Dissociation model of the electrical conductivity of molten salt mixtures
IV. Binary reciprocal univalent systems

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Received 4 September 1989

The dissociation model of the electrical conductivity of molten salt mixtures, based on the assumption of an incomplete dissociation of electrolyte components was applied in some binary reciprocal univalent systems. The systems of alkali halides and the systems of alkali halide and silver halide were verified. It was found that the dissociation model of the electrical conductivity of molten salt mixtures may be successfully applied in the reciprocal systems as well. From the standpoint of the physical interpretation the correctness of the calculation is conditioned by the consistency and the correctness of the molar conductivity values, especially by the correctness of the value of the standard Gibbs energy of the exchange reaction. In the reciprocal systems the most dissociated is always the stable pair of salts. The dissociation degrees of all components are higher than 0.5 in all systems studied.

In [1] the dissociation model of the electrical conductivity of molten salt mixtures, based on the idea of an incomplete dissociation of electrolyte components was proposed and theoretically derived. Owing to the mutual interaction of the components in the systems with a common ion their dissociation degrees are not constant but they change with the composition of the system. Consequently, the content of "free" ions in the system changes as well. In [2] the validity of the dissociation model was verified in a number of binary univalent systems with a common ion. In [3] the dissociation model was applied in some ternary univalent systems with a common ion.

Among the binary univalent systems belong also the reciprocal systems which are the mixtures of salts without a common ion, such as NaCl—KBr. Their properties depend on the properties of the binary mixtures, *e.g.* NaCl—NaBr, KCl—KBr, NaCl—KCl, and NaBr—KBr as well as on the quantities which cannot be derived from the properties of the binary mixtures. Their thermodynamic behaviour was discussed *e.g.* on the basis of various variants of the regular solutions theory [4] and of the theory of conformal ionic solutions [5].

In each binary reciprocal system the exchange reaction of the type

$$\mathrm{AX(l)} + \mathrm{BY(l)} \rightleftharpoons \mathrm{AY(l)} + \mathrm{BX(l)} \qquad (A)$$

takes place, the equilibrium of which is determined by the standard Gibbs energy

$$\Delta G^{\circ}_{\mathrm{ex}} = -RT \ln K_{\mathrm{ex}} = -RT \ln \frac{a(\mathrm{AY})\,a(\mathrm{BX})}{a(\mathrm{AX})\,a(\mathrm{BY})} \qquad (1)$$

where $a(\mathrm{AX})$, $a(\mathrm{BY})$, $a(\mathrm{AY})$, and $a(\mathrm{BX})$ are the equilibrium activities of the constituents. If the standard Gibbs energy of the exchange reaction (*A*) is negative, then the equilibrium is shifted to the right and the binary AY—BX system is stable. In the opposite case the binary AX—BY system is stable. In any case the numerical value of the standard Gibbs energy of the exchange reaction (*A*) determines the equilibrium activities of all four constituents of the reciprocal system.

Procedure and results

Let us consider a binary reciprocal system AX—BY with the composition of $(1 - x)$ moles AX and x moles BY According to eqn (*A*) y moles AY and y moles BX originate in this system. Assuming the ideal behaviour of the system the activities are equal to the mole fractions and for the equilibrium constant of the exchange reaction (*A*) the following equation may be derived (assuming that Henry's constants equal one)

$$K_{\mathrm{ex}} = \frac{y^2}{(1 - x - y)(x - y)} \qquad (2)$$

Solving eqn (*2*) for the known value of K_{ex} (resp. $\Delta G^{\circ}_{\mathrm{ex}}$) and the initial composition of the binary reciprocal system x the equilibrium mole fractions of all four constituents are obtained

$$x_1 = a(\mathrm{AX}) = 1 - x - y,\quad x_2 = a(\mathrm{BY}) = x - y,\quad x_3 = x_4 = a(\mathrm{AY}) = a(\mathrm{BX}) = y$$

The individual constituents of the binary reciprocal system dissociate electrolytically according to the schemes

$$\mathrm{A^{-}\ X^{-}} \rightleftharpoons \mathrm{A^{-} + X^{-}} \qquad (B)$$

$$\mathrm{B^{-}\ Y^{-}} \rightleftharpoons \mathrm{B^{-} + Y^{-}} \qquad (C)$$

$$\mathrm{A\ \ Y^{-}} \rightleftharpoons \mathrm{A^{-} + Y^{-}} \qquad (D)$$

$$\mathrm{B^{-}\ X^{-}} \rightleftharpoons \mathrm{B^{-} + X^{-}} \qquad (E)$$

with the dissociation degrees α_i. In an arbitrary reciprocal mixture the following amounts of individual particles are present

$$
\begin{aligned}
n(\mathrm{A^+\ X^-}) &= x_1(1-\alpha_1) & n(\mathrm{A^+}) &= x_1\alpha_1 + x_3\alpha_3\\
n(\mathrm{B^+\ Y^-}) &= x_2(1-\alpha_2) & n(\mathrm{B^+}) &= x_2\alpha_2 + x_4\alpha_4\\
n(\mathrm{A^+\ Y^-}) &= x_3(1-\alpha_3) & n(\mathrm{X^-}) &= x_1\alpha_1 + x_4\alpha_4\\
n(\mathrm{B^+\ X^-}) &= x_4(1-\alpha_4) & n(\mathrm{Y^-}) &= x_2\alpha_2 + x_3\alpha_3
\end{aligned}
$$

The total amount of all particles in the mixture is $S = 1 + x_1\alpha_1 + x_2\alpha_2 + x_3\alpha_3 + x_4\alpha_4$. For the equilibrium constants of the dissociation reactions K_i we get the following equations

$$K_1 = \frac{(x_1\alpha_1 + x_3\alpha_3)(x_1\alpha_1 + x_4\alpha_4)}{x_1(1-\alpha_1)S} \tag{3}$$

$$K_2 = \frac{(x_2\alpha_2 + x_3\alpha_3)(x_2\alpha_2 + x_4\alpha_4)}{x_2(1-\alpha_2)S} \tag{4}$$

$$K_3 = \frac{(x_3\alpha_3 + x_1\alpha_1)(x_3\alpha_3 + x_2\alpha_2)}{x_3(1-\alpha_3)S} \tag{5}$$

$$K_4 = \frac{(x_4\alpha_4 + x_1\alpha_1)(x_4\alpha_4 + x_2\alpha_2)}{x_4(1-\alpha_4)S} \tag{6}$$

Rearranging eqns (*3—6*) we get for the dissociation degrees of the individual constituents the following relations

$$\alpha_1 = 1 - \frac{(x_1\alpha_1 + x_3\alpha_3)(x_1\alpha_1 + x_4\alpha_4)}{K_1x_1S} \tag{7}$$

$$\alpha_2 = 1 - \frac{(x_2\alpha_2 + x_3\alpha_3)(x_2\alpha_2 + x_4\alpha_4)}{K_2x_2S} \tag{8}$$

$$\alpha_3 = 1 - \frac{(x_3\alpha_3 + x_1\alpha_1)(x_3\alpha_3 + x_2\alpha_2)}{K_3x_3S} \tag{9}$$

$$\alpha_4 = 1 - \frac{(x_4\alpha_4 + x_1\alpha_1)(x_4\alpha_4 + x_2\alpha_2)}{K_4x_4S} \tag{10}$$

The set of implicit eqns (*7—10*) may be solved iteratively. The values of the equilibrium constants K_i are determined by the values of the dissociation degrees of the pure constituents

$$K_i = \frac{\alpha_{0i}^2}{1-\alpha_{0i}^2} \qquad i = 1, 2, 3, 4 \tag{11}$$

The values of the dissociation degrees of the pure salts α_{0i} were chosen as the input values for α_i with advantage.

By analogy with the procedure shown in [1] the following relation can be derived for the molar conductivity of the binary reciprocal mixture

$$\lambda_{\text{mix}} = \sum_{i=1}^{4} x_i \frac{\alpha_i}{\alpha_{0i}} \lambda_i \tag{12}$$

where λ_i are the molar conductivities of the pure salts. The solution of eqns (*7—10*) and (*12*) along with the condition

$$\sum_{j=1}^{k} (\lambda_{j,\text{exp}} - \lambda_{j,\text{calc}})^2 = \text{min} \tag{13}$$

enables to find such values of α_{0i} for which the standard deviation of the experimental values of the molar conductivity from the calculated ones is less

Table 1

The calculated values of the dissociation degrees of the pure salts in the reciprocal systems studied

System	α_{01}	α_{02}	α_{03}	α_{04}	s	$\Delta G^{\circ}_{\text{ex}}$	T/K
	NaCl	KBr	NaBr	KCl			
NaCl—KBr	0.94	0.943	0.69	0.70	0.85	4.914	1073
NaBr—KCl	0.94	0.935	0.675	0.68	1.98	−4.914	1073
	NaCl	KI	NaI	KCl			
NaCl—KI	0.99	0.84	0.74	0.84	1.52	10.964	1070
NaI—KCl	0.99	0.85	0.74	0.84	1.44	−10.964	1070
	KCl	RbBr	KBr	RbCl			
KCl—RbBr	0.93	0.92	0.72	0.85	1.28	4.782	1073
KBr—RbCl	0.93	0.92	0.72	0.85	0.34	−4.782	1073
	KCl	CsBr	KBr	CsCl			
KCl—CsBr	0.70	0.77	0.70	0.94	0.89	−9.818	1073
KBr—CsCl	0.70	0.76	0.70	0.99	0.52	9.818	1073
	NaCl	AgBr	NaBr	AgCl			
NaCl—AgBr	0.93	0.96	0.72	0.71	0.86	10.0[a]	1073
NaBr—AgCl	0.92	0.96	0.72	0.72	0.99	−10.0[a]	1073
	KCl	AgBr	KBr	AgCl			
KCl—AgBr	0.98	0.98	0.54	0.54	2.64	1.0[a]	1073
KBr—AgCl	0.99	0.99	0.59	0.59	7.51	−1.0[a]	1073

s in S cm^2 mol^{-1}; $\Delta G^{\circ}_{\text{ex}}$ in kJ mol^{-1}

a) Estimated values.

than the experimental error for all mixtures with the known value of the molar conductivity.

In the present work the dissociation model of the electrical conductivity of molten salt mixtures was verified in the binary reciprocal systems. The effort was to testify both the stable and the unstable pairs of the salts. The experimental data on the molar conductivity of the binary reciprocal systems are often incomplete in the literature. Even if the conductivity data are known the values of the density or of the standard Gibbs energy of some components are missing. Therefore some reciprocal systems of alkali halides and systems of alkali and silver halides were selected only. The density and conductivity data of the systems under investigation were taken from [6]. The values of the standard Gibbs energies of the respective pure salts were taken from [7].

The calculated values of the dissociation degrees of the pure salts of the studied binary reciprocal systems are given in Table 1. The values of the standard deviations s of the experimental values of the molar conductivity from the calculated ones and the values of the standard Gibbs energies of the exchange reactions used by the calculation are given as well.

Discussion

During the computational procedure it was found that the set of eqns (*7*—*10*) is not too stable. Inputing nonsuitable values of α_{0i} it easily diverges, and α_i attain values of $0 > \alpha_i > 1$, which has no physical meaning. The convergency of the set of eqns (*7*—*10*) depends on the consistency of the molar conductivity and of the standard Gibbs energy of the exchange reaction values. Especially the latter quantity has the greatest influence on the correctness of the calculation for which the agreement of results in both reciprocal pairs of salts is the criterion of the physical relevance. This has been markedly shown especially in the reciprocal systems containing silver halides where the use of the values of the standard Gibbs energies of the exchange reactions (18.37 kJ mol^{-1} for the NaCl—AgBr system and 13.0 kJ mol^{-1} for the KCl—AgBr system) calculated on the basis of the published values of the standard Gibbs energies of the respective salts [7] does not allow to obtain even the rough agreement of the results in both pairs of the reciprocal systems. In both the mentioned systems substantially lower values of the standard Gibbs energies of the exchange reactions were to be used (*cf.* Table 1). Suspicious is also the value of the standard Gibbs energy in the KCl—CsBr system. It is known that the stable pair is always formed by the small cation—small anion salt and the large cation—large anion salt. It means that the KCl—CsBr pair could be stable although the results of the calculation of the dissociation degrees are in relatively good accordance in both reciprocal pairs.

From the results of the calculation it follows that except the KCl—CsBr system the most dissociated is always the stable pair of salts. The content of the unstable pair of constituents in the mixture is always relatively lower and their dissociation degrees are always lower, too. It is remarkable that in all the reciprocal systems studied the dissociation degrees of the constituents are always higher than 0.5. No explanation was found for this fact till now.

From the present work it follows that the dissociation model of the electrical conductivity of molten salt mixtures may be successfully used also in the binary reciprocal systems. By suitable choice of the dissociation degrees of the pure salts and using the correct value of the standard Gibbs energy of the exchange reaction it is possible to describe rationally the course of the molar conductivity in these systems. whereby the standard deviations of the experimental values of the molar conductivity from the calculated ones do not surpass the experimental error. It is evident that for the quantitative conclusions, similarly as in the binary and ternary systems with a common ion, more complete and more precise experimental data are needed.

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Translated by V Daněk