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Theory of Mixed Isoactive Electrolyte Solutions

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The basic laws of the osmotic theory of mixed isoactive solutions of electrolytes are discussed, and the possibilities of calculating the thermodynamic functions of the mixtures from data for the binary isopiestic solutions are considered. The results obtained for the salting-out effect in extraction systems are presented as an illustration of the theory. 94 references.

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I. INTRODUCTION

The theory of isoactive solutions has been applied increasingly in theoretical work and in practical calculations in recent years. Work during the past 10–15 years has produced the first theory able to deal with both dilute and concentrated (up to saturation) solutions of electrolytes. This theory relies on comparisons of the properties of mixed solutions with those of the initial binary systems at constant activity of the solvent (isopiestic method). Electrolyte solutions have many common features, and it seems logical to use the properties of binary solutions to calculate the corresponding properties of electrolyte mixtures. However, in principle, the general conclusions of the theory can be applied to any system.

The theory can be said to have begun in 1936, when Zdanovskii's rule was published[1] (the fundamental relationship in this theory). However, general interest in Zdanovskii's rule became evident only in the 1960's, stimulated by discussions of its physical significance and of its role in solution thermodynamics. We should note that almost all the theoretical foundations of the theory of isoactive solutions were laid by Soviet scientists.

The general thermodynamic relationships used in the isopiestic method are discussed by Kirgintsev[2]. In this review we shall examine the limiting laws and the possibility of calculating the properties of mixed systems from data for the binary solutions.

II. LAW OF IDEAL MIXING OF ISOPIESTIC SOLUTIONS

The deviation from ideal behaviour of the solvent in a solution is usually characterised by an osmotic coefficient. In our studies of salting-out in electrolyte solutions[3–5] we have pointed out that the osmotic coefficient also describes the tendency of the solute to take up solvent (especially water). This tendency is described particularly well by the molal osmotic coefficient ϕ, defined by the expression

$$\ln a_w = -0.001\ M\nu m\varphi, \qquad (1)$$

where a_w is the activity of the solvent, M is its molecular weight, ν is the stoichiometric coefficient of the electrolyte, and m is the molal concentration of the solute.

Formula (1) is written for a binary solution. If the solution contains several solutes the formula becomes

$$\ln a_w = -0.001 M\varphi_m \sum \nu_i m_i. \qquad (2)$$

The osmotic coefficient of the mixed solution (ϕ_m) is a measure of the average tendency to take up solvent for the particular mixture of solutes. In order to determine the contribution of each component we need to consider the limiting case in which the specific interaction between the components is negligibly small, i.e. we must assume that the molecules or ions of the solute experience the same effect from the other components in the mixed solution as in a binary solution with solvent at the same activity (where the effect arises entirely from like molecules or ions). In such a solution the components have the same tendency to take up solvent as in a binary solution of the same activity, since the solvent has the same "lack of attractiveness" in the two media. The numbers of solvent molecules oriented around a given ion remain the same. Under these conditions the osmotic coefficients of a given component in the binary and in the mixed solution having the same solvent activity should be the same[3].

Thus, for this particular limiting case Eqn.(2) can be written as a sum of the contributions of the individual components to the decrease in the activity of the solvent:

$$\ln a_W = -0.001 M \sum \nu_i m_i \varphi_i^*, \qquad (3)$$

where ϕ_i^* is the osmotic coefficient of the binary solution in isopiestic equilibrium with the mixed solution. (Throughout this reivew we shall use an asterisk to denote parameters referring to isopiestic binary solutions.)

From Eqns.(2) and (3) we obtain

$$\varphi_m = \sum \nu_i m_i \varphi_i^* / \sum \nu_i m_i \text{ or}$$
$$\varphi_m = \sum y_i \varphi_i^*, \qquad (4)$$

where y_i is the ion fraction defined as $\nu_k m_k / \Sigma \nu_i m_i$. Thus ϕ_m is an additive function of composition. Therefore, under these conditions the osmotic pressure generated by a given electrolyte in a mixture is proportional to the ionic concentration of the electrolyte over the whole range of ion fractions. The postulated equality of the osmotic coefficients of the component in isopiestic solutions (i.e. Eqn.(4) has been confirmed[5] from the theoretical and experimental results

of many authors[6-15] for various mixed solutions of alkali metal and other chlorides and nitrates. Experimental results agreed within 1–2% with those calculated from data for the isopiestic binary solutions (with total salt concentrations as high as 3.0–5.0 *m*).

Hence, dividing Eqn.(3) by Eqn.(1) for isopiestic mixed and binary solutions, we obtain[3] the expression known as Zdanovskii's rule:

$$\sum_i m_i/m_i^* = 1, \qquad (5)$$

where m_i^* is the molality of the binary solution having a solvent activity identical to that of the mixed solution. Zdanovskii arrived at this rule purely empirically[1], and at first believed it to be approximate and valid in special cases only. Th law states that when isopiestic binary solutions are mixed the activity of the solvent is unchanged in the absence of specific interactions between the solutes.

Dividing (5) by the total molality or by the total ionic concentration gives, respectively,

$$\frac{1}{m} = \sum_i \frac{1}{m_i^*} x_i \text{ and } \frac{1}{\nu m} = \sum_i \frac{1}{\nu_i m_i^*} y_i, \qquad (6)$$

whence we find that the reciprocal total molality and the reciprocal total ionic concentration are additive functions of composition (x is the mole fraction).

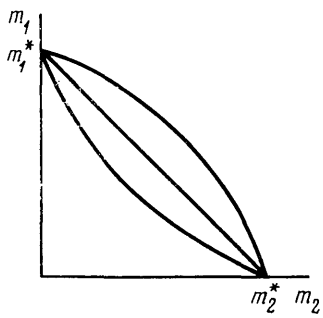


Figure 1. Isotherm–isobars of water in a ternary water–salt system.

For ternary aqueous salt systems with two dissolved electrolytes *1* and *2* Eqns.(5) and (6) take the form

$$m_1/m_1^* + m_2/m_2^* = 1 \qquad (7)$$

and

$$\frac{1}{m} = \frac{1}{m_1^*} x_1 + \frac{1}{m_2^*} x_2. \qquad (8)$$

According to these two equations Zdanovskii's rule can be expressed graphically by straight-line plots (Figs.1 and 2). Its validity has been demonstrated for a large number of systems by Zdanovskii himself and by other workers. Existing experimental information, reported from different laboratories, shows that in mixed solutions of electrolytes with a common anion the deviations from Zdanovskii's rule are usually less than 1–2%. These solutions include the halides, nitrates, and sulphates of the alkali and alkaline-earth metals, and various other salts, at concentrations up to saturation. The fullest bibliography on this topic is given in Ref.16, but it is already seriously out of date.

This discussion of the thermodynamic significance of Zdanovskii's rule allows us to generalise the rule and to conclude that it should apply not only to solutions of salts with a common anion, as had previously been assumed, but also to mixed solutions from any system[3]. This conclusion was confirmed experimentally for solutions with a common cation[3] (including mixtures of strong acids) and for systems without a common ion[17,18]. The latter systems were subsequently studied in detail in our laboratory, following a suggestion by G.I.Mikulin, as quaternary reciprocal systems.

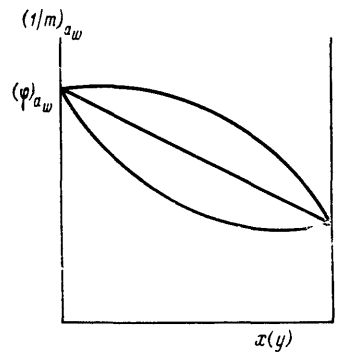


Figure 2. Reciprocal total molality and osmotic coefficient against composition of the ternary solution.

All the available results show that the only condition for the validity of Zdanovskii's rule on mixing binary solutions of electrolytes is the absence of specific interactions between the ions, so that the form of the ions and of their associations is unchanged by the conversion of the binary solution into a mixed solution. Hence no redistribution of the solvent among the components takes place when isopiestic solutions of this type are mixed. For example, large deviations from Zdanovskii's rule are observed[19,20] on mixing solutions of caesium and cobalt chlorides, because the two cations have very different affinities for the chloride ion. On the other hand, isopiestic solutions of cobalt and nickel chlorides can be mixed in exact accordance with Zdanovskii's rule, in spite of the well known chemical interaction between the cations and the anions. This is because of the similarity in properties of the cobalt and nickel ions towards the chloride ion: as a result, there is no redistribution of the chloride ions on mixing, and hence no redistribution of the water.

In the absence of specific interactions between the electrolytes it follows from Eqns.(1)–(3) that the total osmotic activity (as well as the activity of the water) is unchanged when isopiestic solutions are mixed. The total osmotic activity remains equal to the sum of the osmotic activities of the binary solutions, i.e.

$$\sum \nu_i m_i \varphi_i^* = \text{const.} \qquad (9)$$

This expression conveniently characterises the behaviour of solutes on mixing. It is formally similar to the law of constant ionic strength, but it is more strict as well as having greater generality, since it is applicable also to concentrated solutions. If the solutions being mixed have equal (or similar) osmotic coefficients the law of constant osmotic

activity (9) becomes a law of constant ionic concentration, since in this case the isopiestic binary solutions will have identical ionic concentrations and the mixing will affect neither the activity of the water nor the ionic concentration of the resulting mixed solution. This follows from Eqn.(5) for the condition

$$m_1^* = m_2^* = \ldots m_i^*.$$

The direct relationship which we have established between Zdanovskii's rule and the postulate of equal osmotic coefficients of the components in isopiestic solutions, and the resulting additivity of the properties [Eqns.(4) and (6)], suggest that the two laws are identical and are both limiting laws. Additional evidence for this statement comes from the following considerations. Constancy of the solvent activity and of the osmotic activity of the electrolytes on mixing is possible only when the excess Gibbs free energy is zero ($G_m^E i = 0$). Since the activities are related to the chemical potentials, this is a sufficient condition for constancy of the solvent activity, i.e. for the validity of Zdanovskii's rule. However, it follows from the expression

$$G_m^{Ei} = \Delta H - TS_m^{Ei} = \Delta H + T\partial G^{Ei}/\partial T,$$

(where ΔH is the enthalpy of mixing, T is the temperature, and $S_m^E i$ is the excess entropy of mixing) that, in general, we have $\Delta H = 0$ for $G_m^E i = 0$, i.e. that mixing is ideal when Zdanovskii's rule applies. Nevertheless non-ideal mixing with $G_m^E i = 0$ is possible in some cases: this occurs when a small enthalpy change can be compensated (at a given temperature) by the excess entropy term.

Thus, in general mixed solutions free from specific interactions between the dissolved components can be prepared by ideal mixing of binary solutions of the components in isopiestic equilibrium. We have proposed the term isoactive for solutions of this type[18,21].

The first evidence of the ideality of mixing in accordance with Zdanovskii's rule was obtained by Vdovenko and Ryazanov[22,23], who also formulated the analogy between Zdanovskii's rule and Raoult's law. A similar demonstration was later given by Kirgintsev[2] by introducing a new thermodynamic function (the aqueosity of the solution).

It follows that Zdanovskii's rule can no longer be treated as partial and approximate: it is a limiting expression, or, more strictly, a limiting law[24]. Hence, experimental results on mixed solutions cannot be classified as confirming (or not confirming) the generality of this law. Zdanovskii's law is entirely general, and it can be used as a standard of comparison for the properties of real solutions: in other words, the whole of the experimental information can be interpreted from the standpoint of deviations from this law. This is the essential feature common to all limiting laws. No "correction" to Eqn.(5) can increase its generality, since it introduces some indeterminacy arising from the need to determine the correction experimentally for each specific system.

III. ADDITIVITY OF THE PROPERTIES OF MIXED SOLUTIONS OF ELECTROLYTES

The ideal mixing of isopiestic binary solutions of electrolytes allows us to calculate all the thermodynamic properties of mixed isoactive solutions from the properties of the initial binaries. The difference from the calculation of the properties of ideal solutions is that the mixing of individual components is replaced (in the case of isoactive solutions) by the mixing of the appropriate binary solutions in isopiestic equilibrium with the mixed isoactive solution. Thus all the calculations begin with a determination of the so-called isopiestic concentrations m_i^* of the binary solutions, usually by a selection method relying on successive approximations[1]. The concentration dependence of the activity of the water in the binary solutions is first established from tabulated data (Fig.3). A suitable value of the activity of water is then chosen, and the corresponding concentration is inserted into Eqn.(5) (the concentrations of the components in the mixed solution m_i are assumed to be known). If the sum differs from unity the operation is repeated: when the results are satisfactorily consistent the calculated concentrations of the binary solutions will be isopiestic.

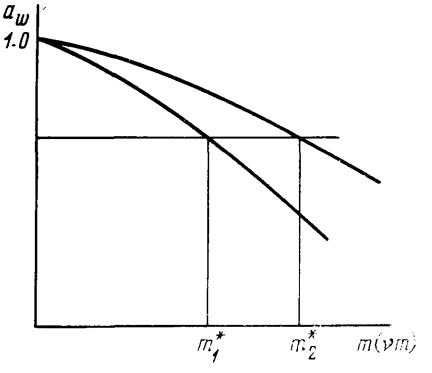


Figure 3. Determination of the isopiestic concentrations m_1^* and m_2^* for a ternary solution.

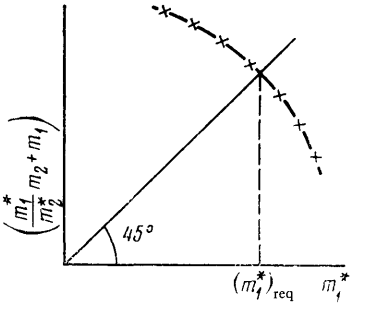


Figure 4. Graphical determination of the required value of m_1^*.

The need for selection can be avoided by using the method proposed in Ref.22. Zdanovskii's law for a ternary solution is written

$$\frac{m_1^*}{m_2^*} m_2 + m_1 = m_1^*.$$

The ratio m_1^*/m_2^* can be taken from tabulations, or alternatively we can use Fig.3 and draw a number of sections for different water activities. We then plot (Fig.4) the function $(m_1^*/m_2^*)m_2 + m_1$ against the corresponding value of m_1^*. The intersection of the resulting curve with a straight line drawn

through the origin at 45° gives the wanted value of m_1^*. The concentration m_2^* is found in a similar way. In extensive calculations it is convenient to establish the approximate $a_W = f(m_i)$ expressions and to solve them simultaneously with Eqn.(5) on a computer[25].

These methods can be used only when the isopiestic concentrations do not exceed the solubility limits of the components. If the isopiestic concentration is higher than the solubility it cannot be determined experimentally. Zdanovskii overcame this problem by graphically extrapolating the $a_W = f(m^*)$ relationships to the supersaturated solution region. In our work[25] the same result was achieved by using analytical expressions as approximations to the experimental data. If experimental values of the activity of water are available for solutions saturated with the first electrolyte, i.e. for point C lying on the m_1^S–m_{12}^S curve of Fig.5, the calculation is possible[26]. If the coordinates of this point are m_1 and m_2 we can solve Eqn.(5) for m_1^* and obtain

$$m_1^* = m_1 m_2^*/(m_2^* - m_2).$$

Therefore the quantity m_1^*, corresponding to a given activity of water, can be found if m_1, m_2, and m_2^* are known. Mikulin[27] carried out calculations of this type in his graphical–analytical treatment of data for the KCl–NaCl–H_2O, KNO_3–$NaNO_3$–H_2O, and NaCl–$CaCl_2$–H_2O systems.

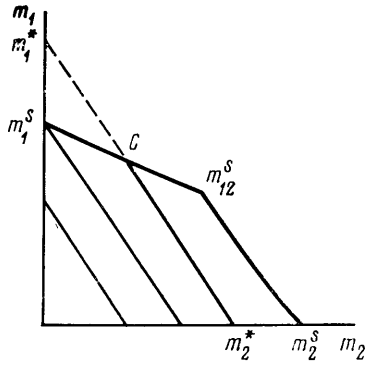


Figure 5. Determination of the isopiestic concentration beyond the solubility limit.

If the isopiestic concentrations of the binary solutions and their properties are known, the corresponding property for the multi-component isopiestic solution is easily calculated. Ideality of mixing is equivalent to zero changes in enthalpy and in volume on mixing: it follows that these properties (and others, related to them) are additive. In mixed isoactive solutions additivity is expected in relation to the isopiestic binary solutions. For example, in order to form a ternary solution of given composition the initial binary solutions have to be mixed in the appropriate proportions. According to Zdanovskii's law (5), in order to prepare a mixture of electrolytes having a common ion in which the concentration of the first electrolyte is m_1 and that of the second electrolyte is m_2 we have to mix m_1/m_1^* parts of the binary solution of electrolyte *1* and m_2/m_2^* parts of the binary solution of electrolyte *2*. The enthalpy of the resulting ternary solution will be[23]

$$H = \frac{m_1}{m_1^*} H_1^* + \frac{m_2}{m_2^*} H_2^* \quad \text{or} \quad H = \sum_i \frac{m_i}{m_i^*} H_i^*. \tag{10}$$

In a similar way we can obtain an expression for the volume:

$$V = \frac{m_1}{m_1^*} V_1^* + \frac{m_2}{m_2^*} V_2^* \quad \text{or} \quad V = \sum_i \frac{m_i}{m_i^*} V_i^*. \tag{11}$$

The additivity of the enthalpy and volume allows us to calculate other properties of the multicomponent solutions derived from these functions. For example, Zdanovskii[28] obtained a similar expression for the specific heat

$$C = \frac{m_1}{m_1^*} C_1^* + \frac{m_2}{m_2^*} C_2^* \quad \text{or} \quad C = \sum_i \frac{m_i}{m_i^*} C_i^* \tag{12}$$

and for the density (the reciprocal of the specific volume)

$$\frac{1}{\rho} = \frac{m_1}{m_1^*} \frac{1}{\rho_1^*} + \frac{m_2}{m_2^*} \frac{1}{\rho_2^*} \quad \text{or} \quad \frac{1}{\rho} = \sum_i \frac{m_i}{m_i^*} \frac{1}{\rho_i^*}. \tag{13}$$

The entropy is defined by the equation

$$S = \frac{m_1}{m_1^*} S_1^* + \frac{m_2}{m_2^*} S_2^* + \Delta S_m \quad \text{or} \quad S = \sum_i \frac{m_i}{m_i^*} S_i^* + \Delta S_m, \tag{14}$$

where ΔS_m is the ideal entropy of mixing. The equation for the Gibbs free energy therefore becomes

$$G = \frac{m_1}{m_1^*} G_1^* + \frac{m_2}{m_2^*} G_2^* + \Delta G_m \quad \text{or} \quad G = \sum_i \frac{m_i}{m_i^*} G_i^* + \Delta G_m, \tag{15}$$

where ΔG_m is a purely entropic term. When the ideality of the mixing of isopiestic solutions has been established Eqns.(10)–(15) can be used in the simplified form shown.

The equation for the change in entropy during ideal mixing of isopiestic binary solutions was obtained by Vdovenko and Ryazov by a statistical method[23]:

$$\Delta G_m = -T\Delta S_m = RT\left(\nu_1 m_1 \ln\frac{\nu_1 m_1}{\nu_1 m_1 + \nu_2 m_2} + \nu_2 m_2 \ln\frac{\nu_2 m_2}{\nu_1 m_1 + \nu_2 m_2} - \right.$$
$$\left. - \nu_{-1} m_1 \ln\frac{\nu_{-1} m_1}{\nu_{-1} m_1 + \nu_{-2} m_2} - \nu_{-2} m_2 \ln\frac{\nu_{-2} m_2}{\nu_{-1} m_1 + \nu_{-2} m_2}\right), \tag{16}$$

where the subscripts −1 and −2 denote the anions of the first and the second electrolyte. If the electrolytes *1* and *2* have no common ion the last two terms drop out of the equation.

All these expressions for thermodynamic properties per mole of solute can be written in the form[29]

$$\Phi^m = x_1 \Phi_1^{m*} + x_2 \Phi_2^{m*} + \Delta\Phi_{m.id.}^m, \tag{17}$$

where Φ_i^m are the thermodynamic functions referred to one mole of solute, and $\Phi_{m.id.}^m$ is the change in the thermodynamic functions caused by ideal mixing of the isopiestic solutions.

If the binary solutions being mixed have the same (or similar) concentration dependences of the water activity, or similar values of the osmotic coefficients under isopiestic conditions, the total ionic concentration in the mixed solution will be equal (or similar) to the ionic isopiestic concentrations in the binary solutions [see Eqns.(1) and (3)]. In this case all the equations for additive functions (Φ) again take a form similar to Eqn.(17):

$$\Phi = x_1 \Phi_1^* + x_2 \Phi_2^* + \Delta\Phi_{m.id.} \quad \text{or} \quad \Phi = \sum_i x_i \Phi_i^* + \Delta\Phi_{m.id.}. \tag{18}$$

The properties of one binary solution may have to be inferred from those of the mixed solution and of the other binary solution. For example, it is difficult (or even impossible) to determine the properties of solutions of salts undergoing hydrolysis. Hydrolysis can be suppressed by adding acid to the solution: if the mixture can be assumed to be an isoactive solution the properties of the binary solution of hydrolysable electrolyte in a hypothetical non-hydrolysed acid-free form[30] can easily be calculated by the above formulae.

The properties of isoactive systems are directly related not only to those of the isopiestic binary solutions but also to those of solutions of any concentration. This is because

when solutions with different solvent activities are mixed only redistribution of the solvent takes place between the electrolytes. "Internal" levelling of the activity occurs, increasing concentration of one component being accompanied by increase ing dilution of another. The process taking place within the solution can be described as a succession of steps: 1) dilution and concentration of the binary solutions to the isopiestic concentration levels, and 2) ideal mixing of the isopiestic binary solutions. Thus, any property of the solution can be expressed as the sum

$$\Phi_i = \Phi_i^* + \Delta\Phi_{m_i - m_i^*} \quad \text{or} \quad \Phi_i^* = \Phi_i - \Delta\Phi_{m_i - m_i^*}, \tag{19}$$

where $\Delta\Phi_{m_i^I - m_i^*}$ is the change in the function for the binary solution upon conversion from the concentration chosen for mixing to the isopiestic concentration.

It has been shown[29] that the thermodynamic functions of mixing can be calculated by expressions similar to (10)–(17):

$$\Delta\Phi_m = \frac{m_1}{m_1^*}\Delta\Phi_{m_1' - m_1^*} + \frac{m_2}{m_2^*}\Delta\Phi_{m_2' - m_2^*} + \Delta\Phi_{m.id.} \tag{20}$$

If the thermodynamic functions are calculated for one mole of electrolyte we have

$$\Delta\Phi_m^m = x_1\Delta\Phi_{m_1' - m_1^*}^m + x_2\Delta\Phi_{m_2' - m_2^*}^m + \ldots + \Delta\Phi_{m.id.}^m \tag{21}$$

Since the mixing effects during formation of isoactive solutions are determined by the solvent redistribution and by the ideal entropy changes which follow the mixing of isopiestic solutions, an appropriate term is added to Eqns.(20) and (21): in the case of functions independent of the entropy of mixing this term is zero. For example, for the enthalpy of mixing we have

$$\Delta H_m^m = x_1\Delta H_{m_1' - m_1^*}^m + x_2\Delta H_{m_2' - m_2^*}^m. \tag{22}$$

This expression was obtained by Zdanovskii and Deryabina[31] for the enthalpy change caused by the redistribution of the solvent. It is evident from Eqn.(19) that the expression for a generalised property of the mixed solution in terms of the properties of binary solutions of arbitrary concentration takes the form of Eqns.(10)–(17):

$$\Phi = \frac{m_1}{m_1^*}(\Phi_1 - \Delta\Phi_{m_1' - m_1^*}) + \frac{m_2}{m_2^*}(\Phi_2 - \Delta\Phi_{m_2' - m_2^*}) + \ldots + \Delta\Phi_{m.id.} \tag{23}$$

If the property is calculated for one mole of the electrolyte the expression becomes

$$\Phi^m = x_1(\Phi_1^m - \Delta\Phi_{m_1' - m_1^*}^m) + x_2(\Phi_2^m - \Delta\Phi_{m_2' - m_2^*}^m) + \ldots + \Delta\Phi_{m.id.}^m \tag{24}$$

Thus, if no specific interactions between the electrolytes are found in the mixed solution (as compared with the binary solutions) the properties of the mixed solution—including the functions of mixing of the binary solutions—can be calculated from the properties of the latter without further experiments.

To conclude this Section we should stress that in principle any mixed solution of electrolytes, even one in which chemical interactions are present, can be treated as isoactive if the compositions of the resulting complexes are known. The analogy with ideal associated solutions[32] is appropriate. By allowing for the chemical interaction we can compare these systems with the binary isopiestic solutions of their components. However, calculation of the thermodynamic properties of the system is possible only if the necessary data for the binary solutions of the initial components and of the resulting components are available. If complexes are formed our formulae will have limited value, since very few data are available on the properties of complex solutions (especially when the stability of the complexes is low). However, this approach offers the possibility of calculating complex formation in solutions[33].

All the arguments presented here follow from the postulate that isoactive solutions can be treated as "an ideal mixture of binary solution quasi-particles"[34]. The quasi-particles can be simple ions, complex ions, or neutral molecules, i.e. any formation known to be present in real solutions. Deviations from the limiting law are a result of the impossibility of allowing for the large number of states in which the dissolved components may exist. If allowance can be made even only for the fundamental states the mixed solutions can be "reduced" to isoactive or almost isoactive solutions. This is clearly shown by our work[35–37] on systems containing sulphuric acid, which has only a weak second dissociation though most of the thermodynamic properties of its solutions have been determined with respect to full dissociation. By ignoring the second dissociation step and treating sulphuric acid as a 1–1 electrolyte we were able to show experimentally[36,37] that mixtures of sulphuric acid and monobasic inorganic acids (nitric, perchloric, hydrochloric) or lithium or potassium hydrogen sulphates can be treated as isoactive with acceptable precision (up to ±3%). In practice, mixtures of lithium sulphate and hydrogen sulphate are also isoactive: the deviations increase with the size of the alkali metal cation. All the thermodynamic parameters of the mixed solutions mentioned above were calculated in our laboratory[37] by using this effect.

IV. ACTIVITY COEFFICIENTS OF ELECTROLYTES IN MIXED ISOACTIVE SOLUTIONS

The condition for the formation of an isoactive mixed solution from isopiestic binary solutions is ideal mixing ($\Delta G_m^E i = 0$). From this condition we can easily obtain an expression for the activity coefficients (γ) of the components in the mixed solution, which vary only as a result of changes in the overall ionic concentration. This involves comparing the chemical potentials, measured from the corresponding standard states[24]:

$$\nu_1 RT \ln a_1 = \nu_1 RT \ln a_1^* + \nu_1 RT \ln \frac{\nu_1 m_1}{\nu_1 m_1 + \nu_2 m_2}.$$

It follows that

$$\gamma_1 = \nu_1 m_1^* \gamma_1^* / (\nu_1 m_1 + \nu_2 m_2) \quad \text{or} \quad \gamma_k = \nu_k m_k^* \gamma_k^* / \sum \nu_i m_i, \tag{25}$$

Eqn.(25) is known as Mikulin's equation.

A formula of this type for 1–1 electrolytes was first proposed[38] as an approximation, obtained from McCay and Perring's[39] general differential equation. Mikulin[40] and, later, Vdovenko and Ryazanov[22], derived Eqn.(25) for mixtures of electrolytes of different valency types by an exact simultaneous solution of McCay and Perring's equations and Zdanovskii's law (5). Mikulin's equation, like Zdanovskii's law, applies with adequate precision to a very large number of different mixed solutions of electrolytes, including solutions at very high concentrations.

In order to formulate the dependence of the activity coefficient of the electrolyte on the composition at constant water activity we shall express Eqn.(25) in terms of the osmotic coefficients, using Eqns.(1), (2), and (4). We obtain[4]

$$\gamma_1/\gamma_1^* = \varphi_m/\varphi_1^* \tag{26}$$

and for a ternary solution

$$\gamma_1/\gamma_1^* = (1 - \varphi_2^*/\varphi_1^*)\, y_1 + \varphi_2^*/\varphi_1^*, \tag{27}$$

$$\frac{\gamma_1}{\gamma_1^*} = 1 - (1 - \varphi_2^*/\varphi_1^*)\, y_2, \qquad (28)$$

or in terms of the isopiestic concentrations

$$\gamma_1/\gamma_1^* = 1 - (1 - \nu_1 m_1^*/\nu_2 m_2^*)\, y_2. \qquad (29)$$

It follows from (26)–(29) that at constant water activity the activity coefficient of the electrolyte is directly proportional to both its own ion fraction and the ion fraction of the second electrolyte. The slope of the straight-line dependence is determined by the difference (or ratio) of the osmotic coefficients of the binary isopiestic solutions (or of the isopiestic concentrations). Eqns.(27)–(29) are reminiscent of Harned's rule[41], though they differ from it in having a thermodynamic foundation and hence in being applicable without exception to all isoactive solutions, i.e. to solutions in which specific interactions between the electrolytes can be neglected.

In order to convert Eqns.(28) and (29) into a form similar to Harned's rule we shall take logarithms [of Eqn.(28), say]. Series expansion of the logarithm on the right-hand side, truncated after the first term, gives

$$\ln \gamma_1 = \ln \gamma_1^* - (1 - \varphi_2^*/\varphi_1^*)\, y_2. \qquad (30)$$

From these considerations we may conclude that a linear dependence of the activity coefficient on composition is characteristic, strictly speaking, of the condition of constant solvent activity (or constancy of osmotic activity), and not constancy of the ionic strength (as required by Harned's rule). We should note that at the water activity corresponding to the intersection of the $a_W = f_1(m_1)$ and $a_W = f_2(m_2)$ plots the coefficient of y_2 is zero, and on either side of this point the coefficient has different signs.

If the osmotic coefficients in the isopiestic solutions of electrolytes being mixed are equal Mikulin's equation for the activity coefficient of one of the components becomes[3]

$$\gamma_k = \gamma_k^* = \text{const}. \qquad (31)$$

This expression follows also from Eqn.(26).

Since the condition of constant water activity in this case, is analogous to constancy of the overall ionic concentration (3), we can infer the following from Eqn.(31): if the electrolytes have equal osmotic coefficients (i.e. equal tendencies for taking up water) their activity coefficients at constant total ionic concentration will be constant (i.e. independent of the component ratio) and equal to the activity coefficient of the component in the binary solution. Eqn.(31) applies strictly, even to concentrated solutions, in the absence of specific interactions between the electrolytes (i.e. for ideal mixing of binary isopiestic solutions of electrolytes). However, the condition of equal osmotic coefficients in the binary solutions is most easily satisfied at low concentrations. We have obtained satisfactory results[3] at total molalities up to 1.5–2.0 for the following systems (which have also been studied by other workers): HNO_3–$CaCl_2$–H_2O, HNO_3–$MgCl_2$–H_2O, HCl–$CaCl_2$–H_2O, HCl–$SrCl_2$–H_2O, HCl–$MgCl_2$–H_2O, HCl–$HClO_4$–H_2O, etc.

The expression (31) is analogous to the ionic strength rule, and yet it reveals the shortcomings of that rule and the advantages of using ionic and osmotic concentrations. The ionic strength rule was confirmed by the Debye–Hückel law, and in some of the contemporary publications[42–44] the law was also compared with Zdanovskii's rule, which had previously been thought to be only an approximation. It was shown[45] that only a special case of Zdanovskii's law, corresponding to equal osmotic coefficients of the components [as in Eqn.(31)], could be compared with the Debye–Hückel law. The Debye–Hückel limiting law describes the ideal mixing of electrolyte solutions to a good approximation only at very high dilutions. The Zdanovskii limiting law also is applicable only to systems without specific interaction between the electrolytes, but its validity is unaffected by the tendency of the electrolytes to take up solvent or by the concentration of the electrolyte.

It is often necessary, especially in radioactive tracer work under industrial conditions, to calculate the thermodynamic activity of a microcomponent in the presence of a macro-component: for example, in the salting-out of micro-components during extraction and adsorption. The application of Eqn.(25) to a micro-component is greatly simplified if the concentration of the micro-component can be ignored in comparison to that of the macro-component. Under those conditions we assume that the total ionic concentration in the denominator of the right-hand side of Eqn.(25) and the isopiestic concentration of the binary solution of the macro-component are equal to the concentration of the macro-component in the mixed solution. Thus, the isopiestic concentration of the micro-component *1* (m_{01}) is determined by the initial concentration of the macro-component *2*, and Eqn.(25) becomes[4]

$$\gamma_{01} = \nu_{01} m_{01}^* \gamma_{01}^* / \nu_2 m_2. \qquad (32)$$

If in one solution substance *1* is the micro-component and substance *2* is the macro-component, and in another solution the roles are reversed, then for equal ionic concentrations of the macro-components the ratio of the activity coefficients of the micro-components in these solutions will be

$$\gamma_{01}/\gamma_{02} = \nu_{01} m_{01}^* \gamma_{01}^* / \nu_{02} m_{02}^* \gamma_{02}^*. \qquad (33)$$

Robinson and Stokes, when discussing mixed solutions of hydrochloric acid and sodium chloride, quote the following "paradoxical result: the activity coefficient of hydrochloric acid in a solution containing effectively only sodium chloride is practically equal to the activity coefficient of sodium chloride in a solution containing effectively only hydrochloric acid"[46]. The explanation of this paradox follows from Eqn.(33). The activity coefficients of the micro-components in these solutions will be similar if the products $\nu m^* \gamma^*$ have similar values. In the case of hydrochloric acid and sodium chloride solutions the ratio of these products is close to unity over a wide range of concentration.

V. THERMODYNAMIC PROPERTIES OF QUATERNARY RECIPROCAL SYSTEMS

It is obvious, from the formulation of the ideal mixing of electrolyte solutions given by Zdanovskii (see Section I), that both the probability and the magnitude of deviations from ideality will be greater if the electrolytes being mixed do not have a common ion. This is mainly the result of ion-exchange interaction in systems without a common ion. Furthermore, in systems which include a like ion the deviations cannot be calculated in terms of the properties of the binary solutions, because the transfer of the ions from one electrolyte to another is accompanied by the formation of complexes which cannot exist in the binary solutions. In systems without common ions the main interaction is ion exchange between the dissolved electrolytes, which can be described by treating the mixture of electrolytes as a system of four reciprocal binary isopiestic solutions, as suggested by Mikulin and Voznesenskaya[47].

Equilibrium in a quaternary reciprocal system is treated as an ionic exchange double decomposition reaction:

$$\underset{1}{AM} + \underset{4}{BN} \rightleftarrows \underset{2}{AN} + \underset{3}{BM}, \qquad (34)$$

Following Mikulin and Voznesenskaya[47], we shall represent a mixed solution of two electrolytes without a common ion in a composition square (Fig.6) relating the concentrations of

the components of the quaternary reciprocal system (34). We shall denote the concentrations of A, B, M, and N by n_A, n_B, n_M, and n_N respectively, and we shall take the total concentrations of electrolytes in the system to be n g-equiv per 1000 g of water. The following relationships will be used for the ion fractions in the case of electrolytes of different valency:

$$x=n_A/n;\ 1-x=n_B/n;\ y=n_M/n;\ 1-y=n_N/n.$$

The concentrations of the electrolytes AM, AN, BM, BN (point S of Fig.6) will be related by the expressions

$$n_1=nxy;\ n_2=nx(1-y);\ n_3=n(1-x)y;\ n_4=(1-x)(1-y). \quad (35)$$

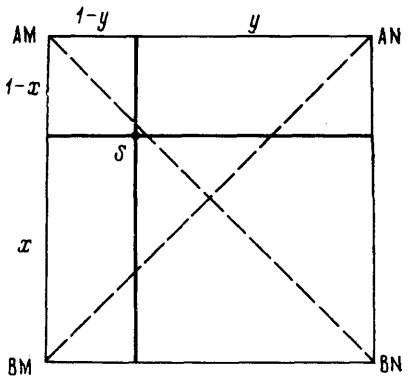


Figure 6. Relationship between the composition of the components in a quaternary reciprocal system (composition square).

We shall also use[48] the expression (4) relating the osmotic coefficient of the mixed solution (ϕ) to the osmotic coefficients in the binary solutions of the electrolytes (ϕ_i^*) at the same water activity. For a quaternary reciprocal system, allowing for the equality

$$\nu_i m_i = \frac{z_i^+ + z_i^-}{z_i^+ z_i^-} n_i = K_i n_i$$

Eqn.(4) becomes

$$\varphi = \sum_i \varphi_i^* K_i n_i / \sum_i K_i n_i. \quad (36)$$

Inserting into this equation the expressions for the concentrations of the electrolytes [Eqn.(35)] we arrive at a formula for the osmotic coefficients of quaternary aqueous reciprocal systems:

$$(\varphi)_{a_w} = \lambda_1\varphi_1^* + \lambda_2\varphi_2^* + \lambda_3\varphi_3^* + \lambda_4\varphi_4^*, \quad (37)$$

where ϕ_i^* are the osmotic coefficients of the binary isopiestic electrolyte solutions which constitute the quaternary reciprocal system (34). The coefficient λ_i (for example, in the case of electrolyte 1) is given by

$$\lambda_1 = xyK_1/[xyK_1 + x(1-y)K_2 + (1-x)yK_3 + (1-x)(1-y)K_4].$$

Eqn.(37) is valid if no chemical interactions other than ion exchange are present in the solution. It is the analogue of Eqn.(4), obtained by postulating equal osmotic coefficients of the components in the isopiestic solutions. It follows that systems of this type can be treated as quaternary reciprocal systems to which Zdanovskii's law applies. Hence, all the equations given in Section II are fully applicable to mixed solutions of electrolytes without a common ion, for example

$$\Delta H = \frac{m_1}{m_1^*}\Delta H_1^* + \frac{m_2}{m_2^*}\Delta H_2^* + \frac{m_3}{m_3^*}\Delta H_3^* + \frac{m_4}{m_4^*}\Delta H_4^*$$

etc.

On the other hand, if we start from the concentrations of two solutions of electrolytes (without common ions) being mixed, the properties of the mixture are parabolically dependent on the relative amount of one of the components. That this should not be interpreted as a deviation from Zdanovskii's law is evident from the work of Mikulin[47], though he himself states[34] that "Zdanovskii's rule applies only to mixed solutions with a common ion, but it follows from this rule that in quaternary aqueous reciprocal systems the equal water activity plots are in general parabolic". Evidently, Mikulin erroneously identifies Zdanovskii's rule not with Eqn.(5), but with the linearity of the water isotherm–isobar for two components, or with the textual formulation of the law in terms of the mixing of two binary solutions.

In order to calculate the thermodynamic functions directly we must start from the concentrations (in the mixture) of the (two) mixed electrolytes, since the concentrations of the four electrolytes in the equilibrium mixture are unknown. In order to simplify the mathematics we shall assume that the ions from all the electrolytes in the system (34) have identical charges (in absolute value): for example, that the electrolytes being mixed are both 1–1, or 2–2. Under these conditions the following equality applies to the AM(1)–BN(4)–H_2O system:

$$x=y=n_1/(n_1+n_2),$$

and Eqn.(4) becomes

$$(\varphi)_{a_w} = (\varphi_1^* + \varphi_4^* - \varphi_2^* - \varphi_3^*)x^2 + (\varphi_2^* + \varphi_3^* - 2\varphi_4^*)x + \varphi_4^* \quad (38)$$

or

$$(\varphi)_{a_w} = Ax^2 + Bx + C. \quad (39)$$

A similar expression was obtained earlier[47] for the reciprocal total molality.

The coefficients A, B, and C can easily be determined from the tabulated values of the corresponding osmotic coefficients of the binary solutions. In this way all the thermodynamic functions of the mixed isoactive solution formed from two solutions of electrolytes without common ions can be calculated. For example,

$$\Delta G = A'x^2 + B'x + C' + \Delta G_M^{id}, \quad (40)$$

where

$$A' = \Delta G_1^* + \Delta G_4^* - \Delta G_2^* - \Delta G_3^*,$$
$$B' = \Delta G_2^* + \Delta G_3^* - 2\Delta G_4^*,$$
$$C' = \Delta G_4^*.$$

Satisfactory agreement between calculation and experiment is obtained for practically all the systems composed of halides and nitrates of alkali and alkaline-earth metals[17,18,49–51].

Formulae for the activity coefficients of the electrolytes (without common ions) in a mixed solution can be obtained from Eqn.(39). In our calculation[48,52] the McCay–Perring equation[39] was first converted into a form consistent with that of the expression for the osmotic coefficients:

$$\ln\frac{(\nu_1 m_1 + \nu_2 m_2)\gamma_1}{\nu_1 m_1^* \gamma_1^*} = \int_0^{\ln a_w} \left[(1-y_1)\left(\frac{\partial\varphi}{\partial y_1}\right)_{a_w} + \varphi + \varphi_1^*\right]\frac{d\ln a_w}{\ln a_w}. \quad (41)$$

Simultaneous solution of Eqns.(39) and (41) for electrolytes with the above limitations on the stoichiometric coefficients gave

$$\ln\gamma_1 = \ln\frac{m_1^*\gamma_1^*}{m_1+m_4} - (1-x)^2\int\frac{A}{\ln a_w}\,d\ln a_w.$$

From the Gibbs–Duhem equation for a binary solution we have

$$\int\frac{\varphi_i^*}{\ln a_w}\,d\ln a_w = \ln a_i^*,$$

whence

$$\ln\gamma_1 = \ln\frac{m_1^*\gamma_1^*}{m_1+m_4} - (1-x_1)^2\ln\frac{a_1^*a_4^*}{a_2^*a_3^*}. \qquad (42)$$

This formula was first obtained[47] by an entirely different approach. In the case of electrolytes of any valency type the McCay and Perring equation must be solved by using the more complex expression (37).

If the coefficient of x^2 in equations of the type of (39) is zero (i.e. $A=0$) it follows that the quaternary system is not only isoactive but also additive with respect to the separate ions: for example, for the system

$$AX_2+2BY=AY_2+2BX$$

we expect to find

$$\varphi_{AX_2}^* + 2\varphi_{BY}^* = \varphi_{AY_2}^* + 2\varphi_{BX}^*. \qquad (43)$$

In this case the affinities of the two cations for the two anions (or of the two anions for the two cations) are the same. Eqn.(43) applies, for example, to the $CaBr_2$–LiCl–H_2O and $CaCl_2$–KBr–H_2O systems[53].

VI. CALCULATION OF THE OSMOTIC COEFFICIENTS AND ACTIVITY COEFFICIENTS OF SEPARATE IONS

The success of our postulate of equal osmotic coefficients for a component in mixed solutions having the same water activity (in the absence of chemical interactions) suggested the possibility of applying the same approach to separate ions. An analogy was formulated[54] between mixed solutions of electrolytes and binary solutions, which were described as mixed by treating the ions as separate components. In keeping with Eqn.(1), which features the mean ionic molal osmotic coefficient, we can introduce the concept of an osmotic coefficient of the ion and replace Eqn.(1) by an expression for the activity of the solvent in the following terms:

$$\ln a_w = -0.001Mm(\nu_+\varphi_+ + \nu_-\varphi_-). \qquad (44)$$

where ν_+ and ν_- are the stoichiometric coefficients of the ions, and ϕ_+ and ϕ_- are the osmotic coefficients of the ions. Like the osmotic coefficients of the components, those of the ions are a measure of the ability of the given species to take up water. Extending the analogy, we assumed that the osmotic coefficients of a given ion in different solutions must be equal if the activity of water in the solutions is the same and if there is no difference between the ionic interactions (in particular, the chemical interactions) in the different solutions. By adopting these hypotheses and taking an arbitrary electrolyte as standard we can easily calculate the osmotic coefficients of the ions in other solutions.

The standard electrolyte is usually chosen so that $\phi_+^0 = \phi_-^0 = \phi_\pm^0$, and therefore it is usually a 1–1 electrolyte. By comparing Eqn.(44) for a solution of the standard electrolyte with the same equation for the unknown binary solution, having an ion in common with the standard, we obtain expressions for the counter-ion in the unknown solution

$$\nu_{+2}\varphi_{+2} = \nu_{\pm 2}\varphi_{\pm 2} - \nu_-\varphi_\pm^0 \quad \text{and} \quad \nu_{-2}\varphi_{-2} = \nu_{\pm 2}\varphi_{\pm 2} - \nu_+\varphi_\pm^0 \qquad (45)$$

and for the 1–1 electrolytes

$$\varphi_{+2} = 2\varphi_{\pm 2} - \varphi_\pm^0 \quad \text{and} \quad \varphi_{-2} = 2\varphi_{\pm 2} - \varphi_\pm^0.$$

For electrolyte solutions not having an ion in common with the standard we use the scheme KCl → CsCl → CsBr.

Using a solution of potassium chloride as standard we have calculated[54] from the above expressions the osmotic coefficients of the ions in binary solutions of various alkali metal halides at concentrations between 1.0 and 2.0 *m*. As a test of the method, we also calculated the mean ionic osmotic coefficients of electrolytes not having an ion in common with the standard, using the scheme KCl → CsCl → CsBr and KCl → KBr → CsBr. The arithmetic means were compared with tabulations[46]: the deviations were found to be within 2%, confirming the correctness of our assumption of equal osmotic coefficients for ions in isopiestic solutions of these electrolytes.

These favourable results justified an attempt to calculate the activity coefficients of individual ions by Mikulin's equation. If two ternary solutions have one electrolyte in common and equal water activities the ratio of the activity coefficients of the electrolytes in the solutions is

$$\gamma_1/\gamma_1' = (\nu_1'm_1' + \nu_3'm_3')/(\nu_1m_1 + \nu_2m_2).$$

In the standard electrolyte solution $\gamma_{+0} = \gamma_{-0} = \gamma_{\pm 0}$, and therefore the expression for the ions (comparing two binary electrolyte solutions with a common ion) becomes

$$\gamma_+/\gamma_{\pm 0} = 2m_0^*/\nu m^* \quad \text{and} \quad \gamma_-/\gamma_{\pm 0} = 2m_0^*/\nu m^*, \qquad (46)$$

i.e. the ratio of the activity coefficients of the ions in the two solutions having identical water activities is equal to the reciprocal of the ratio of the ionic concentrations of these solutions.

Eqns.(46) are easily generalised for multicomponent solutions:

$$\frac{\gamma_{+m}}{\gamma_{+2}} = \frac{\nu_2m_2^*}{\sum_i \nu_im_i} = \frac{\varphi_m}{\varphi_{\pm 2}^*} \quad \text{and} \quad \frac{\gamma_{-m}}{\gamma_{-2}} = \frac{\nu_2m_2^*}{\sum_i \nu_im_i} = \frac{\varphi_m}{\varphi_{\pm 2}^*}, \qquad (47)$$

where γ_{+m} and γ_{+2} are the activity coefficients of the common ion in the mixed and the binary (e.g., the standard) isopiestic solution. For electrolyte solutions without an ion in common we can use the above scheme, which gives (for example) in the case of a $CaBr_2$ solution

$$\gamma_{Ca^{2+}} = \gamma_{\pm CaCl_2}^3(3m_{CaCl_2}^*)^3/\gamma_{\pm KCl}^2(2m_{KCl}^*)^2 \cdot 3m_{CaBr_2}^*,$$
$$\gamma_{Br^-} = \gamma_{\pm KBr}^2(2m_{KBr}^*)^2/\gamma_{\pm KCl}3m_{CaBr_2}^* \cdot 2m_{KCl}^*. \qquad (48)$$

We have calculated[53,54] the activity coefficients of the separate ions in binary solutions of various alkali and alkaline-earth metal halides. The calculations were tested by the scheme used for the osmotic coefficients, but in this case the root mean square values were obtained from pairs of results (because the osmotic coefficients of the ions are additive, and the activity coefficients are multiplicative). The deviation of the calculated mean ionic activity coefficients from the tabulated values[46] was within 1–3% for electrolytes without an ion in common with the standard (potassium chloride).

Bates and coworkers[55] used Robinson and Stokes' hydrate theory to calculate the activity coefficients of separate ions for several solutions of electrolytes. Their results are consistent with ours[54].

For $a_w \to 1$ Raoult's law gives[56]

$$\nu_1m_1^* = \nu_2m_2^* = \sum_i \nu_im_i.$$

Using this expression we find from Eqn.(47) that in very dilute solutions the activity coefficients of the separate ions are a function only of the total ionic concentration, i.e. the

rule of constant water activity becomes an ionic concentration rule[52] reminiscent of Lewis' ionic strength rule but relying on stricter thermodynamic foundations.

Assuming the sulphuric acid–lithium hydrogen sulphate–water system to be isoactive, and assuming equality of the osmotic coefficients of the ions in the isopiestic solutions, we have calculated[35] from data for binary solutions of sulphuric acid and of lithium chloride respectively the dependence of the activity of water on the concentration of lithium hydrogen sulphate (which had not been reported previously). Subsequently[37] the experimental results were compared with calculations: the deviation was less than 1% for isopiestic concentrations, thus allowing all the thermodynamic functions of the system to be calculated by the isoactive solution theory.

If the inter-ionic interactions in the solutions being compared are specific to different extents, more exact values of the osmotic coefficients and of the activity coefficients of the separate ions can be obtained by using quaternary reciprocal systems. Using Eqn.(34) to express the relationship between the osmotic coefficients of 1–1 electrolytes (including the osmotic coefficients of the separate ions) we obtain[24]

$$2\varphi^*_{AM} + 2\varphi^*_{BN} - 2\varphi^*_{AN} - 2\varphi^*_{BM} = ({}^{M}\varphi^*_{A} - {}^{N}\varphi^*_{A}) + \\ + ({}^{B}\varphi^*_{N} - {}^{A}\varphi^*_{N}) + ({}^{N}\varphi^*_{B} - {}^{M}\varphi^*_{B}) + ({}^{A}\varphi^*_{M} - {}^{B}\varphi^*_{M}) = 2A.$$

Averaging gives

$${}^{A}\varphi^*_{M} - {}^{B}\varphi^*_{M} = {}^{1}/_{2}A, \qquad (49)$$

where A has the same significance as in Eqn.(39). In the absence of chemical specificity $A = 0$, and Eqn.(49) reduces to equality of the osmotic coefficients of the ions in isopiestic solutions.

A similar averaging is possible for the activity coefficients of individual ions[24]. In this case we write, using the same scheme, an expression relating the logarithms of the activities of the binary electrolytes having identical solvent activities, and also the corresponding expression in terms of the activity coefficients of the separate ions. The same formula for the activity coefficients of the separate ions can be obtained from Eqn.(42) by treating the ions as separate components:

$$\ln \frac{{}^{A}\gamma^*_{M}}{{}^{B}\gamma^*_{M}} = \ln \frac{m^*_{BM}}{m^*_{AM}} + \frac{1}{4} \ln \frac{a^*_{AM}a^*_{BN}}{a^*_{AN}a^*_{BM}}. \qquad (50)$$

In the absence of chemically specific interactions the expression under the logarithm in the term on the right becomes unity, and formula (50) reduces to (47).

Undoubtedly, the most accurate and general of these equations is[52]

$$\frac{\gamma_{+m}}{\gamma_{+s}} = \frac{\nu_s m^*_s}{\sum_i \nu_i m_i} e^{\Delta} = \frac{\varphi_m}{\varphi_{+s}} e^{\Delta},$$

where Δ is the integral of McCay and Perring's equation for the mixed solution. Extensive information on isopiestic equilibria in ternary solutions with a common ion is available in the literature, and therefore the quantity Δ can be evaluated easily in most cases.

VII. DEVIATIONS FROM IDEAL MIXING IN ISOPIESTIC SOLUTIONS OF ELECTROLYTES

Ideal mixing is a limiting case: all real mixing processes must deviate from ideality to some extent. Aqueous solutions of electrolytes have many features in common, and therefore there is a very large number of pairs of binary solutions which under isopiestic conditions can be mixed with deviations small enough to be ignored. However, mixing operations requiring correction for non-ideality are far from being exceptional. Nevertheless, non-ideal behaviour in mixed systems does not exclude the possibility of limiting cases: for example, in solutions which are dilute with respect to one of the components.

The isotherm–isobars of water in systems with specific interaction between the electrolytes (Figs.1 and 2) are not rectilinear. Substantial curvature of the isotherm–isobars in these systems is usually ascribed to complex formation[57–60], and the curvature is taken as a measure of the intensity of the interactions in the system[61–65]. Even the composition of any compound formed in the mixed solution can be established from the geometry of the isopiestic diagrams[59,60]. We shall examine first of all the general characteristics of the deviations from ideality.

As in the case of mixing individual components, the deviations from ideality in our case can be characterised by excess functions, activity coefficients, and empirical parameters.

Extensive investigations of ternary water–salt systems by Kirgintsev and Luk'yanov, which we have not attempted to list comprehensively among our references[61–65], have shown that the majority of curvilinear isobar–isotherms can be described by the equation

$$1/m = \frac{1}{m^*_1} x + \frac{1}{m^*_2}(1-x) + bx(1-x), \qquad (51)$$

where x is the mole fraction of one of the two electrolytes, and b is an empirical parameter depending on the activity of water and on the concentrations of the components. It follows from (51) that the reciprocal of the total molality is a quadratic function of the composition, in keeping with Robinson's treatment[66].

When $b = 0$ Eqn.(51) reduces to Zdanovskii's law (ideal mixing); when $b > 0$ the system shows positive deviations from ideal mixinge, and when $b < 0$ it shows negative deviations. Inserting Eqn.(51) under the integral in McCay and Perring's equation defines the activity coefficients of the components of the mixture. (The properties of the quantity b and its use in thermodynamic calculations are discussed in detail in Ref.2.) Since our work was based on relationships between osmotic coefficients, we proposed[17,20] that the deviations should be discussed from the standpoint of Eqn.(4). For a real mixture of two electrolytes we have

$$\varphi(a_w, y) = \varphi_1^* y_1 + \varphi_2^* y_2 + \Delta$$

or

$$\varphi(a_w, y) = \varphi_1^* y_1 + \varphi_2^*(1-y_1) + \beta_0 y_1(1-y_1), \qquad (52)$$

where

$$\Delta = \beta_0 y_1 y_2 = \beta_0 y_1(1-y_1).$$

This formulation of the deviations from isoactivity allows for the interactions in the system in terms of the activity of water, which is the criterion for isopiesticity of the solutions, and it permits extrapolation to zero concentration of the electrolytes in calculations of the activity coefficients of the components.

When $\beta_0 = 0$ Eqn.(52) becomes indistinguishable from the ideal mixing condition (4). If $\beta_0 > 0$ the system shows positive deviations, suggesting an increase in osmotic properties on mixing, such as would result from increased dissociation of the electrolytes in the mixture as compared with their respective binary solutions. This case is seldom met, and the deviations are usually small. Negative deviations ($\beta_0 < 0$), due to association in the mixed electrolytes, are far more common. Large negative deviations arise from complex formation. Association lowers the osmotic properties of the mixture, and in order to maintain isopiesticity with the

binary solutions the total concentration of electrolytes in the mixture must be increased.

The quantity β_0 is a measure of the interactions in the ternary solution. In general β_0 depends on the activity of water and on the concentration ratio of the electrolytes. For small values of β_0 we only need to consider the effect of water activity, but when the deviations are large we must consider also the effect of solution composition on β_0. Series expansion in powers of the activity of water gives

$$\beta_0 = -\beta_{01}(\ln a_w) + \beta_{02}(\ln a_w)^2 - \ldots \quad (53)$$

In most cases we do not need to go beyond a linear dependence of β_0 on $\ln a_w$, but in some systems a very complex relationship is observed. For example, in mixtures of nickel, cobalt, or copper chloride with lithium chloride[20] β_0 increases at first, going through a maximum, and then decreases and even changes sign: in other words, deviations from Zdanovskii's law of either sign can take place in these systems, depending on the activity of the water. Composition-independence of the parameter β_0 is recognised by the symmetry of the Δ function (Fig.7).

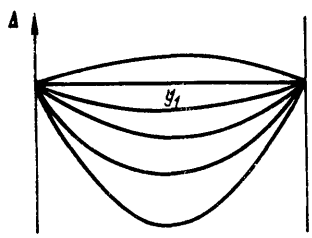


Figure 7. Deviations from isoactivity in ternary water–salt systems.

Whereas the magnitude of β_0 defines the intensity of the interaction, the position of the maximum of the Δ function gives an indication of the composition of the compounds formed in solution. We have used this method to determine, for example, the compositions of the complexes of nickel, cobalt, and copper in chloride and sulphate solutions[20,67,68]. A method of calculating the stability constant of the complex (when only one complex is formed in the solution) was also developed and applied to mixtures of nickel or cobalt nitrate and urea solutions[69]. Results consistent with other methods were obtained.

Experimental determination of Δ or β_0 allows calculation of the excess Gibbs free energies with respect to ideal mixing of the isopiestic solutions ($\Delta G_M^E i$). We have calculated $\Delta G_M^E i$ from measurements of the activity of the solvent only[21,70] by using Scatchard's method[71,73], developed for the isomolal mixing of solutions of 1–1 electrolytes:

$$\Delta G_M^{Ei} - m\partial\Delta G_M^{Ei}/\partial m = -2\Delta RTm.$$

For electrolytes of any valency type this expression becomes (putting $\Sigma\nu_i m_i = \nu_1 m_1 + \nu_2 m_2$)

$$\Delta G_M^{Ei} - \sum \nu_i m_i \frac{\partial \Delta G_M^{Ei}}{\partial \sum \nu_i m_i} = -\Delta RT \sum \nu_i m_i. \quad (54)$$

After converting (54) into

$$-\left(\sum \nu_i m_i\right)^2 \left(\frac{\partial \Delta G_M^{Ei} / \sum \nu_i m_i}{\partial \sum \nu_i m_i}\right)_{\Sigma \nu_i m_i} = -\Delta RT \sum \nu_i m_i$$

we obtain

$$\Delta G_M^{Ei} = \sum \nu_i m_i RT \int_0^{\Sigma \nu_i m_i} \frac{\Delta}{\sum \nu_i m_i} \mathrm{d} \sum \nu_i m_i.$$

Combining this equation with (52) gives

$$\Delta G_M^{Ei} = y_1(1-y_1) RT \sum \nu_i m_i \int_0^{\Sigma \nu_i m_i} \frac{\beta_0}{\sum \nu_i m_i} \mathrm{d} \sum \nu_i m_i. \quad (55)$$

In this expression the excess Gibbs free energy with respect to the isoactive solutions has the dimensions of energy per 1000 g H_2O. We write

$$\beta_0 = \beta'_{01}\left(\sum \nu_i m_i\right) + \beta'_{02}\left(\sum \nu_i m_i\right)^2 + \cdots \quad (56)$$

and, combining (55) and (56), we find

$$\Delta G_M^{Ei} = y_1(1-y_1) RT \left(\sum \nu_i m_i\right)^2 \left[\beta'_{01} + \frac{1}{2}\beta'_{02} \sum \nu_i m_i + \cdots\right] \quad (57)$$

If we retain only the first-order term (i.e. $\beta_0 = \beta'_{01} \Sigma \nu_i m_i$) we have

$$\Delta G_M^{Ei} = \beta_0 y_1(1-y_1) RT \sum \nu_i m_i = \Delta RT \sum \nu_i m_i. \quad (58)$$

Using the relationship between β_0 and b,

$$\beta_0 = -55.51 \ln a_w b\left(\frac{\nu_1 x_1 + \nu_2 x_2}{\nu_1 \nu_2}\right),$$

we obtain an expression for the excess Gibbs free energy with respect to the isoactive solution in terms of the quantity b:

$$\Delta G_M^{Ei} = -x_1(1-x_1) RTmb \cdot 55.51 \ln a_w. \quad (59)$$

In Eqn.(55) the independent variable is the total ionic molality of the mixed solution. It is sometimes convenient to use the activity of water as the independent variable. An appropriate change of variables gives

$$\Delta G_M^{Ei} = y_1(1-y_1) RT \sum \nu_i m_i \int_0^{\ln a_w} \frac{\beta_0}{\ln a_w} \mathrm{d} \ln a_w. \quad (60)$$

Allowing for the dependence of β_0 on the activity of water [Eqn.(53)] we arrive at

$$\Delta G_M^{Ei} = y_1(1-y_1) RT \sum \nu_i m_i \left[\beta_{01}(-\ln a_w) + \frac{1}{2}\beta_{02}(-\ln a_w) + \cdots\right]. \quad (61)$$

Under conditions which justify the approximation $\beta_0 = -\beta_{01} \ln a_w$ we revert to Eqn.(58).

We have used these equations to calculate the excess Gibbs free energies for alkali and alkaline-earth metal halides mixed with cobalt, nickel, and copper chlorides[20] and for alkali metal halides mixed with cobalt, nickel, and alkali metal nitrates[74]. Concurrent measurements of the termal effects in mixing (by Karapent'yants and coworkers[49,75]) have allowed the entropic contributions to be evaluated in most of the mixed solutions.

The most revealing method of expressing the deviations from isoactivity is in terms of the activity coefficients (which are thermodynamic properties of the individual components). A formula for the activity coefficients, obtained from the McCay and Perring equation (41), can be used in conjunction with the expression for the osmotic coefficients.

Eqn.(52) for the osmotic coefficient of the mixed solution can be written as a quadratic function, analogous to (39):

$$\varphi_{(a_w, y)} = Ay^2 + By + C, \quad (62)$$

where $A = -\beta_0$. The difference between this expression and (39) is that the coefficients which appear in (62) can be determined experimentally. In Eqn.(39) they are calculated from the osmotic coefficients of the binary isopiestic solutions. Thus, solution of Eqn.(41) involves operations analogous to those applied to the quaternary reciprocal systems.

By combining Eqn.(62) with the empirical relationship (53) we obtain the following formulae for the activity coefficients:

$$\ln\gamma_1 = \ln\frac{\nu_1 m_1^{\circ}\gamma_1^{\circ}}{\nu_1 m_1 + \nu_2 m_2} + (1-y_1)^2\left[-\beta_{01}\ln a_w + \frac{1}{2}\beta_{02}(\ln a_w)^2 - \cdots\right], \quad (63)$$

$$\ln\gamma_2 = \ln\frac{\nu_2 m_2^{\circ}\gamma_2^{\circ}}{\nu_1 m_1 + \nu_2 m_2} + (1-y_2)^2\left[-\beta_{01}\ln a_w + \frac{1}{2}\beta_{02}(\ln a_w)^2 - \cdots\right].$$

The function β_0 is often linearly related to $\ln a_w$ and independent of composition, allowing the terms in β_{02} to be ignored. Comparing these expressions for the activity coefficients of the components with the excess Gibbs energy [Eqn.(58)] calculated for 1000 g of water and for 1 mole of electrolyte mixture we find

$$g_M^{E_i} = \Delta\mu_1 y_1 + \Delta\mu_2 y_2 = y_1\ln\frac{\gamma_1}{\gamma_1'} + y_2\ln\frac{\gamma_2}{\gamma_2'}. \quad (64)$$

where $\Delta\mu_i$ is the change in chemical potential of the component with respect to the isoactive mixture of electrolytes, and γ_i and γ_i' are the activity coefficients of the i-th electrolyte in the real solution and in the model solution for which Zdanovskii's law is valid.

The advantages of using the osmotic coefficients in the integration of the McCay and Perring equation include more accurate extrapolation to the region of infinite dilutions, since when $a_w \to 1$ we have $\beta \to 0$, i.e. in the case of electrolyte solutions of any valency type the functional dependence of ϕ under isopiestic conditions tends towards Eqn.(4) at high dilutions. It was found experimentally that for $\beta_0 \leq 0.05$ the errors in the calculation of the activity coefficients are less than 1%. The deviations from the limiting expressions (39) for mixtures of electrolytes without a common ion was estimated[51] in terms of the quantities β_0' and b' by using the expressions

$$(\varphi)_{a_w} = Ax^2 + Bx + C + \beta_0' x(1-x)$$

and

$$1/m = A'x^2 + B'x + C' + b'x(1-x). \quad (65)$$

If $b' = D + Ea_w$, integration of the McCay–Perring equation together with Eqn.(65) gives the following formula for the activity coefficients:

$$\ln\gamma_1 = \ln\frac{m_1^{\circ}\gamma_1^{\circ}}{m_1 + m_2} - (1-x_1)^2\left[\ln\frac{a_1^{\circ}a_4^{\circ}}{a_2^{\circ}a_3^{\circ}} + K\ln a_w\right), \quad (66)$$

where

$$K = (D+E)/0{,}018.$$

The deviations of other thermodynamic functions from isoactivity (e.g. ΔH or ΔV) are best determined directly.

From the experimental point of view the isopiestic method of investigation is not a high-sensitivity method, because all the functions are defined in terms of the activity of the solvent, whose concentration in most cases is substantially greater than the concentration of the solutes. The sensitivity decreases markedly as the electrolyte concentration decreases. An attempt was made[77] to determine the excess enthalpy from the temperature dependence of the excess Gibbs energy, but the results had a large scatter and could only be accepted as tentative.

To conclude this Section we shall dwell on real mixed solutions of electrolytes in which one electrolyte is present at low concentration. In view of the analogy between Zdanovskii's and Raoult's laws we could expect an expression similar to Henry's law to apply to real mixed systems including the micro-component *1*. By using the Gibbs–Duhem equation, and assuming the following expression for the activity coefficient of the micro-component in the ternary solution:

$$\gamma_1 = \frac{\nu_1 m_1^{\circ}\gamma_1^{\circ}}{\nu_2 m_2} e^{l_1/\nu_1 RT}, \quad (67)$$

(where l_1 is an energy parameter depending only on the activity of the water and therefore having the significance of an excess function), we replaced[76] Zdanovskii's law (which is obtained when Mikulin's equation is used) by the expression

$$1 - \frac{m_1}{m_1^{\circ}} - \frac{m_2}{m_2^{\circ}} = -0.018\frac{m_1}{RT}\frac{\mathrm{d}\,l_1}{\mathrm{d}\ln a_w}. \quad (68)$$

This equation gives the relationship between (dm/dx) and $dl_1/d\ln a_w$, where $x = m_1/m$:

$$m\left(\frac{1}{m_2^{\circ}} - \frac{1}{m_1^{\circ}}\right) + \left(\frac{x}{m_1^{\circ}} + \frac{1-x}{m_2^{\circ}}\right)\left(\frac{\partial m}{\partial x}\right)_{a_w} = \frac{1}{RT}\frac{\mathrm{d}\,l_1}{\mathrm{d}\ln a_w}\left[x\left(\frac{\partial m}{\partial x}\right)a_w + m\right]. \quad (69)$$

From Eqn.(69) we can obtain the dependence of l_1 on a_w by using isopiestic measurements on ternary systems. It is clear from Eqn.(68) that at constant water activity the deviation from Zdanovskii's law (given by the right-hand side of the equation) is proportional to the molality of the micro-component. Denoting this deviation by bm_1 we can write

$$1/m = x_1(1/m_1^{\circ} + b) + x_2/m_2^{\circ}. \quad (70)$$

Thus the contribution of the micro-component to the reciprocal total molality remains proportional to the mole fraction, but the proportionality coefficient is no longer equal to the reciprocal isopiestic concentration, and depends also on the differential $dl_1/d\ln a_w$. This is where the analogy between our expression and Henry's law appears. The quantity b is a parameter of Eqn.(51), which reduces to Eqn.(70) when $x_1 \ll 1$. In the absence of specific interactions between the dissolved electrolytes Eqn.(67) simplifies to Eqn.(32).

VIII. SALTING-OUT IN EXTRACTION SYSTEMS

Salting-out effects provide one of the most important applications of the theory of isoactive mixed solutions of electrolytes. This was realised by Zdanovskii, Mikulin, and Kirgintsev, all of whom made important contributions in this area. Their work was aimed mainly at the salting-out of electrolytes into a solid phase, i.e. at determining the solubility of some electrolytes in the presence of others. In this review we shall confine our attention to the salting-out problem in extraction systems, where the substance to be separated is distributed between two liquid phases.

The salting-out effect is directly related to the effective concentration (activity) of the solvent. It manifests itself as a change in the activity coefficient of the component being salted out, and therefore salting-out problems can be solved like other problems in the theory of multi-component solutions. The effectiveness of the salting-out agent is determined by its tendency to become hydrated. Ionic hydration is often thought to be determined by the charge and the radius of the ion. However, this view is too simple, and we must think of hydration as the result of a large number of specific properties of the substance whose overall effect

cannot be ascribed merely to the charge and the size of the ion. In recent years the hydration propensity of electrolytes has been quantified in calculations of activity coefficients by using hydration numbers, which give a very good description of specific properties because they are, to some extent, a derived characteristic[46,78]. We know, nevertheless, that experimental values of the hydration number are strongly dependent on the method of measurement, and can vary by a large factor. Furthermore, methods of calculating salting-out effects by relying on constant parameters cannot reflect changes in hydration with concentration, which are characteristic of electrolyte solutions. Hence, these methods can give only a qualitative estimate of changes in systems containing a salting-out agent.

Harned's coefficient is often used as a criterion for salting-out effects. However, Harned's coefficient can be obtained only if experimental data are available for the multi-component system of interest. Furthermore, it is extremely sensitive to the uncertainties in the determination of the activity coefficients. For example, Vdovenko and Ryazanov[79] have shown that an error of 2% in the activity coefficients can produce deviations of up to 10% in the Harned coefficient. We should note that since the "ionic strength" concept lacks strict thermodynamic foundations all attempts at calculating the Harned coefficient theoretically must continue to be unsuccessful.

We have previously suggested[4] the use of the molal mean ionic isopiestic osmotic coefficient as a criterion of the effectiveness of salting-out agents. The osmotic coefficient is, of course, a thermodynamic parameter of the electrolyte solution which characterises its ability to take up water and embodies all the individual properties of the solution. We should stress that the osmotic coefficient takes account also of any interactions between the ions and the molecules of the dissolved electrolyte. The osmotic coefficients of binary solutions have been determined over a wide range of concentrations for most electrolytes of interest and to a high precision. They are tabulated in Robinson and Stokes' monograph[46]. The most significant advantage of the osmotic coefficient as a criterion of salting-out effectiveness is its direct relationship to the theory of mixed isoactive solutions outlined above. The osmotic coefficient, being a thermodynamic criterion of salting-out, can be used as a reference standard for the salting-out parameters given by other solution theories. By combining Mikulin's equation (25) with Eqn.(1) we obtain Eqn.(26), from which it follows that the activity coefficients of the components (or their salting-out properties) are determined exclusively by the osmotic coefficients.

To determine the efficiency of a salting-out agent we simply plot the function $a_w = f(\nu m)$ for the appropriate binary solutions (see Fig.3), which follows from Eqn.(1) and from which it is clear that the relative position of the curves is determined only by the osmotic coefficients of the electrolytes. The higher the osmotic coefficient (or the steeper the curve), the more effective will be the electrolyte as a salting-out agent. For example, magnesium chloride at low ionic concentrations is a less effective salting-out agent than nitric acid. However, the curves intersect at $\nu m \cong 3.3$, and at the higher ionic concentrations magnesium chloride becomes a stronger salting-out agent than nitric acid. This inversion of the relative effectivenss of pairs of electrolytes is encountered fairly often. We note that the plot shown in Fig.3 can be used at the same time to determine the isopiestic concentrations, which are needed to calculate the activity coefficients by Mikulin's equation in accordance with Zdanovskii's law.

Calculations of the salting-out effect (W) can be classified into three possible cases[80]. In the first case addition of the salting-out agent affects the thermodynamic activity of the substance to be separated, but saturation is not reached. The system remains homogeneous, and the concentrations in the phase are unchanged. For a non-electrolyte we can write

$$a_{ns} = m\gamma_{ns};\ a_{ws} = m\gamma_{ws},$$
$$W_a = a_{ws}/a_{ns} = \gamma_{ws}/\gamma_{ns}, \qquad (71)$$

and for an electrolyte

$$a_{ns} = \nu_+^{\nu_+}\nu_-^{\nu_-} m^{\nu}\gamma_{\pm ns}^{\nu},\quad a_{ws} = \nu_+^{\nu_+} m^{\nu_+}(\nu_- m + \nu_{-s} m_s)^{\nu_-}\gamma_{\pm ws},$$
$$W_a = \frac{a_{ws}}{a_{ns}} = \left(\frac{\gamma_{\pm ws}}{\gamma_{\pm ns}}\right)^{\nu}\left(1 + \frac{\nu_{-s} m_s}{\nu_- m}\right)^{\nu_-}, \qquad (72)$$

where a_{ws}, a_{ns}, and γ_{ws}, γ_{ns} are the activities and activity coefficients of the components with and without the salting-out agent respectively, m is the concentration of the main solute, m_s is the concentration of the salting-out agent, and ν, ν_+, and ν_- are the stoichiometric coefficients of the electrolyte, the cation, and the anion respectively.

It follows from (71) and (72) that during salting-out in a homogeneous system the salting-out effect W_a for the non-electrolyte is determined only by the change in the activity coefficients, whereas in the case of the electrolyte the change in concentration of the like ion (in our case, the anion) also has an effect. If the solutions are isoactive the activities of the main electrolyte and the salting-out effects are easily calculated by using the theory of mixed isoactive solutions to obtain the activity coefficients.

The second case relates to salting-out in a heterogeneous system, when the solution is in equilibrium with the main component in the pure state. Addition of the salting-out agent in this case does not alter the activity of the main compound, but it alters its concentration (i.e. the solubility). For a non-electrolyte we have

$$m_{ns}\gamma_{ns} = m_{ws}\gamma_{ws} \text{ and } W_m = m_{ns}/m_{ws} = \gamma_{ws}/\gamma_{ns}, \qquad (73)$$

and for an electrolyte

$$\nu_+^{\nu_+}\nu_-^{\nu_-} m_{ns}^{\nu}\gamma_{\pm ns}^{\nu} = \nu_+^{\nu_+} m_{ws}^{\nu_+}(\nu_- m_{ws} + \nu_{-s} m_s)^{\nu_-}\gamma_{\pm ws}^{\nu},$$
$$W_m = \frac{m_{ns}}{m_{ws}} = \frac{\gamma_{\pm ws}}{\gamma_{\pm ns}}\left(1 + \frac{\nu_{-s} m_s}{\nu_- m_{ws}}\right)^{\nu_-/\nu}. \qquad (74)$$

If the mixed solutions are isoactive we can easily calculate the solubility m_{ws} in the presence of the salting-out agent from Eqn.(74) after determining the activity coefficients of the main compound in the mixed solution by the above formulae. The activity coefficients of non-electrolytes and gases in solutions are inversely proportional to the solubility. If these solutes are indifferent to the salting-out electrolyte we may assume that the solubility (S_0) is proportional to the activity of the solvent, and re-write Eqn.(73) as

$$\ln\frac{S_0}{S} = \ln\frac{m_{ns}}{m_{ws}} = -\ln a_s. \qquad (75)$$

Using Eqn.(1) we obtain[81,82]

$$\lg\frac{S_0}{S} = K_\varphi \nu_s m_s \varphi_s.$$

This formula is the analogue of Sechenov's equation[83], but it differs from it by taking account both of the ionic concentration of the salting-out agent and of its affinity for the solvent (ϕ_s). The constant K_ϕ should be (in the ideal case) independent of the nature of the salting-out electrolyte.

The third salting-out case is distinguished by the fact that addition of the salting-out agent to one phase alters the concentrations of the main substance in both phases. Salting-out in extraction systems is of this type. Whereas in the

first case the concentration was constant, and in the second case the activity, in this case the constant parameter is the distribution constant of the main substance between the phases, given by the ratio of the activities in the two phases[81,82]:

$$K=\bar{a}_{ns}/a_{ns}=\bar{a}_{ws}/a_{ws} \qquad (76)$$

The salting-out effect W_D is the numerical factor by which the distribution coefficient $D=\bar{m}/m$ is increased. For the distribution of a non-electrolyte we have

$$W_D=\frac{D_{ws}}{D_{ns}}=\frac{\bar{m}_{ws}m_{ns}}{m_{ws}\bar{m}_{ns}}=\frac{\gamma_{ws}}{\gamma_{ns}}\cdot\frac{\bar{\gamma}_{ns}}{\gamma_{ws}}. \qquad (77)$$

In the case of electrolytes (assumed undissociated in the organic phase) we obtain

$$W_D=\left(\frac{m_{ws}}{m_{ns}}\right)^{\nu-1}\left(1+\frac{\nu_{-s}m_s}{\nu_-m_{ws}}\right)^{\nu_-}\left(\frac{\gamma_{\pm ws}}{\gamma_{\pm ns}}\right)^{\nu}\frac{\bar{\gamma}_{ns}}{\bar{\gamma}_{ws}}. \qquad (78)$$

Thus, in extraction systems the overall salting-out effect is determined as much by changes in the organic phase as by those in the phase containing the salting-out agent. Furthermore, in the case of electrolytes the effect of the salting-out agent is not only to increase the distribution coefficient but also to alter the shape of the extraction isotherm. Without the salting-out agent the distribution coefficient of the main substance (in the absence of dissociation in the organic phase) tends towards zero as the dilution is increased. In the presence of the salting-out agent the expression for the distribution coefficient becomes

$$D_{ws}=K\nu_+^{\nu_+}m_{ws}^{\nu_+-1}(\nu_-m_{ws}+\nu_{-s}m_s)^{\nu_-}\gamma_{\pm ws}^{\nu}/\bar{\gamma}_{ws}, \qquad (79)$$

where $m_{ws}^{\nu_+-1}=1$ for electrolytes in which the stoichiometric coefficient of the cation is $\nu_+=1$ (which is true of many electrolytes). Therefore when $m_{ws}\to 0$ the distribution coefficient D_{ws} tends towards a constant, non-zero value. This effect has great practical importance in extraction by "neutral" extractants, especially for trace amounts of electrolytes.

Since the extraction of inorganic substances is often due to chemical interaction between these substances and the extractant we can obtain[81,82] equations for the salting-out effect corresponding to different extraction mechanisms[84-86] by equating constants of the extraction reaction with and without the salting-out agent. For example, in the case of molecular extraction, and negligible dissociation in the organic phase, typical of extraction by "neutral" extractants

$$n\bar{A}+B\rightleftarrows A_nB,$$

we have obtained the expression[80-82]

$$W_D=\left(\frac{m_{Bws}}{m_{Bns}}\right)^{\nu-1}\left(1+\frac{\nu_{-s}m_s}{\nu_-m_{Bws}}\right)\left(\frac{\gamma_{\pm Bws}}{\gamma_{\pm Bns}}\right)^{\nu}\cdot\frac{\bar{\gamma}_{A_nBns}}{\gamma_{A_nBws}}\left(\frac{\bar{a}_{Aws}}{a_{Ans}}\right)^{n}. \qquad (80)$$

This expression shows that allowance must be made for changes in the activity coefficient of the resulting complex and in the activity of the extractant caused by the addition of the salting-out agent to the extraction system. Eqn.(80) is most conveniently used in a logarithmic form[80], in which the various contributions to the overall salting-out effect are additive:

$$\lg W_D=\lg W_c+\lg W_{c.i.}+\lg W_{\gamma\pm}+\lg\bar{W}_\gamma+\lg\bar{W}_A, \qquad (81)$$

where W_c is the concentration effect, $W_{c.i.}$ is the common ion effect, $W_{\gamma\pm}$ is an effect due to changes in the activity coefficients of the electrolyte in the aqueous phase, $\bar{W}_\gamma$ is due to the change in the activity coefficients of the complex in the organic phase, and $\bar{W}_A$ is due to the change in the activity of the extractant. Analogous considerations can be applied to the factors affecting the separation of substances (see Ref.87 for a detailed discussion).

These thermodynamic arguments show that calculations of salting-out effects almost invariably reduce to calculations of changes in the activity coefficients of the main substance in the two phases, though on occasions the activity coefficients of other (interacting) components are also relevant. The other contributions to the overall salting-out effect are relatively easy to calculate. In the case of an isoactive aqueous phase the activity coefficients of the electrolytes can be calculated by the equations given above, whereas the calculation of the activity coefficients of the components in the organic phase often requires additional experiments.

The isopiestic method has been found to be useful also in studies of some properties of the organic phase. For example, experimental determination of the activity coefficients of the components in the mixed solution by the distribution method was shown[88] to be possible if the osmotic coefficients of the substance to be extracted and of the salting-out agent are not very different, especially when the solubility of water in the organic phase is appreciable.

The solubility of water in the organic phase depends not only on the nature of the diluent (extractant) but also on the nature of the substance to be extracted. Water can either decrease or increase the association of the components. However, another general feature is the influence of the water on the standard state in the organic phase in the calculation of the activity coefficients of the components. By applying the Gibbs–Duhem equation to a three-component solution we have shown[89,90] that the degree of hydration of the extractant, complex, or distributed component (m_2) is

$$h=(m_3-m_3^0)/m_2,$$

where m_3 is the concentration of water in the extract, m_3^0 is the solubility of water in the diluent, and for $m_2\to 0$ it is a measure of the effect of water on the activity of component 2 when this component is transferred from its binary solutions to solutions containing water. Furthermore,

$$\ln\frac{a_2^0}{a_2}=h \quad\text{or}\quad \ln\gamma(0)=h, \qquad (82)$$

where a_2^0 and a_2 are the activities of the second component in the pure and in the moist diluent (solvent) respectively, and $\gamma(0)$ is the zeroth activity coefficient, characterising changes of standard state. This expression was later confirmed for a large number of systems. A more detailed account of the effect of water and of ways to allow for it in calculations of the component activities in the organic phase can be found in Refs.89 and 90.

Thus, in extracts where the main contribution to the changes in the activity coefficients is that of hydration these coefficients are easily determined if h is known. An independent determination of the salting-out effect in the organic phase is thus possible.

The contributions of the components to the overall salting-out effect have been determined for several systems with different extractants and extracted substances[91-93], including acids and salts. We shall mention only one example: the extraction of nitric acid by *N*-dioctylamine in *o*-xylene[93]. Salting-out by lithium nitrate[93] is illustrated in Fig.8: the effects were determined according to Eqn.(81) for a constant initial acid concentration of 0.25 M. The activity coefficients of nitric acid in the water phase in the presence of the salting-out agent were calculated by Mikulin's equation (25), and the activity of the free extractant was assumed to be equal to its concentration. The ratio of the activity coefficients in the organic phase was determined from the extraction isotherm[94] in terms of the known activities of the acid

in the water phase. It is clear from Fig.8 that all the salting-out effects included in Eqn.(80) play a substantial role in this system. In this case large positive effects are produced by the change in the activity coefficient of the salt formed in the organic phase, due mainly to the increase in the association of the salt with concentration. The common ion effect is even more substantial. All the other effects, including the change in the activity coefficients in the water phase, are negative. Depending on the chosen system, the contributions of the various effects may differ in sign as well as in magnitude.

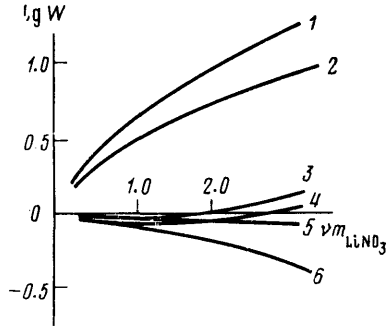


Figure 8. Salting-out effects for nitric acid in the presence of lithium nitrate: *1)* $W_{c.i.}$, *2)* W_D, *3)* $\bar{W}_\gamma$, *4)* W_γ, *5)* W_A, *6)* W_c.

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This review shows that the theory of isoactive solutions is essentially an osmotic theory, since it operates on the osmotic properties of solutions (solvent activity, osmotic acitivities, osmotic coefficients). The validity of isoactive solution theory can no longer be doubted. Experimental studies of mixed solutions at constant activity of the solvent, and isopiestic measurements, have made a valuable contribution to the development of the theory and practice of mixed concentrated solutions.

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