PHYSICAL INTERPRETATION OF SOLUBILITY INTERACTION CONSTANTS FROM THE SERIES EXPANSION OF THE RELATIVE ACTIVITY COEFFICIENTS

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Hydration analysis, which enables information on ionic processes in saturated solutions to be derived from solubility data in ternary systems, was applied to the interpretation of solubility interaction constants from the relative activity coefficient expansion. A close relationship was found between the hydration analysis parameters and the solubility interaction constants characterizing the relative activity of solute, which extends our insight into the ionic behaviour of the system studied by using the values of the interaction constants.

The monograph[1] dealing with solid–liquid equilibria outlines a method of relative activity coefficient expansion allowing phase equilibria of three-component and multicomponent condensed solutions of electrolytes to be calculated using a minimal volume of experimental data. This method has been employed to treat published[2] phase equilibria of a large number of three-component systems, and the correlation equation constants have been tabulated[3,4]. The equilibrium is characterized by so-called interaction constants Q_{ij}, which express the dependence of the relative activity coefficient of the solute forming the saturated solution on the molality of the other solute added. (In the ideal case where the activity coefficient of the former solute is unaffected by the presence of the latter, $Q_{ij} = 0$.) Generally, the majority of systems can be described using one or two interaction constants. The absolute values of the interaction constants Q_{ij} usually decrease with increasing temperature.

The approach in the previous analysis of solubility curves in three-component systems performed by one of us[5,6] was different: within the analysis, parameter P was derived to characterize the difference between the true solubility curve and the solubility curve obtained based on the law of active masses. This is the difference which in the above-mentioned thermodynamic approach was hidden in the "relative activity coefficient" concept. Parameter P characterizes the overall difference between the binary and ternary saturated solutions in terms of the state of water molecules. The par-

ameter has the physical meaning of the mole fraction of water that, due to the addition of foreign ions of component 2, acquired properties different from those of water in the binary saturated solution of component 1. One can imagine that it is contributed to by hydration of the added or newly formed ions in the ternary system on the one hand, and by liberation of water molecules during the formation of ion-pairs or the action of ions with negative hydration on the other hand.

Combination of the two approaches, suggested in the present paper, allows the extensive set of tabulated interaction constants[3,4] to be employed for the study of structure of solutions, and conversely, enables one to estimate the probable shape of the equilibrium solubility curves based on the known ionic behaviour of components of the ternary solution in question.

THEORETICAL

Have a three-component system consisting of water (0) and two solutes, 1 and 2. The method of expansion of relative activity coefficients is based on the equality of chemical potentials of component 1 in the two equilibrium phases, the solid ($'$) and liquid ($''$) phases:
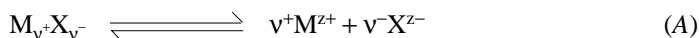
$$\mu_1' = \mu_1'' \ , \tag{1}$$

where we have

$$\mu_1'' = \mu_1^{0''} + RT \ln{(\gamma_1'' m_1)} \ . \tag{2}$$

Similarly, component 2, which is present in the liquid phase solely, obeys the relation

$$\mu_2'' = \mu_2^{0''} + RT \ln{(\gamma_2'' m_2)} \ . \tag{3}$$

For an electrolyte of the $M_{v^+}X_{v^-}$ type which is dissociated according to the equation

$$M_{v^+}X_{v^-} \ \rightleftharpoons \ v^+M^{z+} + v^-X^{z-} \tag{A}$$

we have

$$\mu_1 = \nu_1^+ \mu_1^+ + \nu_1^- \mu_1^- \ . \tag{4}$$

Introduce relative molality as

$$X_i = m_i/m_i^0 \ , \tag{5}$$

(superscript 0 denotes a binary aqueous solution) and the activity coefficient as

$$\xi_i = \gamma_i''/\gamma_i^{0''} \ . \tag{6}$$

Then we have

$$\log X_1 = - \log \xi_1 = \varphi_1 \ \ [T, p, \text{sat}] \ . \tag{7}$$

If the two electrolytes, 1 and 2, have a common ion, Eq. (7) can be modified as follows:

$$\frac{1}{\alpha + \beta} \log \left[X_1^\alpha (X_1 + FB)^\beta \right] = \varphi_1 \ , \tag{8}$$

where α is the number of non-common ions in a molecule of component 1, β is the number of common ions in a molecule of component 1, F is the number of common ions in a molecule of component 2 divided by the number of those ions in a molecule of component 1, and

$$B = X_2 \, m_2^0 / m_1^0 \ . \tag{9}$$

The right-hand side of Eq. (8) can be written in the series expansion form:

$$\varphi_1 = Q_{12} \, m_2 + Q_{122} \, m_2^2 + \dots \ . \tag{10}$$

For the determination of the interaction constants Q it is convenient to divide Eq. (10) by m_2:

$$\varphi_1 / m_2 = Q_{12} + Q_{122} m_2 + \dots \; . \tag{11}$$

A linear relation is thus obtained if higher terms of the expansion can be neglected, which is usually the case.

In the vast majority of electrolyte solutions, a so-called ionic zone can be assumed to form[6,7] around the ion. Within that zone, water molecules are influenced by the charge of the ion, take a different orientation and acquire properties which are basically different from those of pure water. Water with a partly altered structure, so-called destructured water, is a transition between the two limiting states. Such water is always present in the system, even if the ionic zone is absent, as is the case with ions with negative hydration[8] (e.g. K^+, Rb^+, Cs^+, NO_3^- ClO_4^-) or with hydrophobically hydrated ions. The effect of such ions which are incapable of forming the ionic zone consists in facilitating the translation of destructured water. The zone with water's own structure and destructured water vanish if the solution concentration is so high that available water molecules are only sufficient to form the ionic zones, i.e. if the limit of full solvation[9] has been exceeded. The solubilities of many electrolytes are higher than the concentrations corresponding to the limit of full solvation, and in such case, sharing of the hydrate envelopes of the individual ions and ion-pair formation apparently take place. The concept in which ions in the solution affect molecules of water within their reach and alter their properties in comparison with pure water[10] or binary solutions[11] is applicable in all cases.

The relation for the thermodynamic solubility product follows from the thermodynamic equilibrium condition (1). If concentrations are used instead of activities, the relation for the analytical solubility product is obtained as

$$S_0 = (v_1^+)^{v_1^+} (v_1^-)^{v_1^-} (m_1^0)^{(v_1^+ + v_1^-)} \; . \tag{12}$$

If the effect of the common ion in the added component 2 were the same as in component 1, the following equation would hold true in ternary systems (e.g. for the same anion in the two components):

$$S_0 = (v_1^+)^{v_1^+} m_1^{v_1^+} (v_1^- m_1 + v_2^- m_2)^{v_1^-} \; . \tag{13}$$

Deviations from this relation are expressed by parameter P. For deriving this parameter, a concept has been adopted[5,6,11] where the molalities were taken with respect to 1 000 g of such water as is affected by ions in the ternary system to the same extent as in the binary saturated solution of pure component 1. A fraction of the water molecules is

affected by the ions to the extent that it cannot be regarded as solvent. The following equation can be written for the concentration of water remaining as solvent:

$$(w_0)_{\text{solvent}} = \frac{n_1^{1-\nu_{\text{r}}} w_0^0}{(\nu_1^-)^{\nu_{\text{r}}} n_1^0} (\nu_1^- n_1 + \nu_2^- n_2)^{\nu_{\text{r}}} \ . \tag{14}$$

In this equation, n_i is the number of moles of component 1 in 100 g of solution, $\nu_{\text{r}} = \nu_1^-/(\nu_1^+ + \nu_1^-)$, and superscript 0 refers to the binary aqueous solution. Parameter P has the meaning of the mole fraction of water that, on the addition of component 2, acquired properties different from those of water in the binary solution saturated by component 1. This parameter is defined[5,6] as

$$P = \frac{1 - w_1 - w_2 - (w_0)_{\text{solvent}}}{M_{\text{r,H}_2\text{O}} (n_1 + n_2)} \ , \tag{15}$$

where $M_{\text{r,H}_2\text{O}}$ is the relative molecular mass of water ($\approx$ 18). In hydration analysis, parameter P is calculated in each point of the analyzed branch of the isotherm. The dependence of P/x_2 on x_2 was found empirically to be the most illustrative information concerning the ionic processes in the system. No theoretical background for this dependence has been suggested so far. For a crude comparison of systems it is convenient to express this dependence as a power polynomial function of the mole fraction of component 2 (x_2):

$$P = P_{12} x_2 + P_{122} x_2^2 + \dots \ . \tag{16}$$

As above, we divide this equation by x_2, whereby the constants P_{ij} are easier to obtain:

$$P/x_2 = P_{12} + P_{122} x_2 + \dots \ . \tag{17}$$

RESULTS AND DISCUSSION

For the interpretation of the physical meaning of the constants Q, or the parameter P, data of a number of systems where different behaviour could be expected were extracted from the extensive literature dealing with phase equilibria. The selection was governed by the data reliability, suitable concentration regions, and availability of information about the behaviour of the systems.

System No. 1. Solubility branch of NaCl in the NaCl–KCl–H$_2$O system at 25 °C (ref.[12]). In this system, the K$^+$ ion is incapable of competing with the Na$^+$ ion for water or for the chloride ion.

System No. 2. Solubility branch of CdCl$_2$. 5/2 H$_2$O in the CdCl$_2$–CaCl$_2$–H$_2$O system at 25 °C (refs[13–15]). Addition of CaCl$_2$ gives rise to complex anions, the solid phase occurs as hydrate.

System No. 3. Solubility branch of KBr in the KBr–NaBr–H$_2$O system[16]. The strongly hydrated Na$^+$ ions withdraw water as long as all ions are capable of forming their hydrate envelopes to the natural extent. Competitive sharing of hydration spheres takes place at higher Na$^+$ concentrations (approximately at 8 mol H$_2$O/mol salts[5,6,17]).

TABLE I
Results of evaluation of solubility data

System	Q_{12}	Q_{122}	Q_{1222}	P_{12}	P_{122}	Note[a]		
						φ/m_2	P	P/x_2
1	−0.004	–	–	1.26	−0.33	0→	0→	0→
2	0.012	0.008	–	−1.21	−0.87	>0▼	<0▲	<0▲
3	−0.027	–	–	3.58	–	<0→	<0▼	>0⚡
4	−0.053	0.018	–	6.73	−1.50	<0▼	>0▼	>0▲
5	−0.001	−0.074	0.072	3.70	−2.41	<0>	>0<	>0<?
6	0.054	−0.002	–	−7.13	2.13	>0▲	<0▲	<0→
7	−0.108	0.153	–	13.67	−12.00	<0>	0⚡	<0▲
8	0.014	−0.001	–	−1.91	0.12	>0▲	<0→	<0▼

[a] Characteristics of curve in the graph:

0→   approaches zero across the etire region
0⚡   approaches zero, increases slightly, then decreases
>0▼   positive value, increases
>0▲   positive value, decreases
>0⚡   positive value, first constant, then decreases
<0→   negative value, constant
<0▲   negative value, increases in its absolute value
<0▼   negative value, decreases in its absolute value
<0>   passes a minimum
>0<   passes a maximum.

System No. 4. Solubility branch of $CaBr_2 . 6 H_2O$ in the $CaBr_2–MgBr_2–H_2O$ system[18]. The Mg^{2+} ions are hydrated strongly. Both salts are highly soluble, so that only 7.5 mol water per mol salts are available along the entire branch of the solubility curve, which is less than the limiting value for salts of this kind (about 9 mol H_2O/mol salts[5,6]), so that ion-pair formation can be expected.

System No. 5. Solubility branch of $MgBr_2 . 6 H_2O$ in the $MgBr_2–MnBr_2–H_2O$ system[18]. At low Mn^{2+} concentrations, the manganese ions are hydrated by molecules of freely available water, whereas at higher Mn^{2+} concentrations, complex ions with mixed coordination spheres are formed due to the water deficit. The compound $MgBr_2 . 2 MnBr_2 . 12 H_2O$ with a heterogeneous coordination sphere at manganese crystallizes in the neighbouring crystallization field[18].

System No. 6. Solubility branch of $MgBr_2 . 6 H_2O$ in the $MgBr_2–ZnBr_2–H_2O$ system at 25 °C (ref.[19]). Complex anions of the $[Zn_2Br_6]^{2-}$ type are assumed to form in this system[20]. The compound $MgBr_2 . ZnBr_2 . 7 H_2O$ crystallizes in the neighbouring field.

System No. 7. Solubility branch of $MgCl_2 . 6 H_2O$ in the $MgCl_2–FeCl_2–H_2O$ system at 25 °C (ref.[21]). At low concentrations, the ions added are hydrated by water which has not been used up in the formation of the hydration spheres. At higher concentrations, mixed coordination spheres involving water molecules and anions are formed; eventually this formation predominates. The compound $MgCl_2 . FeCl_2 . 8 H_2O$, formulated by Balarev[21] as $[Mg(H_2O)_6]^{2+}[FeCl_4(H_2O)_2]^{2-}$, crystallizes in the neighbouring field.

System No. 8. Solubility branch of $NaCl$ in the $NaCl–NaNO_3–H_2O$ system at 25 °C (ref.[22]). A destructuring effect of the nitrate anion can be expected.

The results of calculation using the relations given in the Theoretical are summarized in Table I and shown in Figs 1 and 2, indicating that the relative activity coefficient expansion method, like the hydration analysis method[5,6], gives data usable in the interpretation of the physical state of three-component electrolyte solutions. The parameters
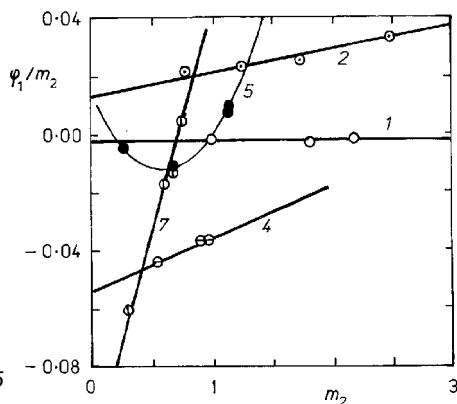

FIG. 1
Plot of φ_1/m_2 vs m_2 for systems No. *1*, *2*, *4*, *5* and *7*

introduced by the two methods are mutually dependent, as the correlation of the Q_{12} and P_{12} constants in Table I demonstrates:

$$Q_{12} = 0.00388 - 0.00771 \, P_{12} \tag{18}$$

(correlation coefficient $r = -0.979$, see Fig. 3).

CONCLUSIONS

The examples treated give evidence that the parameters P (refs[5,6]) and Q (refs[1,3,4]) have a similar physical meaning but parameters Q allow better qualitative distinction of the processes in solutions

If the ion added forms its hydration sphere at the expense of ions of the dissolved equilibrium solid phase or from molecules of water which has not been used up in the hydration of the ions present, the values of the interaction constant Q_{12} are negative along the entire solubility curve. In this treatment, the total number of molecules of water in the saturated solution which are available for the hydration of the ions must be taken into account. A positive Q_{122} value then indicates a situation where the number of water molecules is insufficient and sharing of hydration spheres of the ions present takes place.

A very low Q_{12} value is indicative of a situation where the ion added does not hydrate, nor does it enter into other interactions in the system. Low positive Q_{12} values and, simultaneously, negative Q_{122} values suggest a destructuring effect of the ions added.

Positive Q_{12} values, or simultaneously positive Q_{12} and Q_{122} values, provide information about the formation of ion-pairs or complex ions involving the ion added.
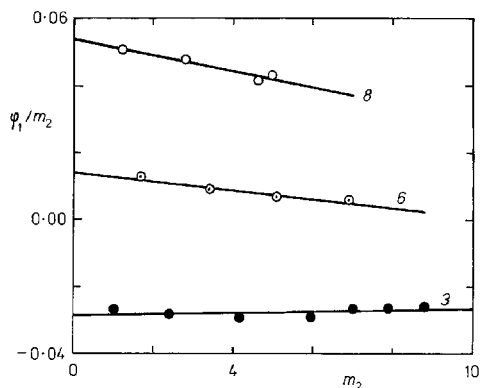

FIG. 2
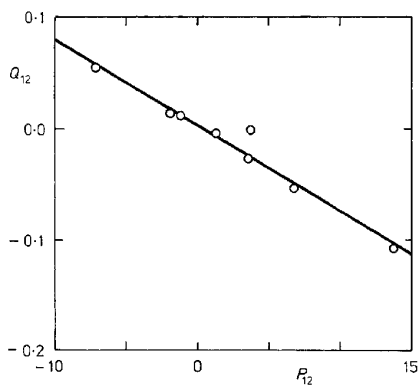Plot of φ_1/m_2 vs m_2 for systems No. 3, 6 and 8

FIG. 3
Correlation of the Q_{12} and P_{12} parameters

The dependences treated are summarized in Table II. It can be concluded that the relative activity coefficient method, using interaction constants tabulated by means of this method for a large series of ternary systems, can be employed to estimate the hydration behaviour of ions in aqueous solutions of electrolytes. The Q parameters enable us to get good qualitative distinction of the processes occurring in solutions.

TABLE II
Physical meaning of interaction parameters

P	P/x_2	Q_{12}	Q_{122}	Q_{1222}	Interpretation
0	0	0	–	–	added ion does not compete, forms no complex
a	a	0	>0	–	solid phase is a hydrate
>0▼	>0→	<0	–	–	the other ion forms its hydration sphere, sufficient amount of water is available
>0▲	▲	<0	>0	–	ion-pair formation
>0	▲	<0	<0	>0	the amount of water available decreases at higher concentrations of component 2
<0▲	▲	>0	–	–	formation of complex ions with a mixed water-containing coordination sphere
<0▲	→	>0	>0	–	formation of complex ions with a homogeneous coordination sphere
b	b	>0	<0	>>0	low concentrations: hydration at a sufficient amount of water / higher concentrations: formation of coordination spheres
<0→	<0▼	>0→<0	<0	–	destructuration

^{a} The P and P/x_2 values are reduced in comparison with systems with the anhydrous equilibrium solid phase; the extent of this reduction and the associated relationships will be discussed elsewhere[23].
^{b} Complex plot with knees, occurrence of extrema is possible.

SYMBOLS

B	relative molality of component 2
F	number of common ions in component 2 divided by the number of common ions in component 1
m_i	molality of i-th component
m_i^0	solubility of i-th component in water (molality)
N_i	number of moles of i-th component

n_i	number of moles of i-th component in 100 g of solution
p	pressure
P	mole fraction of water with altered properties (parameter of the hydration analysis)
P_{ij}	adjustable parameters
Q_{ij}	interaction constants
r	correlation coefficient
R	universal gas constant
S_0	analytical solubility product
T	temperature
w_i	mass fraction of i-th component
X_i	relative molality of i-th component
z	ion charge
α	number of non-common ions in component 1
β	number of common ions in component 1
γ_i	activity coefficient of i-th component
μ_i	chemical potential of i-th component
ν_i^+	number of cations in a molecule of i-th component
ν_i^-	number of anions in a molecule of i-th component
ξ_i	relative activity coefficient of i-th component
φ_1	logarithm of the relative activity coefficient of component 1

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