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Extraction Systems with Associated Extractants

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The review examines the characteristics of the extraction behaviour of extractants with pronounced self-association in the organic solution. The importance of the correct choice of the model of the liquid for an adequate description of the properties of the system is discussed.
The bibliography includes 127 references.

CONTENTS

I. Introduction 263
II. General characteristics of associated substances 263
III. Methods for the description of associated solutions 264
IV. Extraction of substances by highly associated extractants 268
V. Distribution of acids and salts in systems with moderately associated extractants (arylammonium and alkylammonium salts) 270

I. INTRODUCTION

The problem of the processing of nuclear fuel and also the necessity of obtaining in large amounts and with a high degree of purity uranium, thorium, the individual lanthanides, and other rare and widely scattered elements to meet the requirements of nuclear power engineering have led to the vigorous development of certain fields of chemical engineering. The need for special purity of the materials led to the large-scale application of the extraction method for the isolation and purification of metal salts. During the last 10–15 years several hundreds of extractants capable of extracting metal salts and inorganic acids from aqueous solutions have been proposed and used on a laboratory and industrial scale. However, the study of the physicochemical properties of these systems has lagged appreciably behind the practical requirements. Many important details of the chemical behaviour of extractants (the effects of the hydration of the initial compounds and products, their solubilities in the organic phase, the effect of the solvent on the selectivity of the extraction and the stability of the complex extracted, the process kinetics, etc.) have been inadequately investigated.

The capacity of many extractants for self association is of special interest. Association in the organic phase is characteristic of extractants such as high-molecular-weight alcohols and phenols [1-13], carboxylic acids [14-20], alkyl- and aryl-phosphoric acids [21-44], and salts of organic ammonium derivatives [45-78]. Examination of the results of numerous studies on the properties of extraction systems including the extractants enumerated above reveals the following fundamental difficulties relating to the association of the extractant.

a. Conflicting data for the degree of association in the same systems or in systems with components of a similar chemical type obtained by different methods.

b. Unexpectedly simple linear concentration variation of the partition coefficients of metal ions (or acids) despite the non-linearity of the variation of the degree of association of the extractant.

c. Inconsistency of the experimental data for the concentration variation of the average degrees of association of the components with the thermodynamic properties of the model of the solution constituting the basis of the interpretation of these data.

The aim of the present reveiw was to examine the physical significance of models of the solution used for the description of extraction systems in connection with the chemical nature of the compounds present in solution, and also to indicate the principal studies in which ways of overcoming the above difficulties have been outlined.

II. GENERAL CHARACTERISTICS OF ASSOCIATED SUBSTANCES

1. Classes of Extractants with a Tendency towards Association

The capacity of particular substances for marked association in organic solvents is related directly to their chemical nature and the nature of the solvent. Thus alcohols, phenols, carboxylic acids, and organophosphorus acids contain both proton-donating and proton-accepting functional groups [OH, COOH, $OP(OH)_2$, etc.], which leads to the formation of a system of hydrogen bonds in the liquid.

A second mechanism of association, which plays a fundamental role for organic derivatives of ammonium salts, is the dipole–dipole interaction of the polar molecules of the extractants in a medium with a low dielectric constant.

As a rule, in real extraction systems the interaction is complex. Molecules of acid extractants and their metal salts usually have high dipole moments [72-79] and alkylammonium salts are capable of combining with "super-stoichiometric" inorganic acid molecules via hydrogen bonding:

$$R_4N^+.NO_3^- \ldots HNO_3.$$

Extensive experimental data have accumulated concerning the state of the extractant in the organic solvent. Association equilibria have been investigated by methods based on partition between two liquid phases [14-16,30-45,80,81], cryoscopy [21,25,38-42,50-54,80], ebullioscopy [60,82], measurements of the vapour pressure of the solvent [13,19,22-27,30,38,42,46,60-62,82], potentiometric titration [64,65], conductimetry [15,59,63-65], viscometry [21,23,54,59,63,65], light scattering [57,58,62,71], dielectric constant measurements [20,59,63,65,74,77], infrared, ultraviolet, and Raman spectroscopy of the solutions [6,21,25-27,30,32,38,48,59,63], and NMR and ^1H NMR methods [5,41].

Depending on the chemical nature of the extractant and the solvent, the concentration range considered, and temperature, the average degree of association varies within fairly wide limits, but in general one may say that carboxylic and monobasic alkylphosphoric acids are least associated. Their average degree of association is close to two or a little more at high extractant concentrations [16,21,25,29-31,38]. The degree of association of alcohols and phenols increases with concentration more slowly than that of acids, but it reaches much higher values [2-6,13]. The association of dibasic alkyl phosphate is highest; it has been shown [42,43] to reach values of the order of several tens or above at moderate concentrations. The degree of association of alkylammonium salts depends strongly on the nature of the anion and can sometimes reach equally high values [53,57-59,65,71,82]. Evidently, without a far-reaching study of the properties of associated solutions, it is impossible to understand the complex nature of the extraction processes involving the widely employed associated extractants and to predict correctly the effect of different factors on their extraction capacity.

2. Difficulties in the Quantitative Interpretation of Partition Data in Extraction by Associated Extractants

The quantitative interpretation of partition data is complicated by the multiplicity of the reactions. As a rule, the extractants can form with the extracted species not one but a series of complexes with different contents of the extractant per species extracted. For example, in the extraction of uranium by dialkylphosphoric acids [23,39] the complexes UO_2A_2, $UO_2A_2(HA)_2$, and probably $UO_2A_2(HA)_n$ may be present in the organic phase. Most physicochemical research techniques do not permit a direct determination of the number of species formed in solution, since experimental quantities (vapur pressure of the solvent, partition coefficients between the phases, freezing point, etc.) are functions of the overall concentration of all types of species of the solute. Another fundamental difficulty is the non-ideality of both the aqueous and organic solutions. The solute species (hydrated metal ions or acids in the aqueous phase and the set of complexes of different composition and solvated to different extents in the organic phase) interact with one another and with the solvent, which is formally taken into account by the deviation of the activity coefficients from unity. There is an extensive literature on the activity coefficients of electrolytes in aqueous solutions [83,84], but the available data concerning the activities of the components in the organic phase are scanty and are quoted only for individual thoroughly investigated extractants. With increase of the concentration of the extractant and the extracted compound, there is in many cases a marked change in the dielectric constant of the medium, because the majority of extractants are highly polar substances and their dielectric constants are higher by 10–20 units than that of the pure solvent [49,72-78]. In any description of the chemical interaction in the organic phase account must be taken of the change in the properties of the medium when the range of moderate and high solute concentrations is considered. In order to deduce the reasons for the discrepancies in the experimental degrees of association of the extractant obtained over a wide range of concentration, it is necessary to examine in detail model concepts which constitute the basis of the computational equations.

III. METHODS FOR THE DESCRIPTION OF ASSOCIATED SOLUTIONS

1. Model of the Ideal Associated Solution and the Metrics of the Physicochemical Diagram

In the study of the properties of solutions the concept of the ideal associated solution is widely employed, i.e. of a solution in which all kinds of interaction between the species can be divided into two types: strong "chemical" interactions with energies of the order of 2000–10 000 cal mole^{-1} involving the formation of stable configurations and the interactions between the association complexes and the molecules of the surrounding medium; the energies of interactions of the second type are of the same order as the thermal energy (about 600 cal mole^{-1}) and they do not lead to the formation of stable solvates [85]. It is postulated that such a mixture of monomeric solvent molecules and complexes of the solute constitutes an ideal solution at all concentrations (Prigogine and Defay [86], p. 387). The special case of the ideal associated solution [monomeric solvent–associated extractant (its association complexes can include also a third component—the substance extracted)] is of interest for extraction. The following relations can be formulated for such a system:

$$f_A = \frac{\rho}{\rho_0} \cdot \frac{1}{\frac{X_A}{r} + X_B}, \qquad f_B = \frac{1}{\frac{X_A}{r} + X_B} \qquad (1)$$

where f_A and f_B are the activity coefficients in the symmetrical reference system, X_A and X_B are the mole fractions of the extractant and the solvent respectively, ρ_0 is the mole fraction of monomeric molecules in the pure extractant, ρ the mole fraction of the extractant molecules present in solution in the monomeric form, and r the average degree of association of the extractant molecules. Thus it is possible to describe fully the thermodynamic properties of the system, provided that the degree of association of the pure extractant and the law governing its variation with concentration are known. It is usually assumed that the association reactions obey the law of mass action and that the equilibrium constants remain unchanged at all concentrations.

One can assume approximately, in accordance with Mecke's hypothesis [87], which has been proved from the standpoint of statistical thermodynamics [16], that in the standard state the stepwise association constants K_r are independent of the degree of association, i.e.

$$K_2 \simeq K_3 \simeq K_4 \simeq \ldots \simeq K_r = \frac{X_{r+1}}{X_1 \cdot X_r}, \qquad (2)$$

where X_r is the concentration in solution of the association complex containing r monomeric units.

The ideal associated solution model explains the marked positive deviations from Raoult's law which are characteristic of solutions with an associated component (Prigogine and Defay [86], p. 389), but the model itself is very approximate: the solvent in the model is regarded as an inert medium which does not react in any way with the solute and does not affect its association. The concentration association constants are assumed to be independent of concentration and can be determined by studying the pure associated component. In reality the degree of association depends very markedly on the nature of the

solvent, on its dielectric constant, on its capacity to form hydrogen bonds, etc. In particular, association constants cannot remain invariant at high concentrations, since under these conditions there is a marked change in the dielectric constant of the solution and other characteristics of the medium.

Another fundamental defect of the model is the neglect of the difference between the sizes of the species formed in the system. In the case considered the species differ in dimensions by factors of several tens and even hundreds [42,43,53,57,58,67,71,82,88,89]. In such solutions the entropy component of the excess free energy of mixing is of the same order of magnitude as the thermal component, which means that, for a correct interpretation of the experimental data, it is absolutely essential to take into account the influence of the difference between the dimensions of the association complexes and monomeric species, otherwise the calculated average degrees of association will be much too low.

Finally, when the solution is regarded as an ideal associated system, it is impossible to account for its separation into two organic phases [90], which is frequently encountered and is characteristic of systems containing organophosphorus extractants or alkylammonium salts in a hydrocarbon solvent [54,59,67,91].

2. Methods for the Improvement of the Metrics of the Physicochemical Diagram on the Basis of the Lattice Model of the Solution

The study of the thermodynamic properties of high-polymer solutions led to the development of the so called "athermal" model of the solution proposed initially by Fowler in 1937. [92] Subsequently Fowler's ideas were developed by Chang, Miller [93], and particularly Guggenheim [94]. The liquid is regarded as a quasicrystal in the lattice sites of which molecules are located. This approach makes it possible to take into account readily the differences between the dimensions and shapes of the molecules if one assumes that each site can be occupied by either one monomeric species or by one statistical segment of the association complex macromolecule. The lattice is characterised by a statistical average coordination number (subsequently designated by z). The difference between the dimensions of the component molecules is taken into account by the factor R_A—the number of lattice nodes occupies by monomeric molecules of the associated substance. To a first approximation, R_A is determined from the ratio of the molar volumes of the components. Molecular shape is reflected by the quantity q. The product zq characterises the number of contacts between the molecule and its nearest neighbours. By determining z, R_A, and q for any specific system, it is possible to estimate the number of A–A, A–B, and B–B contacts between the component molecules. If long-range forces are now neglected, which is quite admissible for solutions of organic substances in solvents of low polarity, it is possible to relate the enthalpy and entropy of mixing directly to the interaction energies of the molecules, their structure, and chemical nature.

With the aid of the usual methods of statistical mechanics and the lattice model of liquids, it is possible to obtain expressions for the energy and entropy of mixing or for the activity coefficients of the components in solution. Two cases are of special interest: a regular solution, the excess free energy of mixing in which is largely determined by the heat of mixing and the dimensions of the molecules of the components are assumed to be the same, and the opposite type, the so called athermal solution, in which the heat of mixing is negligibly small and the free energy of mixing is determined by the entropy component.

In a regular solution

$$|h^E| \gg T|s^E|, \tag{3}$$

where h^E is the molar heat of mixing and s^E the excess molar entropy of mixing. In the derivation of the fundamental equations it is assumed that the differences in the intermolecular interaction of species of different kinds are fairly small and the distribution of species in the system is random. The concept of the irregular solution was subsequently extended by Hildebrand and Scatchard to mixtures of molecules having different volumes [95] and semiemperical expressions were obtained for the activity coefficients:

$$\begin{aligned} RT\ln f_A &= v_A^0\left(\frac{v_B^0 n_B}{v_A^0 n_A + v_B^0 n_B}\right)^2 \cdot (\delta_A - \delta_B)^2 \quad , \\ RT\ln f_B &= v_B^0\left(\frac{v_A^0 n_A}{v_A^0 n_A + v_B^0 n_B}\right)^2 \cdot (\delta_A - \delta_B)^2 \quad , \end{aligned} \tag{4}$$

where v^0 is the molar volume of the pure component and n_i the number of moles of component i in the system. Eqns. (4) make it possible to calculate the activity coefficients from data for the pure substances, and the regular solution model has been frequently used to describe extraction systems [44,67,96]. However, according to the significance of the assumptions underlying it, the model can describe satisfactorily only a system with intermolecular dispersion interactions and is unsuitable for systems containing species with large dipole moments which are readily polarised or are capable of forming hydrogen bonds. The second fundamental defect of the regular solution model is the by no means complete allowance for the differences between the dimensions of the species. The introduction of molar volumes or of volume fractions as units of concentration corrects only for the differences between the dimensions of the monomeric species of the components, while the formation of polymeric aggregates or molecular chains in solution is disregarded and yet, for a degree of association $r \geq 5$, the contribution of the formation of association complexes to the excess entropy of mixing frequently becomes decisive.

For an athermal solution,

$$T|S^E| \gg |h^E| \tag{5}$$

and all the deviations from the properties of the ideal solution are determined by the difference between the dimensions and shapes of the species. Typical systems of this kind were described by Meyer [97,98]. They all consist of solutions of substances with large molecular weights and chain molecules in a non-polar solvent such as benzene or hexane and are characterised by a negligible heat of mixing and considerable negative deviations from ideality. Since the heat of mixing is small, the activity coefficients of an athermal solution are almost independent of temperature. Miller [93] showed that, in terms of the $z \to \infty$ approximation,

$$\begin{aligned} f_A &= \frac{N_A + N_B}{N_A + R_A N_B} \cdot \exp\frac{(R_A - 1)N_B}{N_A + R_A N_B} \quad , \\ f_B &= \frac{N_A + N_B}{N_A + R_A N_B} \cdot R_A \exp\left[-\frac{(R_A - 1)N_A}{N_A + R_A N_B}\right] \quad , \end{aligned} \tag{6}$$

where N_i is the number of lattice sites occupied by component i.

Eqn. (6) shows that the activity coefficients are smaller than unity. By a slight extension of Eqn. (6) as a result of the introduction of the parameter q, the physical significance of which was defined above, it is possible to take into account directly not only the dimensions but also the shape of the molecules.

In real systems containing an associated extractant in an organic solvent of low polarity, the intermolecular interactions are much more complex than in the limiting cases of regular or athermal solutions discussed above. There are two methods for the description of real associated solutions involving lattice concepts.

Barker [98,99] developed a pure lattice model in which account is taken not only of the van Der Waals forces but also of directional interactions of the hydrogen bond type, which depend on the mutual orientation of the molecules. In Barker's model the different classes of contact regions, corresponding to functional groups are considered, and the interaction energies of all possible combinations of contact regions are specified, the probability of the formation of each contact pair being determined by the condition of the free energy minimum. In other respects the quasichemical method proposed by Guggenheim is employed. The fundamental defect of Barker's model is a lack of theoretical parameters measured by independent methods. The mutual exchange energies employed in the calculations are essentially converted into empirical parameters and their choice as well as the choice of the geometrical characteristic z, q, and R_i is not unambiguous. The mathematical procedure is complex, requiring the use of computers, despite the approximate nature of the physical model itself (neglect of geometrical factors in the calculation of the probability of the formation of different contact pairs, an overestimate of the degree of order in the liquid, the lack of validity of the condition of constant lattice parameters over a wide range of concentrations, etc.).

Certain difficulties of the pure lattice models of solutions can be obviated by considering separately the strong directional interactions, treating them as ordinary chemical association reactions obeying the law of mass action and specifying the law of association, i.e. the dependence of the stepwise association constant K_r on the degree of association r. Weaker non-directional interactions are treated in terms of the lattice approximation, which makes it possible to take into account the influence of the dimensions and shapes of the species.

A version of this model has been proposed [42,89,100] for the description of solutions of highly associated substances—monoalkylphosphoric acids and alkylammonium salts—in a non-polar solvent (benzene, carbon tetrachloride, etc.). In this case the partition function for a binary system can be formulated as follows:

$$Q = G(N_D, N_T)\prod_D \psi_D^{N_D}\exp\left[-\frac{U(N_D, N_T)}{kT}\right], \quad (7)$$

where the subscripts D and T are general symbols defining the kind of all possible species (including association complexes and solvates) in the system, N_D is the number of species of type D, ψ_D the partition function with respect to the internal states of the molecule, $G(N_D, N_T)$ the number of configurations of the system, and $U(N_D, N_T)$ the configuration energy of the system, which depends on the number and class of contacts of all possible species in the system.

$G(N_D, N_T)$ is calculated from the formula

$$\ln G(N_D) = \sum_D \ln\left(\frac{\rho_D}{\sigma_D}\right)^{N_D} - \sum_D \ln N_D! + \frac{\sum_D N_D(r_D-1)}{\sum_D N_D(r_D-q_D)}\ln\left(\sum_D q_D N_D\right)! - \frac{\sum_D N_D(q_D-1)}{\sum_D N_D(r_D-q_D)}\ln\left(\sum_D r_D N_D\right)! \quad , \quad (8)$$

where ρ_D is the number of ways of distributing molecules of type D among r_D sites for a single fixed unit and σ_D is the molecular symmetry factor. A molecule of type D has in the general case surface regions which are not equivalent as regards energy. Suppose that ϵ and ν are general symbols of the class of contact regions on the molecule; the fraction of contact regions on a species of type D in class ϵ is designated by the symbol v_ϵ^D and can be readily calculated in each specific case. The quantity $U_{\epsilon\nu}$ is the energy of the contact formed by regions of classes ϵ and ν on particles of the same (D) or different (D and T) kinds.

It follows from Eqns. (7) and (8) that the chemical potential of species of type D (cyclic structures of association complexes and solvates are absent) is

$$\mu_D = kT\left\{-\ln\frac{\rho_D}{\sigma_D}\psi_D + \ln N_D - \frac{z}{2}q_D\ln\sum_T q_T N_T + r_D\left(\frac{z}{2}-1\right)\ln\sum_T r_T N_T\right\} + \frac{z}{2}q_D\sum_{\varepsilon,\nu}U_{\varepsilon\nu}\cdot(v_\varepsilon^D v_\nu + v_\nu^D v_\varepsilon - v_\varepsilon v_\nu) \quad . \quad (9)$$

For a specific system, account is taken of the association law $K_r = f(r)$, where K_r is the equilibrium constant of the reaction involving the addition of a monomeric unit to an r-mer of the associated component, and of the shape of the association complex (linear, cyclic, bulky, etc. complexes), whereupon it is possible to obtain from Eqn. (9) the relation between the activity coefficient of the solvent and concentration.

Thus, for the simplest case of an athermal associated solution ($K_2 = K_3 = \ldots = K_r$) and linear association complexes, we have

$$f_B = \frac{1}{1+(R_A-1)X_A}\left\{\frac{\frac{2}{z}h(1-X_A)}{(1-h)[1+(R_A-1)X_A]} + \frac{1+\left(\frac{z-2}{z}R_A-1\right)^{-\frac{z}{2}}}{1+(R_A-1)X_A}\right\} \quad (10)$$

where h is the overall effective concentration of all r-mers in solution:

$$h = \frac{[4K_r X_A(1-X_A)+1]^{1/2}-1}{2K_r(1-X_A)} \quad (11)$$

and X_A is the analytical concentration of the solute.

The advantages of this model consist in the direct allowance for the specific interactions and the simplicity of the estimation of the effect of the difference between the dimensions and shapes of the species on the excess thermodynamic functions of mixing. The empirical choice of the interaction constants constitutes the main defect of the model, although, for example, the average degree of association can be estimated also without employing the association constants.

The defects of the lattice approximation have little influence on the final results, since it is used only to introduce corrections to the van der Waals interaction of the association complexes with one another and with the medium.

An interesting method for the description of systems with associated components was proposed by Zagorets and Ochkin [101], who employed certain conclusions of Mayer and McMillan's theory of liquids [102] for the interpretation

of experimental data obtained in a study of the association of alkylammonium salts in benzene and carbon tetrachloride. They obtained a qualitative explanation of the maximum on the curve relating the degree of association to the concentration of the alkylammonium salt and also of the influence of the dimensions of the cation and anion and of temperature on the degree of association.

However, their assessment of the rigor and universality of the proposed method is open to objection. Thus, two expressions obtained by McMillan and Mayer are used as the initial equations:

$$\ln a = \ln \rho - \sum \nu B_{\nu n} \left(\frac{\Delta\alpha}{\gamma}\right)^{\nu-1} C^n \quad , \tag{12}$$

$$P = P_0 + kT\left[C + \frac{\Delta\alpha}{\gamma} - \sum(\gamma + n - 1)B_{\nu n}\left(\frac{\Delta\alpha}{\gamma}\right)^{\nu} C^n \right] \quad , \tag{13}$$

where ρ and C are the volume concentrations of the solvent and solute respectively, P_0 is the vapour pressure of the pure solvent, $B\nu n$ are the virial coefficients characterising the interactions of ν solvent molecules and n solute molecules, $\Delta\alpha = \alpha - \alpha_0$, α_0 being the activity of the pure solvent, and $\gamma = \alpha/\rho$ (here and below the notation used is that in the original report). The authors claim that "Eqns. (12) and (13) are rigorous, i.e. in their derivation no simplifying assumptions were made concerning the structure of the solutions. This constitutes an advantage of McMillan and Mayer's theory over other statistical theories of solutions (for example the lattice theory)". This is only partly true. Very important assumptions are made in Mayer's theory: the potential energy is regarded as the sum of pair interactions; the energy levels are assumed to be continuous, which is inadmissible for strong directional interactions. Apart from these fundamental simplifications of the initial theory, Zagorets and Ochkin introduced a number of further assumptions: in the expression

$$\frac{C^2}{\rho_0 \ln f_a} = \frac{1}{A_2}\left[1 - \frac{A_3}{A_2}C - \left(\frac{A_4}{A_2} - \frac{A_3^2}{A_2^2}\right)C^2 - \ldots\right] \tag{14}$$

they omitted higher terms, which restricts the applicability of subsequent expressions to low concentrations; moreover, a number of simplifying assumptions were made in the numerical calculations of Ochkin and Zagorets.

Comparison of the version of Mayer's theory proposed by Ochkin and Zagorets and the lattice models shows that both approaches constitute a very rough approximation. The simplifications of the lattice models are clearer and their validity is easier to check, while the consequences of certain approximations in the version under consideration are difficult to assess.

The considerable discrepancies between the calculation of the position of the maximum on the $n = f(m)$ curve from the formula proposed by Zagorets and Ochkin [101],

$$m_{\max} \simeq \sqrt{\frac{A_2}{-A_3 \cdot 10^{-3} M_2}} \tag{15}$$

and the experimental data is very instructive.

A similar attempt to apply a virial expansion to the description of solutions of an associated alkylammonium salt in benzene was made by Danesi et al. [62] As above, the authors make a number of simplifications: (1) they replace the second virial coefficient of the binary system (which depends on the concentrations of the components) by the corresponding coefficient for the pure solvent, (2) they neglect the higher terms of the expansion, and (3) they assume the partial molar volume of the mixture to be equal to the partial molar volume of the solvent.

As a result of these simplifications, they consider essentially the model of an ideal associated solution and, what is more, they assume implicitly its infinite dilution. Evidently the calculation of the average degree of association and other properties on the basis of such simplified models cannot yield a picture describing correctly the complex interactions in a real system.

3. Determination of the Degree of Association of Substances by Methods of Physicochemical Analysis

In order to refine the stoichiometry of the reactions, in the study of extraction equilibria many investigators attempted to determine by an independent method the degree of association of the extractant and its complexes with the metal. For these purposes, they employed cryoscopy [25,39,41,42,50–54,80], ebullioscopy [60,82], measurements of the vapour pressure of the solvent [13,19,22–26,30,32,42,61,82], light scattering [57,58,62,71], and viscosity measurements [21,23,54,59,63,65,70]. Data obtained by different methods for the same systems or systems of similar composition reveal very interesting contradictions. The average degree of association determined by cryoscopy, ebullioscopy, and measurements of the vapour pressure of the solvent proved to be appreciably lower than the value calculated from optical measurements and was inconsistent with the appreciably higher viscosities of such solutions compared with the viscosity of the pure solvent. The discrepancies may be very large. Thus, for trialkylammonium (C_7–C_{12}) nitrate solutions in benzene, cryoscopic measurements and measurements of the vapour pressures of the solvent yielded $r = 1.8$–5.0, whereas according to light scattering data [46] $r \simeq 60$. Similarly, for dialkylammonium sulphate solutions in benzene, light scattering data gave $r = 40$–50, which is higher by a power of 10 than the value derived from cryoscopic measurements [57,58,71].

In the determination of the average degree of association of the solute by methods based on the measurement of the activity of the solvent and of r over a wide range of concentrations, $r = \varphi(X)$ curves with a maximum are frequently obtained [47,52], which conflicts with the thermodynamic condition for the stability of the phase from the standpoint of the representation of the solution as an ideal mixture of all possible compounds (Prigogine and Defay [86], p. 404; Storonkin [103], p. 65):

$$\frac{\partial \mu_A}{\partial X_A} > 0 \text{ and } \frac{\partial^2 \mu_A}{\partial X_A^2} > 0 \quad \text{or} \quad \frac{\partial r_A}{\partial X_A} > 0 \text{ and } \frac{\partial^2 r_A}{\partial X_A^2} < 0 \tag{16}$$

Evidently the properties of the above class of solutions cannot be described by the theory of ideal associated solutions.

The reason for all these contradictions can be readily deduced by considering the model concepts used in the derivation of the equations for the activity of the solute. We shall consider in detail the cryoscopic method (ebullioscopy and tensimetry are based on similar postulates).

In the derivation of the computational formula

$$\Delta T = \frac{RT_{0B}}{L_B} \cdot \frac{M_B}{1000} m_A \qquad (17)$$

the following assumptions were made: (a) the components of the solution are completely miscible in the liquid state and do not form solid solutions; (b) the latent heat of fusion of the solvent is independent of temperature; (c) the solution obeys Raoult's law at all the concentrations considered; (d) the solution is very dilute.

All the deviations from properties of the ideal solution are explained by a change in the number of individual species as a result of chemical interactions:

$$r = \frac{m_A}{m_{A,\,eff}}, \qquad (18)$$

i.e. one uses essentially the model of an ideal associated solution, the fundamental disadvantages of which have already been discussed. Refined cryoscopic formulae proposed by Udovenko or Fomin [104] (p. 45) are valid for a wider concentration range but also only for an ideal associated solution.

A method has been proposed [89] for the calculation of the average degree of association of a substance in a monomeric solvent from the activities of the solvent on the basis of the theory of association equilibria in terms of the athermal approximation whereby account can be taken of the dimensions of the association complexes:

$$r = \frac{X_A}{\frac{z}{2}\left\{\left[\frac{1-X_A}{f_B X_B (1-X_A+R_A X_A)}\right]^{z/2} - 1\right\} \cdot [1+(R_A-1)X_A] + R_A X_A}, \qquad (19)$$

and the results of the calculation of the average degree of association in the trioctylammonium mononitrate–benzene system by Eqns. (17), (18), and (19) have been compared. Table 1 shows that neglect of the negative deviations from Raoult's law due to the formation in the solution of large association complexes reduces r by a power of ten. Calculations by Eqn. (19) agree satisfactorily with light scattering data [46, 57, 58, 71].

Table 1. Average degree of association of trioctylammonium nitrate in benzene according to cryoscopic data [105].

X_A	r_A (17, 18)	r_A (19) with $\begin{cases} R_A=5 \\ z=6 \end{cases}$
0.0090	2.1	2.0
0.021	3.1	5.9
0.041	3.3	32
0.068	2.6	50
0.094	2.1	>50

Similar results were obtained for the mono-n-octylphosphoric acid (MOPA)–carbon tetrachloride system from isopiestic measurements of the vapour pressure [42] (Table 2).

It follows from Tables 1 and 2 that the degree of association of the extractant is frequently found to be too low owing to an incorrect interpretation of the data. This factor must be borne in mind in considering the reactions involved in extraction by highly associated extractants.

IV. EXTRACTION OF SUBSTANCES BY HIGHLY ASSOCIATED EXTRACTANTS

1. Experimental Concentration Variation of the Partition Coefficients of Metals

We shall consider monoalkyl or monoaryl phosphoric acid esters as examples of typical highly associated extractants. The characteristic form of the variation of the partition coefficients of metals between the aqueous and organic phases $\alpha = M_{org}/M_{aq}$ and the extractant concentration in the organic phase S is striking; $\lg \alpha$ varies linearly with $\lg S$ over a wide range of compositions of both aqueous and organic phases [43, 100]:

(a) a unit slope of the concentration curve is observed for cations with different structures of the outer electron shell and in particular with different electrovalences (UO_2^{2+}, Am^{3+}, Np^{4+});

(b) the unit slope persists when the concentration of the inorganic acid in the aqueous phase, the supporting salt, and hence the degree of hydration of the cations are varied;

(c) the variation of the extractant concentration in the organic phase within wide limits (from 0.001 to 1.0 M) does not alter the slope of the concentration curve;

(d) the structure of the hydrocarbon group in the alkylphosphate molecule and the nature of the low-polarity solvent do not influence the slope of the concentration curve.

Table 2. Average degree of association of mono-n-octylphosphoric acid in carbon tetrachloride [42].

X_A	r_A (17, 18)	r_A (19) with $\begin{cases} R_A=1.3 \\ z=6 \end{cases}$
0.108	4.9	8.2
0.151	5.1	17.4
0.395	4.3	18.4
0.471	4.4	21
0.648	3.7	30
0.790	3.0	42

The slope changes only when the condition of a high degree of association of the extractant breaks down and also when solvents causing dissociation into monomers are employed, for example alcohols, or when the concentration of the metal extracted is raised above a certain limit [106]. Concentration curves have been obtained [36] for the extraction of trace amounts of europium and americium by MOPA solutions in various solvents (benzene, carbon tetrachloride, chloroform, n-hexane, and butyl chloride) and it was found that not only is the slope of the concentration curve the same in all cases but the numerical partition coefficients are very close at the same extractant concentrations [36]. This supports the hypothesis of a high degree of order in the distribution of the MOPA chain molecules in its association complexes. The $OPO(OH)_2$ polar groups are probably directed inwards and are surrounded by a stable hydration shell, while the organic groups are directed to the outside of the micelles. During extraction, cations pass from the aqueous phase to the hydration shell linked to the $OPO(OH)_2$ groups. The proposed structure provides a qualitative explanation of the independence of the partition coefficients of the nature of the low-polarity solvent and of the very high water

content in organic MOPA solutions. It has been found[42] that in 1 M MOPA solution in carbon tetrachloride up to 27 moles of water per litre dissolved on saturation, with a sharp increase of viscosity and degree of association (Table 3).

Table 3. Relative water content M_{H_2O}/M_{MOPA} in organic MOPA solutions in equilibrium with 2 M aqueous HNO_3 at 20°C.

Solvent	MOPA mole fraction in organic phase					
	0.0025	0.005	0.01	0.02	0.04	0.08
1-Hexanol	1.4	1.7	2.1	2.1	2.1	2.1
n-Butyl chloride	3.7	4.2	4.5	4.6	4.7	5.1
n-Hexane	7.5	12	13	14	15	16

2. Common Methods for the Interpretation of Experimental Relations

The partition of a substance between two immiscible phases has been used for a long time as one of the methods for the determination of the composition of the complex extracted[51,107-110]. The formation of a single compound in the organic phase is usually considered:

$$M_{(aq.)} + \tau S_{(org.)} \rightleftarrows (MS_\tau)_{(org.)} . \qquad (20)$$

The following relation is valid for this reaction:

$$\alpha = K\frac{(f_S S)^\tau f_M}{f_{MS\tau}}, \qquad (21)$$

where α is the partition coefficient of the substance extracted, K the thermodynamic equilibrium constant, S the concentration of the extractant, and f_S, f_M, and $f_{MS\tau}$ are the activity coefficients. It is assumed that at moderate concentrations the activity coefficients of the uncharged species are close to unity and τ, the number of extractant species involved in the reaction, is determined from the slope of the straight line represented by the equation

$$\lg \alpha = \lg K + \tau \lg S . \qquad (22)$$

The activity of the extractant is either found independently by the usual methods[111-113] or the activity coefficients are assumed to be constant. The method described can of course yield satisfactory results only when the properties of the organic phase differ little from those of an ideal solution. Real extraction systems contain as a rule polar extractants which interact strongly with one another and with the solvent. It can be shown[104] that the association of the extractant or its solvation by the solvent reduce the slope of the curve defined by Eqn. (22) and in the general case the slope becomes a complex function of the extractant concentration and the ratio of the association and solvation constants.

In most studies of the extraction of metal ions by highly associated extractants[105,114-116] the hypothesis that the organic phase in the given concentration range contains only one association complex is employed. Its degree of association is determined independently or simply selected in order to account for the experimental relations. Thus the mechanism

$$M^{l+}_{(aq.)} + \frac{2l}{r}(H_2A)_{r(org.)} \rightleftarrows M[H(HA)_2]_{l(org.)} + l\,H^+_{(aq.)} \qquad (23)$$

was proposed in numerous studies by Peppard and coworkers[25-29,31,33,34,38,40] to account for the characteristics of the extraction of a number of lanthanides and actinides by phosphoric acid monoesters. It explains the extraction of lanthanides with $l = 3$ and of actinides with $l = 4$. The slope of the $\lg \alpha = \varphi(\lg S)$ concentration curve, which is unity, seemingly agreed with the average degree of association of the extractant $r = 6-8$ found by cryoscopic measurements in solutions of mono-2-ethylhexylphosphoric acid (M2EHPA) in dry benzene. However, this mechanism does not explain why the slope is also unity in the extraction of UO_2^{2+},[117] which leads to $l = 4$. Moreover, it has been shown[42] that the degree of association of phosphoric acid monoesters in a non-polar solvent in the presence of water is much higher than 6-8 and changes with the concentration of the extractant. The same authors regard the formation of "infinite" polymers in the organic phase,

$$M^{l+}_{(aq.)} + (H_2A)_{r(org.)} \rightleftarrows M(H_{2r-l}A_r)_{(org.)} + l\,H^+_{(aq.)} \qquad (24)$$

as an alternative mechanism. Although the authors note correctly that in this case the slope of the concentration curve will be unity when $r \to \infty$ if only one cation of the metal extracted is linked to each association complex species regardless of the valence of the cation, they unfortunately did not carry out a quantitative analysis of the proposed mechanism. This led to the incorrect conclusion that the slope of the concentration curve depends on the average degree of association of the extractant which may vary with the concentration of the extractant, temperature, and certain other factors. Another possible explanation of the variable slope of the concentration curves is based on the hypothesis of the presence of several extractable complexes with different component ratios; however, here too there are difficulties when an attempt is made to explain why the slope of the curve decreases with increase of the concentration of the extractant[118].

3. Allowance for the Multiplicity of Interactions in the Organic Phase

In considering the mechanism of extraction by highly associated extractants, one or two, more rarely three, fixed values of r are usually taken into account for the description of the state of the extractants in the organic phase in order to simplify the calculations. The constants for equilibria of the monomer–dimer–polymer type are fitted to give the best agreement with experiment. The approximate nature of the model is evident.

A scheme of interactions taking into account the formation in the organic phase of all possible association complexes of the extractant has been proposed[42,43,119]. When trace amounts of the metal extracted are employed, the overall molar concentration of the extractant is

$$S = \sum_r r[A_r] . \qquad (25)$$

If we introduce the equilibrium constant β for the addition of the cation to a specified reaction centre in the association complex and the statistical factor W_r taking into

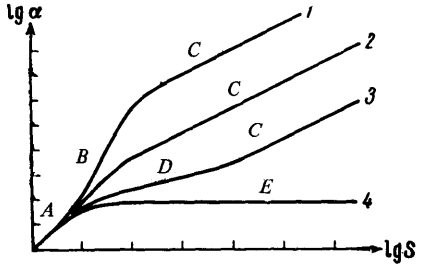
account the number of possible locations of the cation M among the reaction centres of the r-mer, it is easy to obtain the following expression for the partition coefficients:

$$\alpha = \beta f_M \sum_r W_r [A_r] \frac{f_r}{f_{A_r M}}, \quad (26)$$

where $[A_r]$ is the molar concentration of the r-mer and f_M, f_r and $f_{A_r M}$ are the activity coefficients of the M species, the association complex $[A_r]$, and the complex $[A_r M]$. It has been shown[43] that, in terms of the quasi-chemical approximation[94], for a system comprising a solvent and a mixture of r-mers with non-zero mutual exchange energies, $f_r/f_{A_r M} \simeq 1$ provided that $r \geqslant 10$ and $S \leqslant 1$. Moreover, for low concentrations $M_{(org.)}$ the formation of complexes containing several M atoms per association complex $[A_r]$ maybe disregarded. As a result, the following simple expression is obtained for the concentration curve:

$$\alpha = \beta \frac{f_M}{\nu} S, \quad (27)$$

where ν is the number of monomeric units of the association complex $[A_r]$ forming one reaction centre. Eqn. (27) is valid, provided that the condition $S/r \gg M_{(org.)}$ holds, and makes it possible to describe quantitatively the extraction of microconcentrations of metal ions by a highly associated extractant. The limits of the applicability of the ratio $f_M/f_{A_r M} \simeq 1$ depend on the parameters of the specific system; the method of their calculation has been described[119]. When the condition $S/r \gg M_{(org.)}$ breaks down, the relation $\alpha = \varphi(S)$ becomes more complicated and the partition coefficient becomes a function not only of S but also of $M_{(aq.)}$ and, as shown by the same authors[43], analysis of the concentration curve in this case does not lead to determination of the stoichiometry of the reaction.



General form of $\lg \alpha = \varphi(\lg S)$ concentration curves for different values of the parameter b: 1) $b > 1$; 2) $b = 1$; 3) $b < 1$; 4) $b = 0$ ($\partial \lg \alpha / \partial \lg S = \nu$ in region A, $\partial \lg \alpha / \partial \lg S > \nu$ in region B, $\partial \lg \alpha / \partial \lg S = 1$ in region C, $\partial \lg \alpha / \partial \lg S < \nu$ in region D, and $\partial \lg \alpha / \partial \lg S = 0$ in region E).

When the factors influencing the shape of the concentration curves are considered, the problem arises of the influence of the metal ions incorporated into the association complex of the extractant on the bond strength between the monomeric units of the complex[35]. In the general case one can foresee three possibilities: (a) the nature of the bonds in the association complex does not change and the addition of new monomeric units to the complex $[A_r M_i]$ proceeds in accordance with the same law as the addition to the complex without the metal $[A_r]$—the case considered above; (b) the monomeric units in the coordination spheres closest to the metal decrease the strength of bonds with other monomeric units; (c) the bond strength in the association complex increases under the influence of the metal. These effects can be taken into account quantitatively by introducing the bond stabilisation parameter $b = K_i/K_r$, i.e. the ratio of the constants for the addition of a monomeric unit A_1 to the association complex $[A_r]$. As before, the constant K_r is assumed to be independent of the degree of association r. If the bond perturbation zone is assumed equivalent to three coordination spheres closest to the metal atom within which the monomer addition constant $K_i \neq K_r$, the following expression is obtained for the partition coefficient:

$$\alpha = K_{M\nu} f_M \left\{ [A_1]^\nu + \frac{1}{\nu (bK_r)^2} \sum_{j=\nu+1}^{3\nu} j (bK_r)^j [A_1]^j + \frac{b^{2\nu}}{\nu K_r^\nu} \sum_{n=3\nu+1}^{\infty} n [A_1]^n K_r^n \right\}, \quad (28)$$

and

$$S = \sum_{r=1}^{\infty} r [A_r] = \sum_{r=1}^{\infty} r [A_1]^r K_r^{r-1} = \frac{[A_1]}{(1 - K_r [A_1])^2}, \quad (29)$$

where $K_{M\nu}$ is the formation constant of the complex $[MA_\nu]$, $[A_1]$ is the concentration of the monomeric extractant molecules in the organic phase, and j and n are summation indexes; the other symbols have the same significance as before.

The concentration curves calculated for different parameters S, K_r, and b are illustrated in the Figure, which shows that, when the degree of association of the extractant is high, the slope of the concentration curve approaches unity for $b > 0$ owing to the high values of K_r or S. When $b = 0$, the association complex is disrupted by the inserted species and α is independent of S over a wide extractant concentration range. A slope equal to the coefficient ν (the number of monomeric units of the association complex forming a single reaction centre) is obtained only at low concentrations where the degree of association of the extractant is still low. If the bonds in the association complex are appreciably strengthened by the inserted species ($b \gg 1$), the concentration curve shows sections where the slope is higher than ν. It follows from the foregoing that analysis of the shapes of the concentration curves requires a detailed examination of all possible types of chemical interaction in the system over a fairly wide range of concentrations and independent measurements of the degree of association of the extractant and of its solvation by the solvent are necessary.

V. DISTRIBUTION OF ACIDS AND SALTS IN SYSTEMS WITH MODERATELY ASSOCIATED EXTRACTANTS (ARYLAMMONIUM AND ALKYLAMMONIUM SALTS)

1. Certain Contradictions in the Interpretation of Experimental Relations

The considerable success of the methods for the determination of the composition and stability of solvates in extraction systems with neutral organophosphorus and other non-associated extractants left a deep impression on the methods for the interpretation of experimental data obtained with associated extractants. The traditional representation of extraction data in terms of the relation $\lg \alpha = \varphi(\lg S)$, in which the slope is identified with the

solvation number, is transferred without any changes to extraction systems with extractants associated in non-polar solvents such as alkylammonium salts, aryl- and alkyl-phosphoric acids, etc.

It is most surprising that simple linear relations are then obtained. Moreover, the equilibrium distribution of, for example, nitric acid in the extraction system with a trialkylammonium nitrate, may be described [52,120-122,123] by the simple reaction

$$B \cdot HNO_{3(org.)} + H^+_{(aq.)} + NO^-_{3(aq.)} \rightleftarrows B \cdot 2HNO_{3(org.)} \quad (30)$$

(here B = trialkylamine), i.e. seemingly there is no association of the trialkylammonium salt at all. According to the law of mass action, we have for reaction (30)

$$\alpha = K \cdot [B][H^+][NO_3^-] \cdot \frac{f_{\pm}^2 \cdot f_{B \cdot HNO_3}}{f_{B \cdot 2HNO_3}} . \quad (31)$$

However, the condition of a constant f_i usually adopted conflicts with numerous studies on the state of alkylammonium salts in solvents of low polarity. Fairly high association in such systems has been reliably established by cryoscopic [51,53,56] and conductimetric methods [64,65], by dielectric constant measurements [72-74], by light scattering [57,58,71], by viscometric measurements [54,65,70], etc. (particularly if account is taken of the correction for the effect of the difference between the dimensions of the solvent and extractant species on values found by cryoscopic and similar methods). The greater complexity of the equilibria in the extraction of hydrogen halides from aqueous solutions in the form of trialkylammonium salts compared with the simplest reaction

$$B_{(org.)} + H^+_{(aq.)} + X^-_{(aq.)} \rightleftarrows BH \cdot X_{(org.)}, \quad (32)$$

is indicated by the deviation of the $[BHX]_{(org.)} = \varphi\{[B]a_{HX(aq.)}\}$ relation from linearity at fairly low concentrations $[BH.X]_{(org.)} \simeq 0.001$ M, when there is no reason to postulate appreciable changes in f_B and $f_{BH.X}$ due to causes other than association [60,61]. Finally, when no account is taken of the association of the alkylammonium salt, it is difficult to explain the comparatively low capacity of the extractant [124], which deviates appreciably from the capacity expected on the basis of the stoichiometry of reactions (32) and (30).

2. Allowance for the Association of Extractants by a Simplified Procedure

Fomin and Potapova attempted to resolve the contradiction between the results of a cryoscopic study of the trioctylamine–nitric acid–water system and the invariance of the equilibrium constant calculated for reaction (30) without taking into account the association of the extractant. They assume [52] that the reaction equation can be written in the following general form:

$$\frac{y}{x}(BH \cdot NO_3)_{x(org.)} + y\,H^+_{(aq.)} + y\,NO^-_{3(aq.)} \rightleftarrows [B \cdot 2HNO_3]_{y(org.)} \quad (33)$$

and that the equilibrium constant can be expressed thus:

$$K'' = K' \cdot \frac{x^{y/x}}{y} \cdot \frac{1}{[HNO_3]^{2y-2}_{(aq.)} \; [BH \cdot NO_3]^{y/x-1}_{x(org.)}} , \quad (34)$$

where K' is the equilibrium constant for reaction (30). Next it is assumed that, with increase of the concentration of acid in the aqueous phase, the term $[HNO_3]^{2y-2}_{(aq.)}$ will increase and the term $[BH.NO_3]^{y/x-1}_{x}$ will decrease when $x < y$ which leads to the virtually constant value of K' observed experimentally. The main defect of this purely qualitative treatment is that there are no serious grounds for the assumption that the coefficients x and y are constant. They must evidently change with the concentrations of the acid and the amine. In this case too K' and K'' will also be functions of the concentration of the reactants.

Shmidt and coworkers [125] proposed an explanation based on Vanselow's hypothesis [126] according to which the activities of individual groups of the association complex are equal to their fractions relative to all the functional groups of the complex but in the formulation of the fundamental equations account must be taken of the activity coefficients of the association complexes themselves, which was not done by the authors. The conclusion that the degree of association of the alkylammonium salt remains unchanged when it adds to metal salts is also open to objection [69]. This conflicts with statistical considerations, particularly for a high coordination number of the complex-forming agent; Shmidt and coworkers determined the average degree of association of the extractant r by a cryoscopic method, which yielded somewhat low results [89] and, moreover, they failed to examine in detail the important problem of the multiplicity of equilibria, although they do note the constancy of the slope of the concentration curve when the average value of r varies.

Scibona's study [48] is interesting in this respect. The author considers the distribution of a singly-charged anion Y^- or a singly-charged complex anion MX^-_{n+1} between the solution of an electrolyte CX and an organic solution of the corresponding alkylammonium salt RX. The proposed reaction mechanism,

$$\sum_1^I [RX]_{i(org.)} + t\,[Y^-]_{(aq.)} \rightleftarrows \sum_1^I [RY]_{j(aq.)} + \sum_1^A \sum_1^B [(RX)_a (RY)_b] + t\,[X^-]_{(aq.)} \quad (35)$$

takes into account the association of the extractant of the complex extracted. The following equilibria are taken into consideration:

$$[RX]_{(org.)} + [Y^-]_{(aq.)} \rightleftarrows [RY]_{(org.)} + [X^-]_{(aq.)} , \quad K_{(1,X,Y)} , \quad (36)$$

$$i\,[RX]_{(org.)} \rightleftarrows [RX]_{i(org.)}, \quad K(i, X) , \quad (37)$$

$$j\,[RY]_{(org.)} \rightleftarrows [RY]_{j(org.)}, \quad K(j, Y) , \quad (38)$$

$$a\,[RX]_{(org.)} + b\,[RY]_{(org.)} \rightleftarrows [(RX)_a (RY)_b]_{(org.)} \quad K(a, b) . \quad (39)$$

An expression was obtained relating the partition coefficient of the anion Y^- to the concentration of the extractant. The authors extrapolated the partition coefficient (using certain auxiliary functions and not the partition coefficients themselves, which does not alter the essential feature of the procedure) to zero extractant concentration and found the constant $K_{(1,X,Y)}$, the deviations from the linear relation $\lg \alpha = \varphi\{\lg[RX]\}$ being regarded as a consequence of association in the organic phase. Although the authors interpret the experimental relations [48,68] in terms of the formation of only one complex, their equations are valid also when the solution contains a multiplicity of complexes of different compositions. Since an ideal associated solution is assumed and the activity coefficients in the organic phase are set equal to unity, the model cannot be valid over a wide range of concentrations and remains essentially semiempirical.

A similar approach has been developed by Högfeldt and Fredlund [66,127]. In their investigations the set of reactions of the associated alkylammonium salts with the complex metal-containing anion, leading to the formation of a continuous series of extractable complexes having structures of different complexity, was treated in terms of the ideal associated solution approximation. The composition of one or several complexes is chosen on the basis of the results of a two-phase potentiometric titration

whereby one can describe satisfactorily the form of the experimental relations. It has been shown [16] that this approach leads to the "discovery" of non-existent complexes or to the assumption that certain complexes are absent, whereas in reality they are formed.

3. Successive Allowance for the Association of Extractants and Extraction Complexes in the Description of Extraction by Amines

In another attempt to account for the known experimental relations governing the extraction of acids and metal ions by alkylammonium salts, taking into account the association in the organic phase, was made by Komarov and Komarov [55]. Account was taken of all interactions of the type

$$B_{r(org.)} + i\,[HA]_{(aq.)} \rightleftarrows B_r(HA)_{i(org.)}, \quad K_{ri}\ , \tag{40}$$

where B_r is an r-mer of the initial alkylammonium salt, HA a monobasic acid, and K_{ri} the thermodynamic equilibrium constant of reaction (40). If each association complex B_r has r energetically equivalent active centres capable of combining with a molecule of the acid HA, the following relation is valid:

$$K_{ri} = \beta^i W_{ri}\ , \tag{41}$$

where β is the equilibrium constant for the addition of the HA molecule to the specified reaction centre and W_{ri} is the statistical factor. It is now possible to find the concentration of each solvate with the aid of the law of mass action:

$$[B_r(HA)_i] = (\beta a)^i W_{ri}\,[B_r] \cdot \frac{f_r}{f_{ri}}\ , \tag{42}$$

where a is the activity of HA in the aqueous phase and f_r and f_{ri} are the activity coefficients of B_r and $B_r[AH]_i$. Bearing in mind that

$$W_{ri} = \frac{r!}{\sigma_r\,(r-i)!\,i!}\ , \tag{43}$$

where σ_r is the symmetry coefficient, it is easy to find the acid concentration C_H and the concentration of the alkylammonium salt C_B in the organic phase:

$$C_H = [HA] + \sum_{i=1}^{r}\sum_{r=1}^{R} (\beta a)^i [B_r] \cdot \frac{f_r}{f_{ri}} \cdot \frac{r!}{G_r\,(r-i)!\,(i-1)!}\ , \tag{44}$$

$$C_B = \sum_{r=1}^{R} r\,[B_r] + \sum_{i=1}^{r}\sum_{r=1}^{R} (\beta a)^i [B_r] \cdot \frac{f_r}{f_{ri}} \cdot \frac{r!\,r}{\sigma_r\,(r-i)!\,i!}\ . \tag{45}$$

In contrast to the studies enumerated above, in this model the organic phase is not regarded as an ideal associated solution. With the aid of the theory of association equilibria, the value of the following function was found by the present authors:

$$\ln\frac{f_r}{f_{ri}} = iR_B\frac{2-z}{2}\left\{\ln\frac{q_s\sum_D r_D C_D}{r_s\sum_D q_D C_D} + \frac{2}{kT}\left[\omega_{as}\left(v_a^2 + v_n v_a - v_a\right) + \omega_{ns}\left(v_n^2 + v_n v_a - 2v_n - v_a\right) - \omega_{an}\left(v_n v_a - v_a\right)\right]\right\} = i\psi\,(C_H, C_B)\ , \tag{46}$$

where R_B is the number of quasilattice sites occupied by a single molecule of E, z the coordination number of the quasilattice, D a general symbol for a species (solvent molecule, association complex, solvate, etc.), qz the number of nearest neighbours of the species D, C_D the molar concentration of species of type D in the mixture, r_D the number of sites occupied by the corresponding species, a, n, and s are the classes of contact regions (alkyl groups, acid anions, and solvent molecules), v_i is the fraction of contact regions of class i in solution, and ω_{ij} the Guggenheim mutual exchange energy. A numerical estimate of the quantity $\psi(C_H, C_B)$ is possible for specific systems. After carrying out the summation in Eqns. (44) and (45), the following formula is obtained:

$$\beta = \frac{C_H}{(C_B - C_H)\,a}\,e^{-\psi}. \tag{47}$$

Bearing in mind that the multiplier $e^{-\psi}$ is close to unity for low values of C_H, [119] Eqn. (45) can be formally regarded as an expression of the law of mass action for reaction (32), since C_H may be interpreted as the equilibrium concentration of the extractant [B] and $C_B - C_H$ as the equilibrium concentration of the non-polymerised alkyl ammonium salt. It is clear from the above that reaction (30) in no way reflects the entire complexity of the interactions in the system, although simple equations of type (47) are in fact satisfactorily consistent with experimental data.

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The review has demonstrated the exceptional complexity of extraction systems with associated extractants. The authors attempted to emphasise the conflicting nature of the data obtained by different methods for the same systems and to show that this is largely due to the approximate nature of the models of the solution used as a basis for a quantitative interpretation of the results of measurements of macroscopic quantities from the standpoint of the interaction between molecules. In general, one must say that a rigorous interpretation of colligative properties of systems from the standpoint of the determination of the composition and stability of complicated molecular complexes requires also the application of a rigorous theory of the liquid state. However, the only versions of solution theory at present available which meet to the required degree of sophistication are model molecular-statistical theories. Since more rigorous versions of the theory have not been developed at all and have not been used to describe the properties of associated solutions (let alone extraction systems) and in view of their personal preference, the authors attempted to demonstrate that the application of the generalised theory of association equilibria [100] would be definitely useful for the understanding of the characteristics of extraction systems with associated extractants. This standpoint can be readily understood bearing in mind that the models of solutions employed earlier [ideal solution, regular solution (Hilderand model), athermal solution, ideal associated solution, athermal associated solution] are readily described by the fundamental equations of the generalised theory of association equilibria subject to fairly approximate special assumptions concerning the properties of the species in the system.

For example, the general expression for the chemical potential defined by Eqn. (9) has the following properties:

(1) in the absence of specific linkages ($N_i = \sum_{D(i)} N_{D(i)}$, $D(i) \equiv i$, $N_0^i = N_i$) with $r_D = 1$ and $u_{\epsilon\nu} = \frac{1}{2}(u_{\epsilon\epsilon} + u_{\nu\nu})$, the expression describes the chemical potential of the component in an **ideal solution**;

(2) in the absence of specific linkages with $r_D = 1$ and $u_{\epsilon\nu} \neq \frac{1}{2}(u_{\epsilon\epsilon} + u_{\nu\nu})$, the expression can be readily shown to be equivalent to μ_D in a **regular solution**;

(3) in the absence of specific linkages with $r_D \neq 1$ and $u_{\epsilon\nu} = \frac{1}{2}(u_{\epsilon\epsilon} + u_{\nu\nu})$, the expression represents the value for an athermal solution;

(4) in the presence of specific linkages with $r_D = 1$ and $u_{\epsilon\nu} = \frac{1}{2}(u_{\epsilon\epsilon} + u_{\nu\nu})$, the expression descibes an ideal associated solution;

(5) in the presence of specific linkages with $r_D > 1$ and $u_{\epsilon\nu} = \frac{1}{2}(u_{\epsilon\epsilon} + u_{\nu\nu})$, the expression corresponds to an athermal associated solution;

(6) in the presence of specific linkages with $r_D > 1$ and $u_{\epsilon\nu} \neq \frac{1}{2}(u_{\epsilon\epsilon} + u_{\nu\nu})$, the expression corresponds to the non-athermal associated solution model.

The study of extraction systems with associated extractants is being rapidly expanded and their practical importance is growing. In this field many surprises and difficulties await the investigator, the overcoming of which may involve a wide-scale employment of modern advances of the statistical theory of solution and an extension of the range of research techniques employed (dielectric constant measurements, Rayleigh light scattering, resonance spectroscopy, diffusion, the dynamo-optical method, measurement of ultrasonic velocities, etc.).

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