practically constant. This shows that in the sulphuric acid–water–benzene–TOA extraction system at low concentrations of the acid, the main factor responsible for the non-ideal behaviour of the organic phase is the hydration of TOA sulphate.[91]

The solubility of water increases considerably with increase in the concentration of trilaurylammonium halides. Thus the "anomalous" relationships observed by Mueller and Diamond[20] are also apparently due to hydration of the salts, and not their association.

Allowance for the influence of hydration on the activity of TOA sulphate also made it possible to eliminate the contradiction between data on the composition of the extracted complex of uranyl sulphate obtained by the saturation and equlibrium-displacement methods.[98] The slope of the plot of $\lg D$ against $\lg a_2$ is close to 2, indicating the formation of the complex $(R_3NH)_4UO_2(SO_4)_3$ in this system. The composition of the complex found in this way is identical to that established by the saturation method.

In a number of studies,[99–101] the activity coefficients of various ammonium salts were found from the isotherm of the surface pressure at the interface between water and a solution of the salt in an aromatic hydrocarbon. With change in the anion of the salt R_3NHX, the values of γ_2 decrease in the order perchlorate < iodide < bromide < chloride. From this it was concluded that the salts whose anions are least effectively extracted are most highly associated.[17,18] This does not agree, however, with data on the association of the salts in dry solutions, obtained by independent methods.[99] It is understandable that

the inversion of this series is due to hydration of the salts, which increases sharply with increase in the proton affinity of their anions and which makes a larger contribution to the non-ideal behaviour of the solutions than association of the salts.

The inversion of the order of activity of the salts in ternary solutions compared with the binary solutions is also observed in other cases. Thus as a consequence of the marked differences in the hydration of ammonium salts with different degrees of substitution, the observed extraction features often cannot be explained on the basis of the reactivity of the amines and the ammonium salts in their dry solutions.

It was pointed out above that the extraction of metals from sulphuric acid solutions increases in the order quaternary < tertiary < secondary alkylammonium. At the same time, spectroscopic studies show that the electron-donor properties of the anions of ammonium salts increase with increase in the degree of substitution at the nitrogen atom of the bases.[102] This "anomalous" dependence of the extraction of metal salts from sulphuric acid solutions on the nature of the cation of the ammonium salt is often related to a steric effect.[8,9] It has been shown, however, that the observed regularity is also due to the influence of hydration on the activity of the ammonium salts.[1] Thus at identical concentrations of secondary and quaternary alkylammonium sulphates, their degrees of hydration differ by approximately 7 units. From the stoichiometry of the complex formed, it can be shown that a decrease in the distribution coefficient should be observed in this order as a result of the difference in the hydration of the salts. For uranyl sulphate, for example, it decreases by a factor of approximately 10^6.[103] The difference actually observed in the extracting power of ammonium salts of the series being considered is appreciably lower, because of the increase in reactivity with increase in the degree of replacement at the nitrogen atom of the bases.

Methyldialkylamines and dimethylalkylamines are weaker bases than trialkylamines, so that the extraction constants for the extraction of acids by these compounds should be slightly lower. In fact, the extraction constant for the extraction of nitric acid by TOA solutions is slightly higher than that for extraction by solutions of methyldioctylamine.[104] The opposite picture is observed, however, for the extraction of hydrochloric and sulphuric acids.[5] The "anomalous" increase in the extraction constants for extraction by methyl-substituted tertiary amines corresponds quantitatively to the difference in the degrees of hydration of the chlorides and sulphates of these amines and those of the corresponding TOA salts in non-polar solvents.[12]

Thus the "anomalous" features observed up to the present in systems containing amines and ammonium salts can be explained only by taking account of the influence of hydration on the activity of the components of the organic phase. In extraction systems containing amines, the part played by hydration generally increases with decrease in the intensity of the acid–base reaction between the components. Hydration has a levelling action on the extraction of inorganic acids. The distribution of the salts between the phases is usually accompanied by displacement of water from the organic phase. Thus hydration facilitates the extraction of inorganic acids by amines, but depresses the extraction of metal salts.

2. The solvation of ammonium salts

To interpret data on the extraction equilibrium in systems containing modifiers, it is necessary to have data on the activity of the components in ternary solvent–ammonium salt–alcohol and solvent–alcohol–water systems and in quaternary solvent–ammonium salt–water–alcohol systems.

In the thermodynamic study of ternary solvent–ammonium salt–alcohol solutions, usually only the activity of the solvent is determined, and the activity of the salt is calculated using the cross relationships (23) and (24). The close analogy between the phenomena of the hydration of ammonium salts and their solvation by alcohols makes it possible to simplify the calculation of the activity of the salt. Eqn. (33) can then be written as:[105,106]

$$m_{al}\gamma^*_{al} = a_{al}(1 + k_s m_2), \tag{44}$$

where a_{al} and m_{al} represent respectively the activity and molality of the alcohol in the ternary solution, γ^*_{al} the activity coefficient of the alcohol in the binary solution ($m_2 = 0$) at the same concentration m_{al}, and k_s the solvation parameter.

Since it is difficult to determine the activity of alcohols in ternary solutions, Eqn. (44) cannot be confirmed experimentally. Only the equations for the activity of the ammonium salt and the solvent, obtained using Eqn. (44), can be verified.

In the derivation of the equation for the activity of the ammonium salt,[105] the cross relatonship (23) was used in the form

$$(\partial \ln a_2/\partial m_{al})_{m_2} = (\partial \ln a_{al}/\partial m_2)m_{al}. \tag{45}$$

Differentiating Eqn. (45) with respect to m_2 and integrating with respect to m_{al} gave the equation

$$\ln a_2 = \ln a_2^0 - \frac{k_s}{1 + k_s m_2} m_{al}. \tag{46}$$

Substituting Eqns. (44) and (46) in the Gibbs-Duhem equation (19) and integrating gives the following equation for the activity of the solvent.[106]

$$\frac{10^3}{M_1} \ln \frac{a_1}{a_1^0 a_1^*} = \frac{k_s m_s m_{al}}{1 + k_s m_2}, \tag{47}$$

where a_1^0 and a_1^* are the activities of the solvent in the corresponding binary solutions for $m_{al} = 0$ and $m_2 = 0$. Eqns. (44), (46), and (47) have been generalised to multicomponent solutions.[94]

Eqn. (47) has been used for the treatment of the results of cryoscopic measurements[49] in the three-component benzene–trioctylammonium sulphate–n-octanol and benzene–trioctylammonium sulphate–methanol systems by the isomolar-series method. These results were prevoiusly described assuming that a trioctylammonium disolvate is formed.[49] The calculated values of the stability constants of the disolvates varied from 393 to 783 for the first system, and from 1020 to 4800 for the second. The range of change in the solvation parameters k_s calculated from the same data was much smaller: from 11.6 to 17.1 for the first system, and from 21.1 to 25.4 for the second. Thus Eqn. (47) provides a better description of the experimental data on the solvation of the ammonium salts than equations based on stoichiometric considerations.

At low alcohol concentrations, Eqn. (47) is simplified and becomes

$$\frac{10^3}{M_1} \ln \frac{a_1}{a_1^0} = -\frac{m_{al}}{1 + k_s m_2}. \tag{48}$$

Eqn. (48) has been used to calculate solvation parameters from ebulliometric data. The results, given in Table 1, show that the solvation parameters of the ammonium salts decrease with increase in temperature, and also with increase in the radius of the anion and the length of the alkyl group of the cation of the salt. To compare data on the influence of "inert" solvents, the solvation parameters of the salts were calculated on the molar concentration scale $k'_s = k_s/d_0$, where d_0 is the density of the solvent. With change in the solvent, the values of k'_s decrease in the order n-pentane < cyclohexane < tetrachloromethane < benzene, that is with increase in the polarity of the solvent. Similar relationships were previously observed for the hydration of ammonium

salts,[15,90] indicating that the phenomena of solvation and hydration are similar. Certain differences are also observed, however; in the solvation by alcohols of trioctylammonium sulphate and methyldioctylammonium and tetrapentylammonium chlorides, a phenomenon analogous to the non-linear hydration detected for these systems is not observed.

Table 1. Solvation parameters k_s of ammonium salts by n-tetradecanol.

Salt	Temperature, °C	k_s	Δk_s	Refs.
Solvent tetrachloromethane				
$(C_{12}H_{25})_3NHCl$	78.6	8.95	0.97	[105]
$(C_{12}H_{25})_3NHCl$	45	15.83	0.79	[105]
$(C_{12}H_{25})_3NHCl$	35	37.8	2.0	[108]
$CH_3(C_8H_{17})_2NHCl$	78.6	11.04	0.19	[106]
$(C_{12}H_{25})_3NHBr$	35	23.98	0.98	[108]
$(C_8H_{11})_4NCl$	78.6	48.3	2.8	[109]
$[(C_{12}H_{25})_3NH]_2ZnCl_4$	35	15.6	1.3	[107]
$(C_8H_{13})_4NI$	78.6	7.41	0.24	[105]
$(C_8H_{13})_4NI$*1	78.6	7.30	0.19	[107]
$(C_8H_{13})_4NI$*2	78.6	7.45	0.65	[107]
$(C_8H_{17})_4NI$	78.6	6.91	0.40	[109]
$(C_4H_9)_3C_8H_{17}NI$	78.6	9.65	0.44	[109]
$(C_4H_9)_3C_8H_{17}NI$	78.6	22.0	2.90	[107]
$[(C_{12}H_{25})_3NH]_2CoCl_4$	78.6	20.8	1.8	[107]
Solvent benzene				
$[(C_8H_{17})_3NH]_2SO_4$*3	5.5	14.46	0.74	[106]
$[(C_8H_{17})_3NH]_2SO_4$*4	5.5	23.20	0.60	[106]
$[C_6H_5(C_{10}H_{21})NH_2]SO_4$*3	5.5	3.93	0.22	[106]
$(C_{12}H_{25})_3NHCl$	80.6	4.2	1.3	[108]
$(C_{12}H_{25})_3NHCl$	35	14.20	0.43	[108]
$(C_{12}H_{25})_3NHBr$	35	9.75	0.55	[108]
$(C_4H_9)_4NI$	80.6	4.15	0.41	[108]
$(C_8H_{17})_4NI$	80.6	3.64	0.26	[108]
$(C_4H_9)_3C_8H_{17}NI$	80.6	4.88	0.57	[108]
$(C_8H_{17})_3C_8H_{17}NBr$	80.6	8.1	1.7	[108]
$(C_5H_{11})_4NCl$	80.6	22.3	1.1	[108]
Solvent cyclohexane				
$(C_{12}H_{25})_3NHCl$	35	30.4	2.9	[108]
$[(C_{12}H_{25})_3NH]_2CoCl_4$	35	11.3	1.3	[107]
Solvent n-pentane				
$(C_{12}H_{25})_3NHCl$	36	28.4	2.5	[108]
$[(C_{12}H_{25})_3NH]_2ZnCl_4$	36	12.0	1.8	[107]

*1Solvation by n-decanol; *2by n-hexadecanol; *3by n-octanol; *4by methanol.

There are few published data on the hydration of alcohols in non-polar solvents. The solubility of water increases slightly in the presence of alcohols. The distribution of water at relatively low alcohol concentrations is described by Eqn. (33), and the degree of hydration of the alcohols is usually low. Thus for $a_w = 1$, the degree of hydration of n-octanol h_{al} in benzene is 0.052[110] or 0.049,[107] and that in tetrachloromethane is 0.043.[110] These data show that the addition of alcohols to non-polar solvents does not lead to a significant change in the activity of water in the organic phase.

The Gibbs–Duhem equation for a four-component solvent–ammonium salt–water–alcohol system can be written as

$$\frac{10^3}{M_1}\frac{\partial \ln a_1}{\partial m_{al}}dm_{al}+m_2\frac{\partial \ln a_2}{\partial m_{al}}dm_{al}+m_w\frac{\partial \ln a_w}{\partial m_{al}}dm_{al}+m_{al}\frac{\partial \ln a_{al}}{\partial m_{al}}dm_{al}=0, \quad (49)$$

The possibility of transforming this equation to a form convenient for calculations is determined by the nature of the dependence of the solubility of water on the alcohol concentration. The experimental study of the hydration of ammonium salts in the presence of alcohols shows the existence of two types of dependence of m_w on m_{al}.[107,110–112] For some systems at low alcohol concentrations and a constant activity of water the following equation is applicable:

$$m_w = m_w^0 + hm_2 + h_{al}m_{al}. \quad (50)$$

For other systems, when an alcohol is added, m_w decreases at first, after which it passes through a minimum and then increases slowly. The degree of displacement of water by the alcohol increases with increase in the proton affinity of the anion of the salt.[112] The last section of the curve can be described by Eqn. (50). In systems of the first type, $h \leqslant 1$, whereas in systems of the second type, the minimum solubility of water corresponds to $h \simeq 1$.

For systems in which the hydration of the salts is described by Eqn. (50), the derivative $\partial \ln a_w/\partial m_{al} \simeq 0$, since the values of h_{al} are usually low. In this case, Eqn. (49) becomes the Gibbs–Duhem equation for a three-component system. This means that in these sysems, the hydration and solvation of the ammonium salts take place independently of one another, and in the calculation of the influence of alcohols on the activity of the ammonium salts in the presence of water it is possible to use the same equations and solvation parameters as for anhydrous solutions.

The solubility of water in solvent–ammonium salt–metal complex–alcohol systems can also in a number of cases be described by Eqn. (50). The following equation has been proposed[107] for the description of the influence of solvation on the activity of the components in systems of this kind:

$$m_{al}\gamma_{al}^* = a_{al}(1 + k_{2s}m_2 + k_{3s}m_3), \quad (51)$$

where k_{2s} and k_{3s} are the solvation parameters of the ammonium salt and the metal complex respectively. This equation has been used[107,113] for the description of the extraction of micro-quantities of metals, and this has made it possible to eliminate the influence on the equilibrium of the change in the concentration of the extracting agent as saturation takes place. In this case, $m_3 \to 0$, and from Eqn. (51), using the cross relationship (45), it is possible to obtain the expressions

$$\ln(a_2/a_2^0) = -k_{2s}m_{al}/(1 + k_{2s}m_2) = \ln(\gamma_2/\gamma_2^0) \quad (52)$$

and

$$\ln(a_3/a_3^0) = -k_{3s}m_{al}/(1 + k_{2s}m_2) = \ln\gamma_3, \quad (53)$$

where γ_2 and γ_3 are the activity coefficients of the ammonium salt and the metal complex respectively in the presence of the alcohol, γ_2^0 the activity coefficient of the ammonium salt in the binary solution, and $\gamma_3^0 = 1$. At a constant composition of the aqueous phase and a constant concentration of the ammonium salt, substituting Eqns. (52) and (53) in Eqn. (9) gives the equation

$$\ln D = \ln D_0 - \frac{qk_{2s} - k_{3s}}{1 + k_{2s}m_2}m_{al}, \quad (54)$$

where D_0 is the distribution coefficient of micro-quantities of the metal in the absence of the alcohol.

Eqn. (54) has been used to describe the influence of n-tetradecanol on the extraction of micro-quantities of iron(III), cobalt(II), and zinc chlorides by solutions of tridodecylammonium chloride in tetrachloromethane.[107,113] In these systems the introduction of the alcohol has practically no influence on the hydration of the extracting agent. The

treatment of the experimental data was carried out using the linear regression equation

$$\ln D = \ln D_0 - bm_{al}. \quad (55)$$

The calculation using Eqn. (55) and the solvation parameters given in Table 1 gives values of b which are practically identical to those obtained from experimental distribution data.

The description of systems in which the addition of an alochol leads initially to a decrease in the hydration of the ammonium salt is even more complex.[52] In this case the distribution coefficient of the metal salt passes through a maximum with increase in the alcohol concentration. The position of the maximum coincides with the position of the minimum on the curve giving the dependence of the concentration of water in the organic phase on the alcohol concentration. The ascending branch of the dependence of the distribution coefficient of the metal salt on the alcohol concentration is due to the increase in the activity of the ammonium salt as a result of the decrease in its hydration when the alcohol is added, and the descending branch is due to the decrease in the activity of the salt as a result of its solvation. This descending branch of the curve is described by equations of type (54) and (55). The calculated increase in the activity of the ammonium salt corresponds to the observed increase in the distribution coefficient of the metal salt.

Thus the non-stoichiometric model of the hydration and solvation of ammonium salts developed by the present authors makes possible a fairly simple description and interpretation of data on the extraction equilibrium. The results obtained using this model are consistent with the results of independent physicochemical measurements.

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