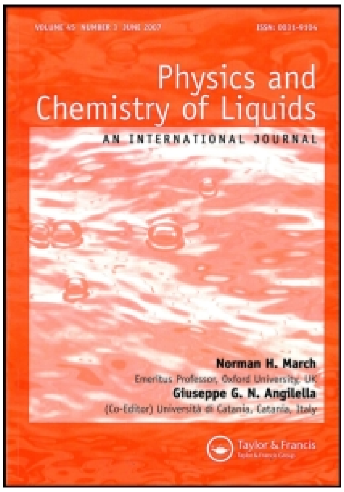

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Concentration Fluctuations and Ionic Core Polarization in Molten Salt Mixtures

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The activity coefficient and the heat of mixing of molten alkali-halide mixtures with a common ion are analyzed through the use of thermodynamic fluctuation theory and of a charged-hard-spheres model for the ionic interactions. A strain contribution is isolated and evaluated with the help of experimental data, and a Coulomb contribution is estimated within the mean spherical approximation. The difference between these contributions and experiment is attributed to electronic polarizability of the ionic cores by displaying its correlation with appropriate polarization parameters.

1 INTRODUCTION

Mixtures of molten alkali halides with a common ion are known[1] to conform rather closely to the model of regular solutions, i.e. the excess entropy of mixing over the ideal value is small and the heat of mixing is approximately a parabolic function of composition. A single interaction parameter w thus suffices in a first approximation to describe the heats of mixing and the activity coefficients. The experimentally determined values of this parameter[1] are mostly negative for the mixtures with a common anion and mostly positive in those with a common cation.

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Various attempts, which are reviewed in the book of Lumsden,[1] have been made to estimate w on the basis of crystalline-like models for the structure of these solutions. These models do not account for strain contributions, which are intrinsically positive, and are not reliable in their estimates of the other contributions. Lumsden[2] has suggested by such a model a sizable contribution to w, in mixtures with a common anion, from effects of electronic polarization of the ionic cores. This term is, of course intrinsically negative.

A number of thermodynamic properties of solutions, and in particular the interaction parameter w for a regular solution, are in fact related to their structural properties by thermodynamic fluctuation theory, as developed by Kirkwood and Buff.[3] This method was previously used[4] to extract from the available thermodynamic data some information on the state of ordering in molten alkali-halide mixtures. We use the method in the following to isolate and evaluate the strain contribution to w. We also estimate the contribution arising from the Coulomb interactions between the ions by a calculation of partial structure factors at long wavelengths for a mixture of charged hard spheres in the mean spherical approximation.[5] Comparison with experiment then allows us to demonstrate the role of electronic polarization of the ionic cores in the concentration fluctuations and the heat of mixing.

2 THERMODYNAMIC FLUCTUATIONS AND MEAN SPHERICAL APPROXIMATION

We consider a molten alkali-halide mixture of composition $A_{1-c}B_cC$ and shall conventionally refer to the three ionic species by indices 1, 2 and 3, with the index 3 denoting the common ion. The activity γ_1 of the "solvent" is defined by writing its chemical potential as

$$\mu_1 = \mu_{10} + k_B T \ln[(1-c)\gamma_1]. \tag{2.1}$$

The Gibbs–Duhem relation yields

$$k_B T\left(\frac{\partial \ln \gamma_1}{\partial c}\right)_{T,P} = \frac{k_B T}{1-c} - \frac{c}{1-c}\left(\frac{\partial \mu_2}{\partial c}\right)_{T,P} \tag{2.2}$$

where μ_2 is the chemical potential of the "solute". In the case of a regular solution one has for the heat of mixing ΔH and for the activity of the solvent the approximate relation

$$\Delta H = k_B T \ln \gamma_1 = wc^2, \tag{2.3}$$

which introduces the interaction parameter w characterizing the solution at any concentration. This parameter is related through Eq. (2.2) to the derivative $(\partial\mu_2/\partial c)_{T,P}$ of the chemical potential of the solute, which is in turn related by thermodynamic fluctuation theory[3] to the long-wavelength limit of the partial structure factors in the solution.

We show in the Appendix that thermodynamic fluctuation theory yields the expression

$$\left(\frac{\partial\mu_2}{\partial c}\right)_{T,P} = -(1-c)n\frac{(v_2-v_1)^2}{K_T} + \frac{k_BT}{c}\lim_{k\to 0}\,[1-c_{cc}(k)] \tag{2.4}$$

where n is the number density of ion pairs, K_T is the isothermal compressibility, v_1 and v_2 are the partial volumes of the components, and $c_{cc}(k)$ is the direct correlation function for concentration fluctuations[6] in the solution. From Eqs. (2.2) and (2.3) we then get for a regular solution

$$w = \tfrac{1}{2}n\frac{(v_2-v_1)^2}{K_T} + \frac{1}{2}\frac{k_BT}{c(1-c)}\lim_{k\to 0} c_{cc}(k). \tag{2.5}$$

The first term in this expression clearly represents the elastic strain contribution to w, as the elastic work involved in the replacement of an A ion by a B ion. This term, which has been omitted in previous theories of molten alkali-halide mixtures, is intrinsically related to the observed variation of the molar volume of the solution with concentration, since

$$n(v_2-v_1) = \frac{1}{V}\left(\frac{\partial V}{\partial c}\right)_{T,P}. \tag{2.6}$$

The second term in Eq. (2.5), on the other hand, can be viewed as an internal potential driving long-wavelength concentration fluctuations at constant volume, if one recalls the usual asymptotic relation between the direct correlation function in a liquid and the negative of the interaction potential divided by k_BT. This term involves the detailed ionic interactions, including in the present case short-range effects from the Coulomb interactions. The long-range Coulomb terms do not enter the present problem as is shown in the Appendix.

Thermodynamic fluctuation theory also relates the partial volumes and the isothermal compressibility to the long-wavelength limit of the partial structure factors in the solution. We show in the Appendix that, as far as density fluctuations within the first two ionic components are concerned, the theory is isomorphous to that for a two-component mixture of neutral particles. We find it convenient for calculational purposes to adopt the following expressions, which are discussed in the Appendix:

$$(nK_T)^{-1} = n\sum_{\alpha,\beta=1}^{3} c_\alpha c_\beta \mu_{\alpha\beta}, \tag{2.7}$$

$$\frac{(v_2 - v_1)}{K_T} = n \sum_{\alpha=1}^{3} c_\alpha(\mu_{\alpha 2} - \mu_{\alpha 1}) \tag{2.8}$$

and

$$\frac{k_B T}{c(1-c)} \lim_{k\to 0} c_{cc}(k) = \frac{k_B T}{c(1-c)} - n(\mu_{11} + \mu_{22} - 2\mu_{12}). \tag{2.9}$$

Here $c_1 = 1 - c$, $c_2 = c$, $c_3 = 1$, and

$$\mu_{\alpha\beta} = \left(\frac{\partial \mu_\alpha}{\partial n_\beta}\right)_{T, n_{\bar{\beta}}} \tag{2.10}$$

is the derivative of the chemical potential of the α component with respect to the number density n_β of the β component at constant temperature and all other number densities $n_{\bar{\beta}}$.

It is now our task to carry out the evaluation of Eqs. (2.7)–(2.9) and hence of w. We are, of course unable to handle a refined model of the ionic interactions but we can draw on recent work concerning structural properties of pure molten salts. Specifically, we can estimate the strain term and the Coulomb contribution to the second term in Eq. (2.5) by resorting to a model which represents each ion as a charged hard sphere. This model, which can be solved analytically in the framework of the mean spherical approximation,[5] yields a resonably good account of the structure of pure molten salts when the hard sphere diameters are adjusted to reproduce their compressibility.[7] Analytic expressions for the chemical potentials in this scheme have already been given elsewhere,[8] and it is a straightforward though lengthy calculation to derive analytic expressions for the quantities $\mu_{\alpha\beta}$ introduced in Eq. (2.10). We thus pass immediately to discuss the numerical results for solutions.

We adopt for the ionic hard-sphere diameters the values reported by Senatore *et al.*,[8] which ensure good agreement of Eq. (2.7) for $c = 0$ and $c = 1$ with the measured values of the compressibility. Rather little is known experimentally about the compressibility of alkali halide solutions as a function of concentration: Figure 1 illustrates a comparison of our results with experiment.[9] Comparatively small deviations from a linear interpolation between the values for the pure components are apparent, and are reasonably reproduced by the theory. The theory is less accurate in its predictions for $(v_2 - v_1)$, a serious drawback for our calculation of w since this quantity enters the strain term in Eq. (2.5) as a square power. The experimental information available[10–12] for the variation of molar volume with concentration indicates, however, that a linear interpolation between the values for the pure components is quite accurate. Our best estimate for the strain contribution to w, which is reported in the first column of the table for a few

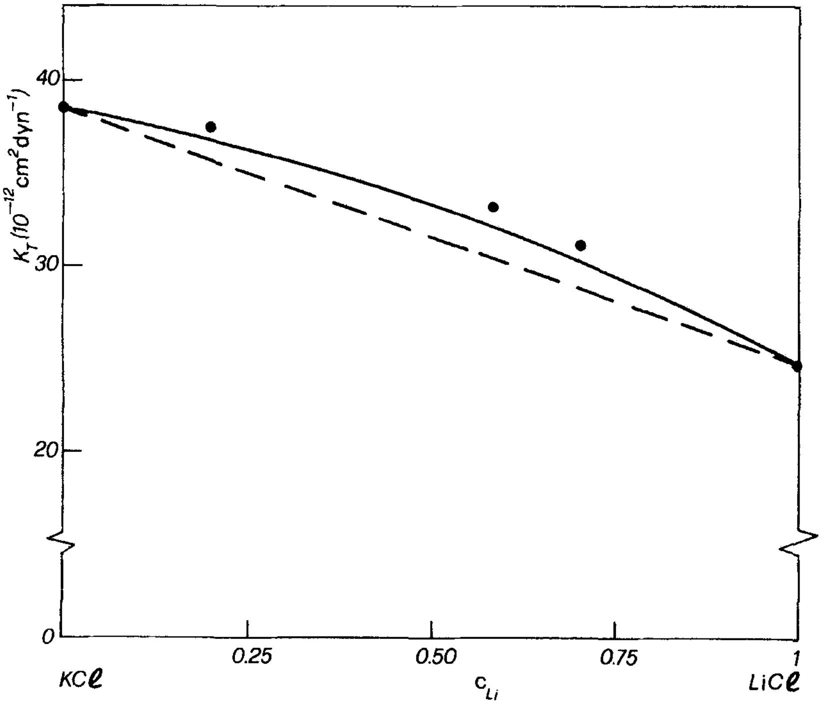

FIGURE 1 Isothermal compressibility versus concentration of Li in the (K, Li) Cl system. Full curve: theory; dots: experiment, from Ref. 9. The broken line is the linear interpolation between the values for the pure components.

TABLE I

Contributions to the interaction parameter w (in units of $\frac{1}{2}k_B T$)

System	w_{strain}	w_{Coulomb}	Δw
(Li, Na) Cl	0.7	0.2	2.0
(Li, K) Cl	3.5	−0.4	6.1
(Li, Cs) Cl	8.9	−2.6	10.8
(Na, K) Cl	1.0	−0.3	1.2
(Na, Cs) Cl	3.7	−1.2	3.2
(K, Cs) Cl	1.0	−0.3	0.5
(F, Br) Na	5.6	−2.2	3.0
(Cl, Br) Na	0.5	−0.2	0.2
(Cl, I) Na	2.3	−1.0	0.7
(F, I) Na	8.1	−3.4	4.1

representative systems at concentration $c = 0.5$, is consequently based on the theoretical values for K_T and on values for $(v_2 - v_1)$ obtained from Eq. (2.6) under the assumption of a linear dependence of the molar volume on concentration. The second column of the table reports the values of the Coulomb contribution to w as calculated from Eq. (2.9).

3 CORRELATION WITH CORE POLARIZATION

Although the numerical results reported in the table should not be taken too seriously from a quantitative viewpoint, we can draw from them some qualitative conclusions. First, the Coulomb contribution to w is mostly negative and quite small. Secondly, the strain contribution is quite important, and clearly leads to a positive value for w if these two are the only contributions. This latter result is, however in contrast with experiment: as we noted in the introduction, the observed values of w are mostly negative for the solutions with a common anion and mostly positive, but much smaller than the sum of w_{strain} and w_{Coulomb}, for the solutions with a common cation. We report in the third column of the table the difference Δw between $w_{\text{strain}} + w_{\text{Coulomb}}$ and the observed values of w.

We must clearly look for an additional negative contribution to the second term in Eq. (2.5) from parts of the ionic interaction potentials that we have not included in the preceding calculations. Contributions to w from London dispersion forces, which have been estimated by Lumsden,[2] are rather small and positive. The only possible source for a large negative contribution is from core polarization effects.

To test this conjecture we plot in Figure 2, for mixtures with a common anion, the quantity $2\Delta w/k_B T$ against a suitable parameter A_-, which is suggested by the work of Lumsden[2] as representative of the effects of core polarization. This parameter is defined as

$$A_- = \frac{\alpha_- e^2}{k_B T}\left(\frac{1}{r_{AC}^2} - \frac{1}{r_{BC}^2}\right)^2 \tag{3.1}$$

where α_- is the electronic polarizability of the anion and r_{AC}, r_{BC} are the first neighbour distances in the pure components. A_- measures the polarization energy of the anion in the electric field arising from the presence of different cations. It is apparent from the figure that the correlation between Δw and A_- is quite good, and can be approximately represented by the linear relation

$$\frac{2\Delta w}{k_B T} \simeq 4.5 A_- . \tag{3.2}$$

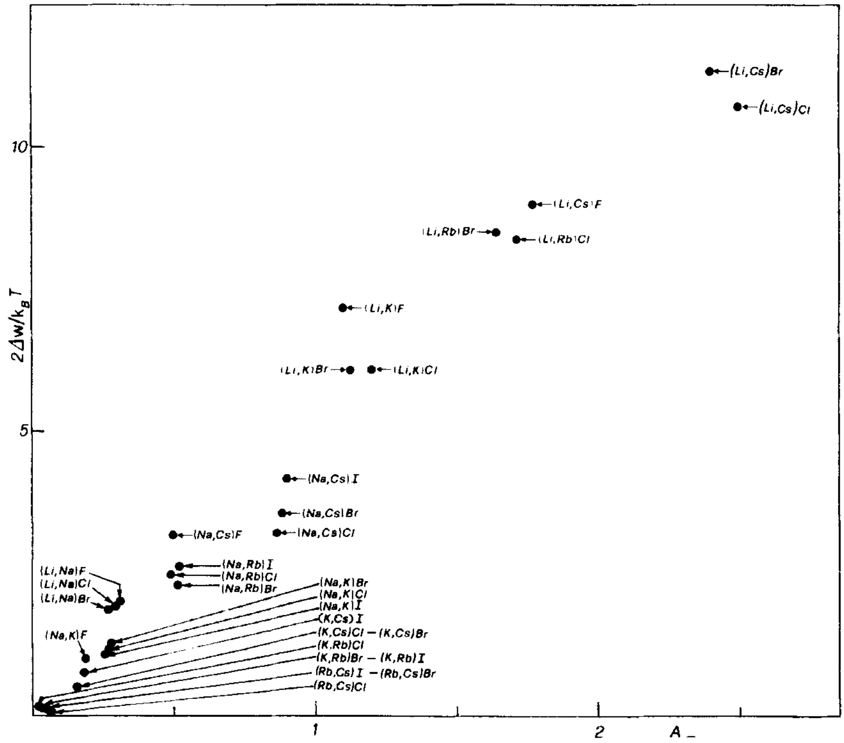

FIGURE 2 Correlation between $2\Delta w/k_BT$ and the anion polarization parameter A_- in molten alkali-halide mixtures with a common anion.

We feel that this correlation demonstrates the role of electronic polarization effects in concentration fluctuations in these systems.

A similar plot is reported in Figure 3 for the mixtures with a common cation, the parameter A_+ being defined by an expression analogous to Eq. (3.1) with the polarizability α_+ of the cation replacing that of the anion. The correlation is less good than in Figure 2, and can be roughly represented by

$$\frac{2\Delta w}{k_BT} \approx 8A_+. \tag{3.3}$$

The larger numerical factor seems to suggest that the core polarization of the solvent and solute negative ions, which are endowed with large polarizabilities, is also relevant in the disordered structures of these liquid mixtures.

An accurate study of these problems would clearly require the use of computer simulation techniques, which are unfortunately very expensive

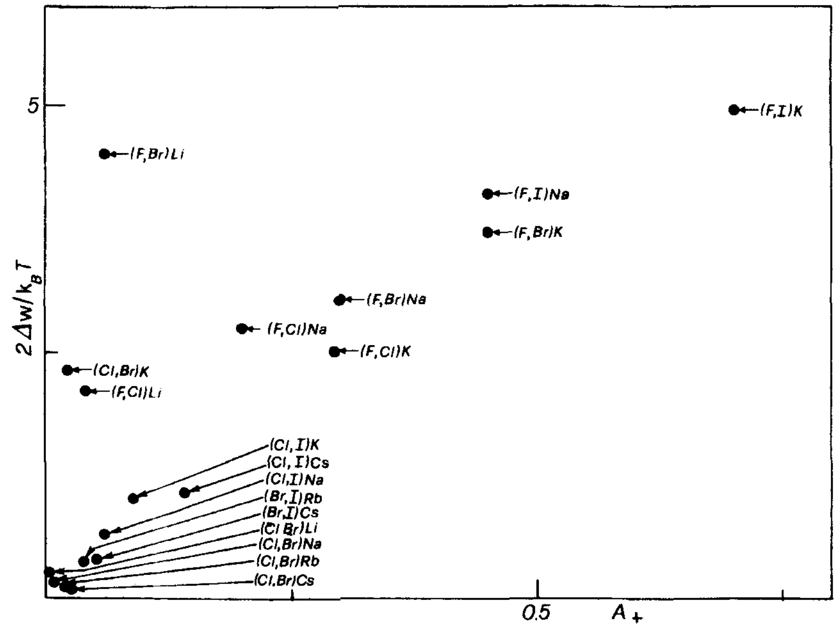

FIGURE 3 Correlation between $2\Delta w/k_BT$ and the cation polarization parameter A_+ in molten alkali-halide mixtures with a common cation.

when electronic polarization effects need to be included. The present approach and the empirical relations (3.2) and (3.3) may, however, already prove useful for other ionic solutions.

Acknowledgment

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Appendix

THERMODYNAMIC FLUCTUATIONS IN A MOLTEN ALKALI-HALIDE MIXTURE WITH A COMMON ION

The relations of Kirkwood and Buff[3] between thermodynamic and structural properties are derived for mixtures of neutral particles, on the assumption of short-range forces between the particles. The structural properties of interest are the direct correlation functions $c_{\alpha\beta}(k)$ in the limit $k \to 0$. These are related to the partial structure factors $S_{\alpha\beta}(k)$, defined by

$$S_{\alpha\beta}(k) = \delta_{\alpha\beta} - n(c_\alpha c_\beta)^{1/2} \int d\mathbf{r} e^{i\mathbf{k}\cdot\mathbf{r}} [g_{\alpha\beta}(r) - 1] \tag{A.1}$$

in terms of the radial distribution functions $g_{\alpha\beta}(r)$, by the inverse-matrix relation[13]

$$c_{\alpha\beta}(k) = \delta_{\alpha\beta} - S^{-1}_{\alpha\beta}(k). \tag{A.2}$$

The difficulty in the case of Coulomb forces is that the long-wavelength form of $c_{\alpha\beta}(k)$ contains a Coulomb divergent term,[14]

$$\lim_{k \to 0} c_{\alpha\beta}(k) = \delta_{\alpha\beta} - \frac{n(c_\alpha c_\beta)^{1/2}}{k_B T} \left[\frac{4\pi Z_\alpha Z_\beta e^2}{k^2} + \mu_{\alpha\beta} \right] \tag{A.3}$$

where Z_α are the ionic valences (in the present case $Z_1 = Z_2 = -Z_3$ with $|Z_\alpha| = 1$ and $\sum_{\alpha=1}^{3} c_\alpha Z_\alpha = 0$) and $\mu_{\alpha\beta}$ are the quantities defined in Eq. (2.10). Some discussion is thus needed before we can apply the Kirkwood–Buff theory to a molten alkali-halide mixture.

The crucial point is that the Coulomb divergences cancel by charge neutrality when we proceed to evaluate the long-wavelength limit of $S_{\alpha\beta}(k)$ by matrix inversion of Eq. (A.3). The result for the partial structure factors describing density fluctuations within the first two ionic components is

$$\lim_{k \to 0} S_{\alpha\beta}(k) = \frac{k_B T}{c_1 c_2 n D} \begin{pmatrix} c_2 \tilde{\mu}_{22} & -(c_1 c_2)^{1/2} \tilde{\mu}_{12} \\ -(c_1 c_2)^{1/2} \tilde{\mu}_{12} & c_1 \tilde{\mu}_{11} \end{pmatrix} \tag{A.4}$$

where

$$\tilde{\mu}_{\alpha\beta} = \mu_{\alpha\beta} + \mu_{33} + \mu_{3\alpha} + \mu_{3\beta} \tag{A.5}$$

and $D = \tilde{\mu}_{11}\tilde{\mu}_{22} - \tilde{\mu}_{12}^2$. Equation (A.4) has the same form as for a two-component neutral mixture, allowing us to introduce through a further matrix inversion a set of "screened" direct correlation functions $\tilde{c}_{\alpha\beta}(k)$, given by

$$\lim_{k \to 0} \tilde{c}_{\alpha\beta}(k) = \delta_{\alpha\beta} - \frac{n(c_\alpha c_\beta)^{1/2}}{k_B T} \tilde{\mu}_{\alpha\beta} \quad (\alpha, \beta = 1, 2). \tag{A.6}$$

The Kirkwood–Buff relations can now be used for this two-component "screened" mixture, and in particular they lead immediately to Eqs. (2.7) and (2.8) in the main text.

The quantity $(\partial\mu_2/\partial c)_{T,P}$ in Eq. (2.2) can be written through the use of the Gibbs–Duhem relation as

$$\left(\frac{\partial\mu_2}{\partial c}\right)_{T,P} = N_1\left[\left(\frac{\partial\mu_1}{\partial N_1}\right)_{T,P,N_2} + \left(\frac{\partial\mu_2}{\partial N_2}\right)_{T,P,N_1} - \left(\frac{\partial\mu_2}{\partial N_1}\right)_{T,P,N_2} - \left(\frac{\partial\mu_1}{\partial N_2}\right)_{T,P,N_1}\right] \tag{A.7}$$

where $N = N_1 + N_2$ and N_1, N_2 are the total numbers of ions in the first and second component. Transformation of the derivatives at constant pressure into derivatives at constant volume yields

$$\left(\frac{\partial\mu_2}{\partial c}\right)_{T,P} = -n(1-c)\frac{(v_2 - v_1)^2}{K_T} + n(1-c)(\mu_{11} + \mu_{22} - 2\mu_{12}). \tag{A.8}$$

Equations (2.4) and (2.9) of the main text follow at once through the use of either Eq. (A.3) or Eq. (A.6), when one defines[6] the concentration-concentration direct correlation function $c_{cc}(k)$ as

$$\begin{aligned} c_{cc}(k) &= c_2 c_{11}(k) + c_1 c_{22}(k) - 2(c_1 c_2)^{1/2} c_{12}(k) \\ &= c_2 \tilde{c}_{11}(k) + c_2 \tilde{c}_{22}(k) - 2(c_1 c_2)^{1/2} \tilde{c}_{12}(k). \end{aligned} \tag{A.9}$$