

Incomplete Dissociation and Electrical Conductivity in Binary Molten Salt Mixtures with Common Ion

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The present work is a continuation of our previous attempts to modelling electrical conductivity in molten salt mixtures with common ion. The basic assumption of the proposed model is the concept of incomplete dissociation of the two salts due to the competition between the two different ions to form neutral ionic associations. Starting from the relationship between the dissociation probabilities of two dependent processes and probability of the common dissociation process, some expressions are proposed for the dissociation probabilities of the salts forming the mixture. We assume that equilibrium constants of the dissociation processes may be used just as probabilities in order to describe more successfully the incomplete dissociation (or ionic association) and its influence on mixture electrical conductivity. We point out the fact that one of the model versions leads to the same value for the dissociation degree of a component, irrespective of the second salt in the mixture.

Because the electrical conductivity measurements in molten salts are rather difficult to perform, the results reported by different authors for the same systems are often scattered. Among the solutions proposed to solve this problem, some efforts have been registered in the last decade to imagine theoretical models enabling the calculation of the mixture electrical conductivity on the basis of conductivities of individual components [1–4].

Our previous attempts [3–5] to modelling electrical conductivity in binary molten salt systems with common ion were based on the assumption, firstly proposed by *Klemm* [6] and then employed by *Daněk* [1, 2], of an incomplete dissociation of the two (or more) salts forming a mixture. According to *Klemm*, in a binary mixture of charge-symmetric salts with a common ion, the salt with smaller cation is more associated (or otherwise, less dissociated) than the other salt at all concentrations. The redistribution of anions between the two different cations is responsible for an increased ionic association of both salts: the salt with the smaller cation is more associated (less dissociated) than the one with the bigger cation.

The experimental conductivity data were satisfactorily rendered by our previous theoretical models [3–5] but on the occasion we also signaled their major drawback: the widely varying values of dissociation degrees found for the same salt depending on the second salt with which it was combined to form a binary system.

A similar observation has been lately made by *Klemm* and *Schaefer* [7] when they tried to use a simple model for ion-counterion interactions (association-dissociation ionic processes) in order to explain the

occurrence of the Chemla effect of the ionic mobilities [8], that is equal internal mobilities of the cations at a certain mixing ratio of two salts.

In the present contribution we propose a method for avoiding the simplifying assumption used in the previous models [1–5], according to which binary molten salt mixtures are similar to diluted aqueous solutions of two additive, monovalent salts where the equilibrium constants between electrically charged and respectively, neutral species are independent of the mixture concentration. In the model we propose here, the equivalence between the dissociation equilibrium constants in the two pure salts and those in the mixture is replaced by a dependence relationship.

A Model for Ion-Coion Interactions in Binary Molten Salt System

If we consider a molten binary system with common ion, $AX-BX$, and admit that each component is incompletely dissociated in the melt, then the mixture consists of five kinds of particles, three of which are charged and two are neutral, *i.e.* A^+ , B^+ , X^- , and AX and BX



Four equilibrium constants correspond to the above equilibria established between the ionic pairs AX or BX and the "free" ions A^+ , X^- and B^+ , X^-

$$K_{01} = \alpha_{01}^2 / [1 - \alpha_{01}^2] \quad (3)$$

$$K_{02} = \alpha_{02}^2 / [1 - \alpha_{02}^2] \quad (4)$$

$$K_1 = \alpha_1(x_1\alpha_1 + x_2\alpha_2) / [(1 - \alpha_1)(1 + x_1\alpha_1 + x_2\alpha_2)] \quad (5)$$

$$K_2 = \alpha_2(x_1\alpha_1 + x_2\alpha_2) / [(1 - \alpha_2)(1 + x_1\alpha_1 + x_2\alpha_2)] \quad (6)$$

where K_{01} , K_{02} and α_{01} , α_{02} are the equilibrium constants and respectively dissociation degrees for the two pure salts, K_1 , K_2 and α_1 , α_2 are the same quantities in the mixture and x_1 , x_2 are mole fractions. According to dissociation models [1, 2], additive binary molten salt mixtures behave like diluted aqueous solutions where the equilibrium constants are considered to be independent of concentration, and therefore

$$K_{01} = K_1 \quad K_{02} = K_2 \quad (7a, b)$$

In those models, by eliminating α between the two thus obtained second-order equations, one gets a cubic equation in which α is then solved numerically.

In the following, we propose a different algorithm for computing the intrinsic dissociation degrees by starting from the observation that eqns (7) are not justified in the real case of molten salt mixtures.

We denote as:

$P(1)$ probability for process $\textcircled{1}$, dissociation of neutral AX into A^+ and X^- free ions;

$P(2)$ probability for process $\textcircled{2}$, dissociation of neutral BX into B^+ and X^- free ions;

$P(1 \cup 2)$ probability for process $\textcircled{1} \cup \textcircled{2}$, dissociation of both AX and BX species in the mixture. As in the mixture the first two processes condition each other, one may use the mathematical relations

$$P(1 \cup 2) = P(1) + P(2) - P(1 \cap 2) \quad (8)$$

$$P(1 \cap 2) = P(1|2) \times P(2) \quad (9a)$$

$$P(1 \cap 2) = P(2|1) \times P(1) \quad (9b)$$

where $P(1|2)$ and $P(2|1)$ are respectively, the probability of the dissociation process $\textcircled{1}$ in the presence of the dissociation process $\textcircled{2}$ and *vice versa*. Finally from eqns (8) and (9) one obtains

$$P(1 \cup 2) = P(1) + P(2) - P(1|2) \times P(2) \quad (10)$$

$$P(1|2) \times P(2) = P(2|1) \times P(1) \quad (11)$$

Thus, the whole matter reduces to determining the above introduced probabilities.

The first step is to consider, according to Bjerrum's theory of the ionic associations [9], that probabilities for the dissociation processes (1) are the very dissociation degrees

$$P(1) = \alpha_{01} \quad P(2) = \alpha_{02} \quad (12a, b)$$

By using eqns (3) and (4), one obtains the relationships between the equilibrium constants of the dissociation processes and their respective probabilities

$$P(1) = 1/\sqrt{(1 + 1/K_{01})} \quad P(2) = 1/\sqrt{(1 + 1/K_{02})} \quad (13)$$

In order to establish the probability of the unified processes, $P(1 \cap 2)$, we introduce the dissociation equilibrium constant in the mixture, K

$$K = \alpha_1\alpha_2(x_1\alpha_1 + x_2\alpha_2) / [(1 - \alpha_1)(1 - \alpha_2)(1 + x_1\alpha_1 + x_2\alpha_2)] \quad (14)$$

which subsequently allows us to determine $P(1 \cup 2)$, the probability for the unified dissociation processes $\textcircled{1} \cup \textcircled{2}$ from the constant K by means of an expression similar to (13)

$$P(1 \cup 2) = 1/\sqrt{(1 + 1/K)} \quad (15)$$

or, after introducing eqn (14)

$$P(1 \cup 2) = [\alpha_1\alpha_2(x_1\alpha_1 + x_2\alpha_2) / \{\alpha_1\alpha_2(x_1\alpha_1 + x_2\alpha_2) + (1 - \alpha_1)(1 - \alpha_2)(1 + x_1\alpha_1 + x_2\alpha_2)\}]^{1/2} \quad (16)$$

Similarly, we can calculate the probability $P(1|2)$ for the dissociation process $\textcircled{1}$ in the presence of the dissociation process $\textcircled{2}$ starting from the K_1 constant, by employing eqns (13) and (15)

$$P(1|2) = 1/\sqrt{(1 + 1/K_1)} \quad (17)$$

By replacing K_1 in eqn (17) with its expression given by eqn (5), it results

$$P(1|2) = \sqrt{\alpha_1(x_1\alpha_1 + x_2\alpha_2) / (1 - x_2\alpha_1 + x_2\alpha_2)} \quad (18)$$

Following the same pattern, the probability of the dissociation process $\textcircled{2}$ in the presence of the dissociation process $\textcircled{1}$ is

$$P(2|1) = \sqrt{\alpha_2(x_1\alpha_1 + x_2\alpha_2) / (1 + x_1\alpha_1 - x_1\alpha_2)} \quad (19)$$

Finally, one introduces in eqns (10) and (11) the probabilities $P(1)$, $P(2)$, $P(1 \cup 2)$, $P(1 \cap 2)$, $P(1|2)$, and $P(2|1)$ as computed above and writes

$$[\alpha_1\alpha_2(x_1\alpha_1 + x_2\alpha_2) / \{\alpha_1\alpha_2(x_1\alpha_1 + x_2\alpha_2) + (1 - \alpha_1)(1 - \alpha_2)(1 + x_1\alpha_1 + x_2\alpha_2)\}]^{1/2} = \alpha_{01} + \alpha_{02} - \alpha_{01}[\alpha_2(x_1\alpha_1 + x_2\alpha_2) / (1 + x_1\alpha_1 - x_1\alpha_2)]^{1/2} \quad (20)$$

$$\alpha_{01}^2\alpha_2(x_1\alpha_1 + x_2\alpha_2) / (1 + x_1\alpha_1 - x_1\alpha_2) = \alpha_{02}^2\alpha_1(x_1\alpha_1 + x_2\alpha_2) / (1 - x_2\alpha_1 + x_2\alpha_2) \quad (21)$$

Expression (21) can be rearranged as a second-order equation of the variable α_2

Table 1. Comparison between Experimental Data, λ_{exp} , and Conductivity Values as Calculated according to Series-Dissociation Model, Versions I and II, for Iodide Mixtures at 950 K

System	$x(\text{LiI})$	λ_{exp}	λ_{SD}	σ_{SD}	$\varepsilon(\lambda_{\text{SD}})$	$\alpha_{01}; \alpha_{02}$	λ_{SD}	σ_{SD}	$\varepsilon(\lambda_{\text{SD}})$	$\alpha_{01}; \alpha_{02}$	
		S cm ² mol ⁻¹	S cm ² mol ⁻¹	S cm ² mol ⁻¹	%		S cm ² mol ⁻¹	S cm ² mol ⁻¹	%		
						I					
											II
LiI—NaI	1.0	218.31	218.77		-0.21		215.77			1.16	
	0.757	179.44	179.44		0.00	0.435	181.55		-1.17	0.445	
	0.552	165.38	164.97	0.47	0.25		167.99	1.10	-1.58		
	0.504	164.85	163.79		0.64	0.995	166.81		-1.19	0.995	
	0.298	150.86	153.40		-1.68		155.57		-3.12		
	0.0	132.06	132.46		-0.31		132.17		-0.08		
LiI—KI	1.0	218.31	224.25		-2.72		221.57		-1.49		
	0.716	152.97	144.76		5.37	0.679	145.51		4.88	0.489	
	0.650	136.51	135.65	1.76	0.63		136.46	1.44	0.04		
	0.514	118.65	118.49		0.14	0.839	119.23		-0.49	0.685	
	0.231	89.33	88.59		0.83		88.98		0.39		
	0.0	82.23	84.95		-3.30		85.12		-3.51		
LiI—RbI	1.0	218.31	227.60		-4.26		225.67		-3.37		
	0.910	176.30	165.04		6.39	0.625	165.45		6.15	0.469	
	0.552	101.26	94.35	3.45	6.82		94.95	3.16	6.23		
	0.271	76.49	81.47		-6.52	0.809	81.69		-6.80	0.675	
	0.0	68.28	71.83		-5.19		71.71		-5.03		
LiI—CsI	1.0	218.31	229.61		-5.17		226.55		-3.77		
	0.946	155.70	159.13		-2.20		158.50		-1.79		
	0.780	116.16	97.09		16.41	0.565	97.22		16.30	0.465	
	0.532	82.95	75.49	3.49	8.99		75.39	3.29	9.12		
	0.284	73.47	68.94		6.16	0.815	68.52		6.73	0.675	
	0.243	70.21	68.36		2.63		67.89		3.30		
	0.0	62.44	66.57		-6.61		65.79		-5.36		

λ – molar conductivity; σ – standard deviation; α_{01}, α_{02} – dissociation degrees of pure salts; ε – relative error.

$$x_2 \alpha_{01}^2 \alpha_2^2 + [\alpha_{01}^2 (1 - x_2 \alpha_1) + x_1 \alpha_{02}^2 \alpha_1] \alpha_2 - \alpha_{02}^2 \alpha_1 (1 + x_1 \alpha_1) = 0 \quad (22)$$

If eqn (22) is subsequently rearranged as an explicit function of α_2 and then introduced in eqn (20), an equation of an order higher than two is obtained which consequently can be solved numerically.

RESULTS AND DISCUSSION

The dissociation degrees of the two individual components, α_{01} and α_{02} , were computed by employing our own experimental conductivity and density data [10] by means of the expression given by the series-dissociation model, also proposed by us in a previous paper [4]

$$\lambda = V^2 / [x_1 V_1^2 \alpha_{01} / \alpha_1 \lambda_1 + x_2 V_2^2 \alpha_{02} / \alpha_2 \lambda_2] \quad (23)$$

under limiting condition

$$\sum_{i=1}^N [\lambda_{\text{exp}}(i) - \lambda(i)]^2 = \min \quad (24)$$

In the above expressions, λ , λ_1 , and λ_2 are molar conductivities of the mixture and respectively the two

pure salts, V , V_1 , and V_2 are molar volumes. We have to mention here that eqn (23) has been worked out in our previous papers [3–5] on the basis of two premises: the incomplete dissociation of the two salts proposed by *Daněš* [1, 2] and respectively the analogy suggested by *Fellner* [11, 12] between an equivalent circuit of electrical resistors and the melt resistance, the latter being calculated as a sum of contributions of the individual components which are linked together either in series or in parallel. Therefore, the equation used by *Daněš* in [1] can be obtained according to the *Fellner* model for parallel coupling of the salts in the mixtures [11] by multiplying molar conductivities λ_1 and λ_2 of the pure salts by dissociation degree ratios α_1 / α_{01} and α_2 / α_{02} . We have shown [4] that eqn (23) renders the experimental data for alkali iodide mixtures better than the *Daněš* expression does. Because neither eqn (22) nor its derivatives against α_{01} and α_{02} can be expressed as explicit functions of α_1 and α_2 , a searching algorithm is employed for finding the condition of minimum. The results thus obtained for 950 K are listed in those columns of Table 1 marked with I.

It can be seen that the proposed model predicts quite satisfactorily the molar conductivity experimental data, with standard deviations between 0.47–3.49

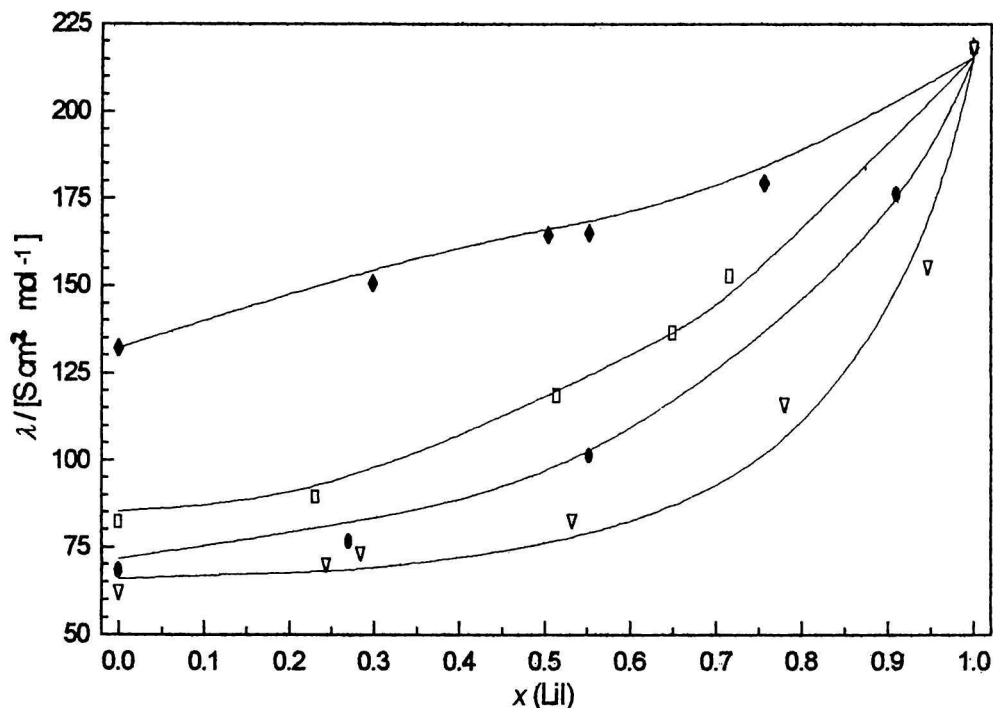


Fig. 1. Molar electrical conductivity calculated according to version II of the model (full lines); the points represent experimental values; LiI—NaI (\blacklozenge), LiI—KI (\square), LiI—RbI (\bullet), LiI—CsI (∇).

$\text{S cm}^2 \text{ mol}^{-1}$, much lower than those registered when using the original "dissociation" model [2] (for example, in the case of LiI—CsI mixture, Daněk reported $\sigma(950 \text{ K}) = 12.77 \text{ S cm}^2 \text{ mol}^{-1}$). The α_0 values for LiI vary depending on the second salt with which it is combined and they range between 0.435—0.679.

Some more pertinent results were obtained when we considered the dissociation constants as being the probabilities themselves of the dissociation processes, respectively:

$P(1) \rightarrow K_{01}$ and $P(2) \rightarrow K_{02}$ for dissociation process ① and ② in the simple salts;

$P(1|2) \rightarrow K_1$ and $P(2|1) \rightarrow K_2$ for the dissociation process taking place in the mixture, that is ① in the presence of ② and ② in the presence of ①, respectively;

$P(1 \cup 2) \rightarrow K$ for the common dissociation process ① \cup ② in the mixture.

Therefore, after replacing the equilibrium constants in eqns (10) and (11) it results

$$\begin{aligned} \alpha_1 \alpha_2 (x_1 \alpha_1 + x_2 \alpha_2) / [(1 - \alpha_1)(1 - \alpha_2)(1 + x_1 \alpha_1 + x_2 \alpha_2)] = \\ = \alpha_{01}^2 / [1 - \alpha_{01}^2] + \alpha_{02}^2 / [1 - \alpha_{02}^2] - \{ \alpha_{02}^2 / [1 - \alpha_{02}^2] \} \times \\ \times \{ \alpha_1 (x_1 \alpha_1 + x_2 \alpha_2) / [(1 - \alpha_1)(1 + x_1 \alpha_1 + x_2 \alpha_2)] \} \end{aligned} \quad (25)$$

and then

$$\begin{aligned} \{ \alpha_{01}^2 / [1 - \alpha_{01}^2] \} \alpha_2 (x_1 \alpha_1 + x_2 \alpha_2) / \\ [(1 - \alpha_2)(1 + x_1 \alpha_1 + x_2 \alpha_2)] = \\ = \{ \alpha_{02}^2 / [1 - \alpha_{02}^2] \} \alpha_1 (x_1 \alpha_1 + x_2 \alpha_2) / \\ [(1 - \alpha_1)(1 + x_1 \alpha_1 + x_2 \alpha_2)] \end{aligned} \quad (26)$$

From eqn (26), one obtains for α_2 the expression

$$\alpha_2 = \alpha_{02}^2 (1 - \alpha_{01}^2) \alpha_1 / [\alpha_{01}^2 (1 - \alpha_{02}^2) (1 - \alpha_1) + \alpha_{02}^2 (1 - \alpha_{01}^2) \alpha_1] \quad (27)$$

and after introducing it in eqn (25) one writes a fourth-order equation which can be solved numerically.

The theoretical molar conductivities and α_{01}, α_{02} values were computed like in the version I and they are listed in Table 1 in the columns marked with II, while the calculated molar conductivities are shown in Fig. 1 (the points represent experimental values). It is easily noticed that the improvement is achieved when using the version II of the model, namely that α_{01} values of LiI are almost similar for all four systems as they lie in the range 0.445—0.489. Again, the calculated conductivity values II are in good agreement with the experimental data, as standard deviations are close to those obtained when using version I of the model.

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