Association in Molten Salts and Mobility Isotherms

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A change with concentration in the height of the first peak of the pair distribution function g_{+-} of a salt in a mixture of molten salts indicates a change in the degree of association of that salt. It is shown that the changes in association observed this way from MD-simulations of binary mixtures of charge symmetric salts with a common anion are qualitatively consistent (i) with the requirements for the occurrence of the crossing of mobility isotherms (Chemla effect) and (ii) with the ideal law of mass action.

In this article, the change in the association of a salt with its concentration is considered to be a property which parallels the change in the height of the first peak of the salt's partial pair distribution function g_{+-} with its concentration.

We are going to deal with melts consisting of a small cation 1, a large cation 2 and an anion 3, all ions being monovalent. The functions g_{13} and g_{23} of such mixtures in their dependence on the mole fraction x_{23} of the salt 23 have been obtained from MD-simulations for (Li, Rb) Cl by Okada, Takagi, and Kawamura [1], and for (Li, K) Cl by Caccamo and Dixon [2] and by Lantelme and Turq [3]. Their results, as to the heights of the first peak of the functions g_{13} and g_{23}, are summarized in Table 1.

From Table 1 it is seen that

(i) the salt 13 is more associated than the salt 23 at all concentrations,
(ii) the association of both salts increases with increasing mole fraction x_{23},
(iii) this increase is more pronounced for the salt 13 than for the salt 23 (cf. last column of Table 1).

Perie and Chemla [4], having discovered systems in which the internal mobility isotherms b_{13} (x_{23}) and b_{23} (x_{23}) cross in the way indicated in Fig. 1 (a), did suggest that association effects are responsible for this phenomenon. The three above observations meet exactly the requirements for this suggestion:

(i) The internal mobility b_{13} of the pure salt 13 is greater than the internal mobility b_{23} of the pure salt 23. However, salt 13 is more associated than salt 23 at all concentrations.

(ii) Both b_{13} and b_{23} decrease with increasing x_{23}, which is in line with the increasing association of both salts.
(iii) b_{13} decreases faster with increasing x_{23} than does b_{23}, because the association of salt 13 increases faster with increasing x_{23} than does the association of salt 23.

In the following it shall be shown that the associative behaviour expressed by the points (i), (ii) and (iii) is consistent with the law of mass action. As the simplest conceivable example which is liable to show these trends, we consider the

Table 1. MD-simulation results on the heights of the first peaks of pair distribution functions g_{+-} for various mole fractions x_{23} of the salt 23.

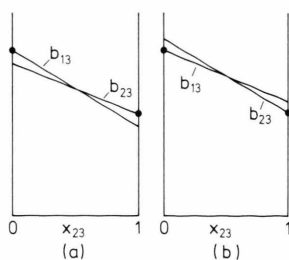| System	Ref.	Temp. (K)	x_{23}	Pair	Height	Height ratio
1 = Li			0	1 – 3	3.69	
						1.56
2 = Rb			0.5	1 – 3	5.77	
	[1]	1100				
3 = Cl			0.5	2 – 3	3.00	
						1.34
			1	2 – 3	4.06	
1 = Li			0.16	1 – 3	4.23	
						1.59
2 = K			0.90	1 – 3	6.73	
	[2]	1036				
3 = Cl			0.16	2 – 3	2.52	
						1.43
			0.90	2 – 3	3.61	
1 = Li			0.10	1 – 3	3.91	
						1.57
2 = K			0.90	1 – 3	6.15	
	[3]	1096				
3 = Cl			0.10	2 – 3	3.02	
						1.46
			0.90	2 – 3	3.32	

Fig. 1. Internal mobility isotherms of binary molten salt mixtures vs. the mole fraction x_{23} of the salt 23. (a) The normal way of crossing (Chemla effect); (b) An alternative way of crossing not observed so far.

chemical equilibrium in a mixture of independent particles consisting of the free ions 1, 2 and 3, and the neutral salt molecules 13 and 23. If the relatively small consequences of volume changes are neglected, one has in this case

$$X_4/X_1 X_3 = K_{13}, \quad X_5/X_2 X_3 = K_{23}. \quad (1\,a, b)$$

Here X_1, X_2, X_3, X_4 and X_5, are the mole fractions of the free ions 1, 2 and 3, and the neutral salt molecules 13 and 23, respectively. One has

$$X_1 + X_2 + X_3 + X_4 + X_5 = 1, \quad (2)$$

and due to the condition of neutrality

$$X_1 + X_2 = X_3. \quad (3)$$

From (2) and (3) follows

$$X_4 + X_5 = 1 - 2 X_3, \quad (4)$$

and from (1 a, b), (3) and (4)

$$X_2 = \frac{-1 + 2 X_3 + K_{13} X_3^2}{(K_{13} - K_{23}) X_3}. \quad (5)$$

The mole fractions of the salts are (cf. (2))

$$x_{13} = 1 - x_{23}, \quad x_{23} = \frac{X_2 + X_5}{1 - X_3}. \quad (6\,a, b)$$

From (6 b) with (1 b) and (5) one obtains

$$x_{23} = \frac{(1 + K_{23} X_3)(-1 + 2 X_3 + K_{13} X_3^2)}{(K_{13} - K_{23}) X_3 (1 - X_3)}. \quad (7)$$

Equation (7) can be written in the form

$$f = g \quad (8)$$

with

$$f = -1 + 2 X_3 + K_{13} K_{23} X_3^3 \quad (9)$$

and

$$g = [K_{13} x_{23} + K_{23}(1 - x_{23})]\, X_3 \\ - [K_{13}(1 + x_{23}) + K_{23}(2 - x_{23})]\, X_3^2. \quad (10)$$

Since cation 1 is supposed to be smaller than cation 2, due to the Coulomb interaction the salt 13 will be more associated than the salt 23, i.e.

$$K_{13} > K_{23}. \quad (11)$$

From (9) follows

$$f(X_3 = 0) = -1, \quad df/dX_3 > 0, \quad (12\,a, b)$$

and from (10) and (11)

$$g(X_3 = 0) = 0, \quad dg/dx_{23} > 0. \quad (13\,a, b)$$

The topology of the functions $f(X_3)$ and $g(X_3)$ given by (12 a, b) and (13 a), together with (8) and (13 b) allows us to see that

$$dX_3/dx_{23} > 0. \quad (14)$$

Figure 2 shows by way of an example how this conclusion has been reached.

Now the degrees of association, A_{13} and A_{23}, of the two salts shall be introduced:

$$A_{13} = X_4/(X_1 + X_4), \quad A_{23} = X_5/(X_2 + X_5). \quad (15\,a, b)$$

From (1 a, b) and (15 a, b) one obtains

$$A_{13} = \frac{K_{13} X_3}{1 + K_{13} X_3}, \quad A_{23} = \frac{K_{23} X_3}{1 + K_{23} X_3}. \quad (16\,a, b)$$

From (11), (14) and (16 a, b) it follows that

(i) $A_{13} > A_{23}$,

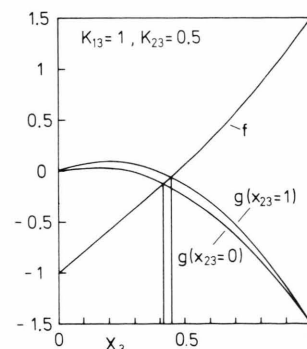(ii) $dA_{13}/dx_{23} > 0, \quad dA_{23}/dx_{23} > 0$,

Fig. 2. The functions f, $g (x_{23} = 0)$ and $g (x_{23} = 1)$ according to (9) and (10) for $K_{13} = 1$, $K_{23} = 0.5$ vs. X_3, showing that $dX_3/dx_{23} > 0$.

(iii) $\mathrm{d}A_{13}/\mathrm{d}x_{23} > \mathrm{d}A_{23}/\mathrm{d}x_{23}$ for $0 < A_{13} + A_{23} < 1$,

(iv) $\mathrm{d}A_{13}/\mathrm{d}x_{23} < \mathrm{d}A_{23}/\mathrm{d}x_{23}$ for $1 < A_{13} + A_{23} < 2$,

since $\mathrm{d}A_{13,23}/\mathrm{d}\ln X_3 = K_{13,23} X_3/(1 + K_{13,23} X_3)^2$, and $A_{13} + A_{23} = 1$ implies $K_{13} X_3 = 1/K_{23} X_3$.

The points (i), (ii) and (iii) are quite analogous to the corresponding points (i), (ii) and (iii) found for the molten salt mixtures discussed above. Point (iv) suggests that mixtures of highly associated salts might show a crossing of the mobility isotherms as depicted in Figure 1 (b). This has never been observed so far, but it might occur in mixtures of badly conducting salts or in mixtures of ordinary salts at elevated temperatures. Note that in molten salts at constant pressure the association increases with temperature [5].

An example for a mixture obeying the points (i), (ii) and (iii) is shown in Fig. 3, where the degrees of dissociation, $\alpha_{13} = 1 - A_{13}$ and $\alpha_{23} = 1 - A_{23}$, as evaluated by means of (7) and (16 a, b) for the case $K_{13} = 1$, $K_{23} = 0.5$, are plotted vs. x_{23}.

It must be kept in mind that the law of mass action for independent particles, which is valid in gases and diluted salt solutions, is not really applicable in molten salt mixtures. However, the conclusions reached for the ideal case might be helpful in rationalising the experimentally observed crossovers of mobility isotherms in molten salts.

Our results can be summarized as follows:

In a binary mixture of charge-symmetric salts with a common anion, the salt with the smaller cation is more associated than the other salt at all concentrations. If in such a mixture some of the smaller cations are replaced by the bigger cations, a redistribution of the anions takes place, resulting in an increased association of both salts. If the average association of the two salts is far from saturation, this incrase is greater for the salt with the smaller cation than for the salt with the bigger cation. Since in the pure salts the mobility of the smaller cation is greater than that of the bigger cation, and in the mixtures the cationic mobilities decrease the more, the more the respective salts associate, a cross-over of the mobility isotherms in the sense of Fig. 1 (a) becomes possible.

In closing it should be remembered that the decrease of both b_{13} and b_{23} with increasing x_{23} is not only due to the increasing association of the salts but partly also to the intercationic drag effect: The fast cations are hampered in their migration by
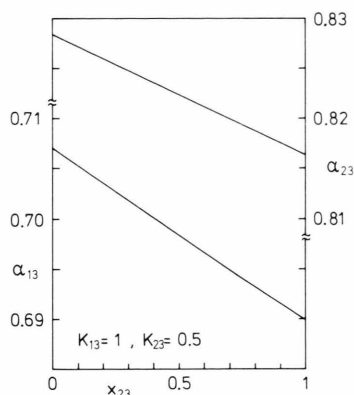

Fig. 3. The degrees of dissociation, α_{13} and α_{23}, of dissociating gas molecules 13 and 23 in their dependence on the mole fraction x_{23} of the salt 23, if the equilibrium constants K_{13} and K_{23} are taken to be 1 and 0.5, respectively.

the slow cations, and the migration of the slow cations is accelerated by the fast cations. If the two cations are isotopes, there are only negligible changes in association (the association of both salts may decrease somewhat with increasing concentration of the heavy salt.), and the drag effect alone remains effective. For instance, the difference between the mobilities of ^{6}Li and ^{7}Li in molten chlorides and nitrates of lithium with the natural isotopic composition (7% ^{6}Li, 93% ^{7}Li) has been found to be only about 40% of the difference between the mobilities of ^{6}Li in pure ^{6}Li-salt and ^{7}Li in pure ^{7}Li-salt [6].

Mixtures containing mono- and divalent cations

If salt 13 is less associated than a less conducting salt 23, as is to be expected if cation 2 is divalent while cation 1 is monovalent, according to our previous reasoning in mixtures of such salts the association of both salts should decrease with increasing x_{23}, and for sufficiently dissociated salts this decrease should be faster for salt 23 than for salt 13. This, in combination with the intercationic drag effect, should result in mobility isotherms having selected general features as shown in Figure 4.

The curves in Fig. 4 have been evaluated by assuming that

$$b_{13,23} = (1 - d)\, b_{13,23}\, (d = 0) \tag{17}$$
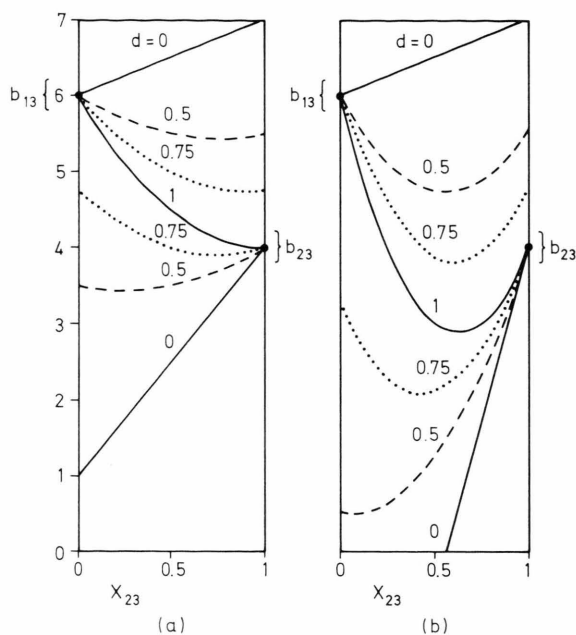$$+ d\, [b_{13}\, (d = 0)\, (1 - x_{23}) + b_{23}\, (d = 0)\, x_{23}] ,$$

Fig. 4. Hypothetical mobility isotherms resulting from a combination of association effects and intercationic drag effects in case of mixtures of salts with monovalent and divalent cations.

where d describes the magnitude of the intercationic drag effect $(0 < d < 1)$, and that in adequate common units

$$b_{13} (d = 0) = 6 + x_{23},$$
$$b_{23} (d = 0) = 1 + 3 x_{23} \qquad \text{(Fig. 4 (a))},$$
$$b_{23} (d = 0) = -5 + 9 x_{23} \qquad \text{(Fig. 4 (b))}.$$

Mobility isotherms with trends shown in Fig. 4, especially isotherms with minima, have indeed been observed for mixtures of alkali halides with alkaline earth halides (cf. e.g. [7]). For such systems crossovers of mobility isotherms have not been observed and are not to be expected from our simple point of view.

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