A simple lattice model for the mixing properties of molten $K_x(KCl)_{1-x}$ solutions

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Abstract. A very simple lattice model is presented for mixtures of alkali metals and alkali halides, like K$_x$(KCl)$_{1-x}$. The valence electrons are assumed to be excluded from the Wigner–Seitz spheres associated with the anions, while they are uniformly distributed over the cation Wigner–Seitz spheres. The calculated excess volume of mixing turns out to be positive over most of the concentration range, in qualitative agreement with experiment, provided the surface energy of the electrons, associated with the boundary of the anion Wigner–Seitz spheres, is taken into account. The results of this model differ considerably from earlier predictions based on linear electron screening theory.

1. Introduction

Solutions of alkali metals in alkali halide melts, of the form M$_x$(MX)$_{1-x}$, where x denotes the mole fraction of metal, undergo a continuous metal–non-metal transition, as the concentration x varies from the pure metal end ($x = 1$, metallic liquid) to the pure salt ($x = 0$, ionic liquid). This transition indirectly shows up in the qualitative change of the pair structure, as measured by neutron diffraction experiments [1], in the appearance of a miscibility gap for certain melts, like K$_x$(KCl)$_{1-x}$, and in the rapid change of the collective density fluctuation spectra, as measured by inelastic neutron scattering experiments [2] or by molecular dynamics simulations [3].

The change in electronic structure renders a theoretical description of metal–salt solutions a difficult task. A systematic but rather naive approach is to assume that the Coulombic interactions between ions are linearly screened by the gas of degenerate valence electrons at all concentrations x. This approach is known to be valid for the pure metal ($x = 1$) [4], but becomes questionable in the presence of anions ($x < 1$). Nonetheless linear screening theory, which is equivalent to second-order perturbation theory in the ion–electron coupling, has been applied to K$_x$(KCl)$_{1-x}$ solutions [5]. The resulting pair structure and phase diagram are in rough, qualitative agreement with experimental data, but the theory is incapable of reproducing the finer details, like the long-wavelength concentration fluctuations, as probed by the small-angle diffraction experiments, or the magnitude and sign of the excess molar volume of mixing. Whereas the theory predicts large *negative* excess volumes at all concentrations, careful thermodynamic measurements lead to a much smaller

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positive excess volume at intermediate concentrations [6]. This qualitative discrepancy between theory and experiment is almost certainly due to the inadequacy of the linear screening approximation, which treats anions and cations on an equal footing, while it is quite clear that the former strongly repel the valence electrons and the latter tend to build up an excess density of valence electrons in their vicinity.

The aim of this paper is to present a very simple model which accounts for the anion–cation asymmetry and to show that this model is capable of predicting at least the right sign of the excess molar volume.

2. The model

One mole of $M_x(MX)_{1-x}$ contains $N_1 = N_{Av}$ M^+ cations, $N_2 = (1-x)N_{Av}$ X^- anions and $N_0 = N_1 - N_2 = xN_{Av}$ valence electrons (N_{Av} denotes Avogadro's number). In our model, the $N = N_1 + N_2$ ions are distributed on the N sites of a simple cubic lattice. Each ion is assumed to be fixed at the centre of a spherical Wigner–Seitz (WS) cell of volume $v = V/N$ and of radius $a = (3v/4\pi)^{1/3}$. The valence electrons occupy the volume $V' = N_1 v = V - N_2 v$, i.e. they are assumed to be excluded from the WS cells associated with the anions. The effective electron density is hence

$$n_0 = \frac{N_0}{N_1 v} = \frac{x}{v} \tag{1}$$

and the usual dimensionless electron density parameter is

$$r_s = \frac{(3/4\pi n_0)^{1/3}}{a_B} = \frac{a}{a_B x^{1/3}} \tag{2}$$

where a_B is the Bohr radius. It is convenient to define a similar parameter associated with the ion density, namely:

$$R_s = \frac{a}{a_B} = x^{1/3} r_s. \tag{3}$$

In the pure salt limit ($x \to 0$), r_s diverges, as there are no valence electrons left, while R_s remains finite. Each WS cell associated with an anion carries a charge $-e$, while each cell associated with a cation carries a charge $+e$ $(1-x)$. Moreover, the valence electrons are assumed to be uniformly spread over the cation WS cell, i.e. they are not polarized by the cation at the centre. Neglecting van der Waals interactions between ions, the total energy U of the model is the sum of an electrostatic Madelung term U_M, a Born repulsion term U_B between neighbouring ions of opposite charge, and an electronic term U_{el}

$$U = U_M + U_B + U_{el}. \tag{4}$$

These three terms are evaluated as follows.

(i) The Madelung energy results from N_1 positive point ions of effective charge e $(1-x)$, and $N_2 = (1-x)N_1$ negative point ions of charge $-e$, which are distributed on a simple cubic lattice. The Madelung energy is of the form

$$\frac{U_M}{N} = -\frac{e^2}{a} u(x) \tag{5}$$

where $u(x) = 0$ for $x = 1$, while for $x = 0$, $u(x)$ equals the Madelung constant of the NaCl structure, i.e. $0.8738 \times (3/4\pi)^{1/3} = 0.542\,06$. For intermediate concentrations, $u(x)$ has been determined by choosing among all possible distributions of positive and negative ions on the simple cubic lattice, the one that yields the lowest electrostatic energy. The optimization was achieved by starting from the known lowest-energy structure at $x = 0$.

The metal concentration was then progressively increased and oppositely charged ions were permuted within a zero-temperature Monte Carlo scheme for periodic samples of $N = 64$ and 216 ions. The results of these calculations are plotted in figure 1 and may be fitted to a simple parabolic form according to

$$u(x) = \left(\frac{3}{4\pi}\right)^{1/3} [0.8738 - 1.2374x + 0.3636x^2]. \tag{6}$$

The Madelung energy in Rydberg units, which are used throughout, becomes

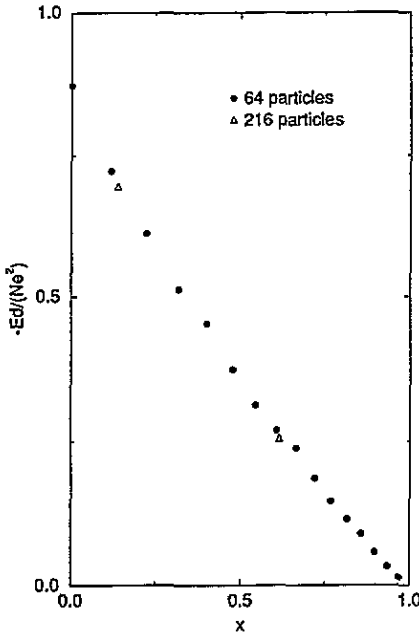$$\frac{U_M^*}{N} = -\frac{2u(x)}{R_s}. \tag{7}$$

Figure 1. Madelung energy, as defined in (5), multiplied by $(4\pi/3)^{1/3}$ versus metal concentration x. Thus, $-U_M/N$ is given in units of e^2/d, where d is the cubic lattice constant. The black dots are the results from the Monte Carlo optimization for a periodic sample of 64 particles, while the open triangles are for a sample of 216 particles.

(ii) The Born term results from the exponential repulsion between oppositely charged nearest-neighbour ions. Each cation is surrounded, on average, by $v(1-x)/(2-x)$ anions. For a simple cubic lattice the coordation number v is equal to 6. The Born repulsion energy per ion in Rydberg units reads:

$$\frac{U_B^*}{N} = A_B^* \, v \frac{(1-x)}{(2-x)} \, e^{-\alpha R_s}. \tag{8}$$

The reduced parameters for a KCl pair are taken at their usual Tosi–Fumi [7] values, i.e. $A_B^* = 131.26$ and $\alpha = 2.530$.

(iii) The electronic contribution to the energy is the sum of a bulk term and a surface term. The bulk term corresponds to the N_1 partially filled WS cells associated with the cations. The surface term results from the N_2 empty WS cells associated with the anions, which may be regarded as spherical cavities 'cut' into the electronic 'jellium':

$$U_{el}^* = N_1 \epsilon_b(r_s) + N_2 \epsilon_s(r_s). \tag{9}$$

The bulk energy ϵ_b and the surface energy ϵ_s may be taken at their ground state values, since the electron Fermi temperature T_F far exceeds the thermodynamic temperature ($T \simeq 10^3$ K), except at very low metal concentration ($r_s \gg 1$), where the electronic contribution becomes vanishingly small. These ground state values depend only on the density parameter r_s.

Since the fractional number of valence electrons in each cation WS cell is x, the bulk energy $\epsilon_b(r_s)$ is of the form

$$\epsilon_b(r_s) = x\epsilon_0(r_s) + \epsilon_{ext}(r_s) + \epsilon_{coul}(r_s) \tag{10}$$

where $\epsilon_0(r_s)$ is the ground state energy per electron of the uniform jellium, $\epsilon_{ext}(r_s)$ the interaction energy of the electron gas with the cation at the centre of the spherical WS cell and $\epsilon_{coul}(r_s)$ is the Coulomb energy of the electron gas uniformly distributed over this cell. The ground state energy per electron $\epsilon_0(r_s)$ splits into the usual kinetic, exchange and correlation contributions and reads in Rydberg units as follows:

$$\epsilon_0(r_s) = \epsilon_k + \epsilon_{ex} + \epsilon_{corr} = \frac{2.21}{r_s^2} - \frac{0.916}{r_s} + \epsilon_{corr}(r_s). \tag{11}$$

For $\epsilon_{corr}(r_s)$ we have used the standard parametrization of the Monte Carlo data of Ceperley and Alder [8]:

$$\epsilon_{corr}(r_s) = \frac{2\gamma}{1 + \beta_1\sqrt{r_s} + \beta_2 r_s} \tag{12}$$

with $\gamma = -0.1423$, $\beta_1 = 1.0529$ and $\beta_2 = 0.3334$. Assuming a simple Ashcroft 'empty core' ion–electron pseudopotential with core radius r_c [4], the 'external' contribution reads:

$$\epsilon_{ext} = \frac{3x}{R_s}\left[\frac{r_c^2}{R_s^2} - 1\right] \tag{13}$$

where r_c is in atomic units. Finally, the Coulomb contribution can easily be calculated:

$$\epsilon_{coul} = \frac{6}{5}\frac{x^2}{R_s}. \tag{14}$$

The surface energy $\epsilon_s(r_s)$ in (9) is the product of the surface s of a WS cavity and the surface energy σ of the jellium model. If the latter is expressed in Rydbergs divided by the square of the Bohr radius a_B, the surface energy $\epsilon_s(r_s)$ is

$$\epsilon_s(r_s) = s\sigma = 4\pi R_s^2\sigma. \tag{15}$$

σ has been calculated for a planar interface [9] and the results for $r_s \geqslant 5$, which are relevant in the present study, may be approximately fitted by the simple power law

$$\sigma(r_s) = \frac{\sigma_0}{r_s^\eta} \tag{16}$$

with $\eta = 2.75$ and $\sigma_0 \simeq 10^{-2}$ Ryd/a_B^2. However, curvature corrections are expected to be quite important in view of the atomic size of the WS spheres, so it is preferable to treat the factor σ_0 as an adjustable parameter in the subsequent calculations.

With $\epsilon_b(r_s)$ and $\epsilon_s(r_s)$ given by formulae (10)–(16), the electronic energy per ion finally reads

$$\frac{U_{el}^*}{N} = \frac{1}{(2-x)}\epsilon_b(r_s) + \frac{(1-x)}{(2-x)}\epsilon_s(r_s). \tag{17}$$

3. Concentration dependence of the excess molar volume

The molar volume V_m at constant pressure P is calculated for each concentration x by solving the equation

$$\frac{d(U^*/N)}{dR_s} = -8\pi R_s^2 P^* \tag{18}$$

where $R_s = x^{1/3}r_s$, $P^* = Pa_B^4/e^2$ is the imposed pressure in atomic units and U^*/N is the total energy per ion in Rydbergs, as calculated along the lines laid out in the previous section. From the value of R_s which solves (18), the molar volume V_m may be calculated according to

$$V_m = N_{Av}(2 - x)4\pi a^3/3 = 0.3733(2 - x)R_s^3 \text{ cm}^3. \tag{19}$$

In the limiting case $x = 0$ (pure salt), the electronic contribution vanishes and with the Born repulsion parameters appropriate for KCl a molar volume $V_m(x = 0)$ of 39 cm^3 is found at zero pressure ($P^* = 0$ in (18)). This lies about 10 cm^3 below the experimental value at $T = 1123$ K [6].

This discrepancy should not be surprising, since the present lattice theory amounts to a zero-temperature calculation. The difference between theory and experiment can hence be traced back to thermal expansion and to the volume change on melting, which is particularly large in KCl, nearly 20%.

In the pure metal limit, the calculated molar volume depends sensitively on the pseudopotential radius r_c. The standard value for r_c is determined from conductivity measurements at melting (i.e. close to room temperature) and is equal to 2.23 in atomic units. This value for r_c leads to a molar volume at zero pressure of about 41 cm^3, which lies roughly 20 cm^3 below the experimental values [6]. However, there is no compelling reason for which the phenomenological value of r_c should be the same at room temperature and at $T = 1123$ K. Hence, we have rescaled r_c in order to achieve a molar volume of the pure metal which lies about 10 cm^3 below the experimental value, as was also the case for the pure salt. For the pure metal a molar volume V_m of 49 cm^3 is obtained by using $r_c = 2.4$ atomic units. This value for r_c was kept throughout our calculations.

For intermediate concentrations ($0 < x < 1$), the surface energy σ of the electron gas turns out to play a crucial role. If this term is neglected in the electronic contribution to the energy (see (9)), the excess molar volume

$$\Delta V_m(P^*, x) = V_m(P^*, x) - x V_m(P^*, x = 1) - (1 - x)V_m(P^*, x = 0) \tag{20}$$

turns out to be invariably negative as shown in figure 2. This situation, which contradicts the experimental findings [6], is reminiscent of the result obtained from linear screening theory [5]. However, the absolute values of the excess molar volume are considerably smaller than in the latter case and this points, hence, to an improvement due to the approximate inclusion of non-linear screening effects within the present model.

Using (15) and (16), the surface energy per electron in Rydbergs reads

$$\epsilon_s(r_s) = s_0 \frac{x^{2/3}}{r_s^{3/4}} \tag{21}$$

where $s_0 \simeq 0.132$, for a planar surface. However, as pointed out earlier, this value is irrelevant in view of the strong curvature of the WS spheres. We make the assumption that the functional form of $\epsilon_s(r_s)$ remains the same for a curved interface, but that curvature renormalizes the prefactor s_0. Since the radius of the WS sphere changes only slightly in going from the pure metal ($x = 1$) to the pure salt ($x = 0$), a constant value of s_0 is
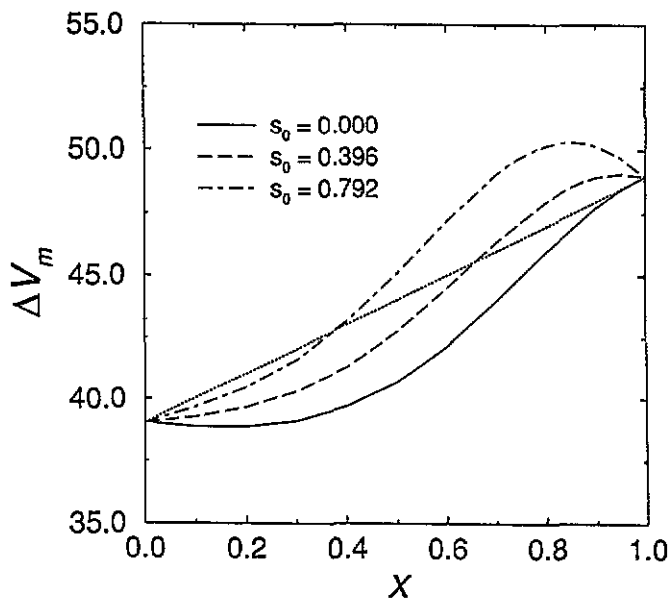
Figure 2. Molar volume V_m (in cm^3) versus metal concentration x, calculated with different values for the surface energy scale factor s_0 in (21): $s_0 = 0$ (full curve), 0.396 (dashed curve) and 0.792 Ryd (dashed-dotted curve).

assumed. Molar volumes calculated with two different values of s_0 (equal to three and six times the planar surface value) are compared in figure 2 with the predictions of the theory when $s_0 = 0$. It shows that ΔV_m becomes increasingly positive, at least on the metal-rich side, as s_0 increases. When $s_0 = 0.792$, ΔV_m is positive over most of the concentration range in qualitative agreement with experiment.

The influence of the pressure on the molar volume may be expected to be strongly underestimated in our zero-temperature model, which should be much less compressible than the melt above 10^3 K. Indeed we found that, in order to reproduce the experimentally observed variations of the molar volume with pressure [6], the experimental pressures had to be multiplied by roughly a factor of 5. The x-dependence of the resulting molar volume, calculated with $s_0 = 0.792$, is plotted in figure 3 for $P = 0$, 4000 and 8000 bar.

4. Discussion

The present simple lattice model for metal–salt solution has been designed to account in a highly phenomenological way for non-linear screening of the ionic Coulomb interactions by valence electrons. Once the interaction parameters have been fixed to ensure reasonable molar volumes of the pure phases (bearing in mind that this is a zero-temperature calculation), the only adjustable parameter is the scale of the surface energy of the electron gas (jellium). It is shown that positive excess molar volumes over most or all of the concentration range are obtained for reasonable values of the surface energy. However, the agreement with experimental molar volume data can only be regarded as, at best, qualitative. These data indicate vanishing excess molar volumes ΔV_m in the vicinity of the pure phases ($x \simeq 1$ and $x \simeq 0$), whereas the present calculation predicts a rapid increase of ΔV_m as x departs from 1. On the salt-rich side, the model leads to small negative values of ΔV_m, other than for sufficiently large surface energy scales which strongly exaggerate the absolute
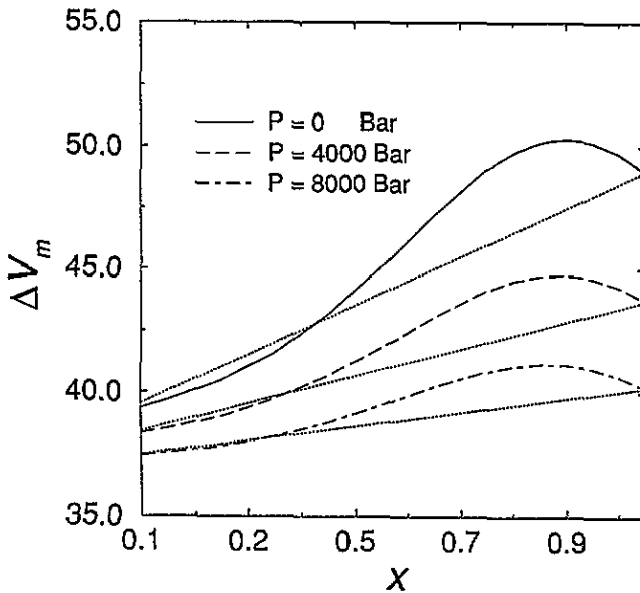
Figure 3. Molar volume V_m (in cm³) versus metal concentration x, for $P = 0$ (upper curve), 4000 (middle curve) and 8000 bar (lower curve).

values of ΔV_m. It is interesting to note that a cross-over from positive to negative molar volumes on the salt-rich side was in fact reported in preliminary measurements [10]. This was not confirmed by subsequent experiments of the same authors [6], although their error bars (roughly $\Delta V_m/V_m \simeq 1\%$) do not completely rule out such a behaviour. It should also be noted that with the choice of $s_0 = 0.792$ Ryd for the scale factor of the surface energy, the maximum excess molar volume is about 3 cm³, which is roughly a factor two larger than the experimental values. This is probably again a consequence of the zero-temperature nature of the calculation.

The present model could be refined in many ways. Thermal expansion effects could be included, at least at a mean field level. Polarization of the electron density inside the cation WS spheres could be described within a simple density functional formulation. More importantly, a more accurate treatment of the surface energy, beyond the rescaled *ansatz* in (21), would be desirable, since the molar volume is very sensitive to this energy. Finally localized electron states, like F centres, could also be accommodated in the present model by introducing a third category of WS cells containing no ion. However, such refinements would necessarily spoil the simplicity of the present calculation, which already leads to the desired qualitative result, namely a positive excess volume of the right magnitude in contrast to a linear screening description.

Acknowledgments

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