STRUCTURE AND THERMODYNAMICS OF METAL-SALT SOLUTIONS:
THE THEORETICAL VIEWPOINT

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ABSTRACT

The structure and thermodynamics of solutions of alkali metals and their halides are calculated on the basis of a simple two-fluid (ion-electron) reference system and a second order perturbation expansion in the ion-electron coupling. The miscibility gap observed in these solutions is reproduced theoretically and explained in terms of screening lengths and correlation lengths, for which we obtain explicit expressions.

I. THE MODEL

The metal-salt solutions are regarded as being composed of \(N_1\) positive ions of charge \(Z_1e\) and \(N_2\) negative ions of charge \(Z_2e\) in a volume \(\Omega\); the corresponding number densities and concentrations are defined as \(\rho_\alpha = N_\alpha / \Omega\) and \(x = N_\alpha / N(\alpha=1,2)\), with \(N = N_1 + N_2\). The excess of positive charge is compensated by the conduction electrons which are assumed to provide a rigid, uniform background of charge \(e\rho_0\), ensuring overall charge neutrality:

\[
\rho_1 Z_1 + \rho_2 Z_2 + \rho_0 = \bar{\rho} Z + \rho_0 = 0 \quad \text{(1)}
\]

The total hamiltonian of the system is written as the sum of three terms (1):

\[
H = H_{ii} + H_{ee} + V_{ie} \quad \text{(2)}
\]

where \(H_{ii}\) is the hamiltonian for the ions in a neutralizing uniform background, \(H_{ee}\) is the familiar jellium hamiltonian for the electrons in a uniform background which exactly cancels the previous one, while \(V_{ie}\) describes the ion-electron interaction minus the interaction energy of the ions with their associated background.

I.1 THE IONIC HAMILTONIAN

The ions are assumed to interact pairwise via the simple model potential:

\[
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\]
\[ U_{\alpha\beta}(r) = Z_\alpha Z_\beta e^z/r + V_0(r) \]  \[ 3 \]

where the short range repulsion \( V(r) \) acts only between oppositely charged ions, and is taken to be of exponential form:

\[ V_0(r) = (\lambda - \delta_{\alpha\beta}) \alpha \exp \left\{ -r/r_0 \right\} \]  \[ 4 \]

The potential \[ 3 \] is a simplified version of the usual Born-Huggins-Mayer potential. For the parameters \( \lambda \) and \( r_0 \), we have chosen the values of the complete Tosi-Fumi potential corresponding to the pure molten salt \[ 3 \].

The ion-ion Hamiltonian hence finally reads:

\[ H_{ij} = K_i + \frac{1}{2\Omega} \sum_{\alpha\beta} \frac{4\pi e^2}{\varepsilon^2} \left[ \rho^*_\alpha \left( \rho^*_\beta - N \right) \right] + \frac{1}{\Omega} \sum_{i=1}^{N_\alpha} \sum_{j=1}^{N_\beta} V_0(|\vec{r}_i - \vec{r}_j|) \]  \[ 5 \]

where \( K_i \) represents the kinetic energy of the ions and \( \rho^*_\alpha \) denotes the Fourier component of the ionic charge density. The corresponding ionic pair correlation functions \( g_{\alpha\beta}(r) \) and their Fourier transforms transform the ionic structure factors \( S_{\alpha\beta}(K) \) have been calculated in the framework of the hypernetted chain equations (HNC), supplemented by the Ornstein-Zernicke relations between the direct correlation functions \( C_{\alpha\beta}(r) \) and the total correlation functions \( h_{\alpha\beta}(r) = g_{\alpha\beta}(r) - 1 \):  \[ 6a \]

\[ \left\{ \begin{array}{l} g_{\alpha\beta}(r) = \exp \left\{ -\beta U_{\alpha\beta}(r) + \frac{1}{\beta} \frac{d}{dr} C_{\alpha\beta}(r) \right\} \quad \text{HNC} \\
    \frac{d}{dr} C_{\alpha\beta}(r) = C_{\alpha\beta}(r) + \frac{2}{\beta} \int_{-\infty}^\infty \int_{-\infty}^\infty \left[ C_{\alpha\beta}(r') C_{\alpha\beta}(r - r') \right] dr' \quad \text{OZ} \end{array} \right. \]  \[ 6b \]

Figure 1 compares the structure factors issued from the model Hamiltonian \[ 5 \] with the experimental results obtained by neutron diffraction for K-KCl and Rb-RbBr(8). The poorer agreement for Rb-RbBr is the consequence of the higher polarisability of this system, not included in our model.
I.2. THE ION–ELECTRON INTERACTION

The term $V_{ie}$ of eqn. [2] can be split in two terms:

$$V_{ie} = -\frac{1}{\Omega} \sum_{\alpha=1}^{2} \sum_{K \neq 0} \hat{V}_{\alpha}(K) \rho_{\alpha}^{*} \rho_{\alpha} + U_0$$  \hspace{1cm}[7]

where $\hat{V}_{\alpha}(K)$ is the dimensionless Fourier transform of the ion-electron pseudopotential $V_{\alpha}(r)$, and $U_0$ is the structure independent contribution (1,4):

$$U_0 = -\frac{1}{\Omega} \sum_{\alpha=1}^{2} \lim_{K \to 0} \left[ \hat{V}_{\alpha}(K) + \frac{4\pi Z_{\alpha} e^2}{K^2} \right] \rho_{\alpha}^{*} \rho_{\alpha} = \frac{2}{\Omega} \sum_{\alpha=1}^{2} N_{\alpha} \int_{0}^{\infty} \left[ V_{\alpha}(r) + \frac{Z_{\alpha} e^2}{r} \right] r^2 dr$$  \hspace{1cm}[8]

The hamiltonian specified by eqns. [2], [5], [7] is in fact quite general and describes a number of coulombic systems besides metal-salt solutions $M_{x}MX_{1-x}$: liquid metals (limit $x=1$), molten salts (limit $x=0$), binary alloys (for which $Z_{1},Z_{2}>0$), and binary ionic mixtures, in which the short range repulsive term may be omitted, the electron-ion interaction being purely coulombic.

For the ion-electron pseudo-potentials occurring in eqns. [7], [8], we have chosen the Ashcroft empty core form [7] for the cation, with a core diameter determined at the melting point of the pure metal, using the sum rule for the compressibility (5). The anion-electron pseudo-potential has been chosen to be an interpolation between the Ashcroft and Shaw (6) forms (7):

$$V_{\alpha}(r) = -\frac{\xi Z_{\alpha} e^2}{r_{c_{\alpha}}} \quad ; \quad r < r_{c_{\alpha}}$$  \hspace{1cm}[9]

$$= -\frac{Z_{\alpha} e^2}{r} \quad ; \quad r > r_{c_{\alpha}}$$

For $r_{c_{2}}$ we have chosen, somewhat arbitrarily, the ionic Pauling radius. $\xi$ will be the only adjustable parameter in our perturbation theory. The coordinates of the critical point which terminates the miscibility gap will depend sensitively on $\xi$, as we will see later. Let us note that the special case $\xi=0$ corresponds to the empty core.
I.3 THE ELECTRON GAS

The thermodynamic properties of the uniform electron gas depend on the usual density parameter $r_s$ and the degeneracy parameter $\zeta$ defined by:

$$r_s = \left(\frac{3}{4\pi n_0}\right)^{1/3}; \quad \zeta = \frac{kT}{kT_F}$$

where $a_B$ is the Bohr radius and $kT_F = e^2 \varepsilon_0^{1/3}$ is the Fermi temperature. In the Metal-salt solutions, as the metallic mole fraction decreases, the density parameter $r_s$ increases ($r_s = \infty$ in the pure salt!) while the Fermi temperature decreases. As a consequence, the electron gas becomes more and more correlated while finite temperature corrections become non-negligible. To describe this weakly degenerate electron gas, we have used the most accurate equation of state presently available, calculated in a wide range of densities (10).

II. THERMODYNAMICS

The thermodynamic properties of the metal-salt solutions described by the hamiltonian [2] are calculated by a perturbation expansion in the ion-electron coupling $V_{ie}$. In the zeroth order the electronic and ionic components, neutralized by their respective uniform backgrounds, are assumed to be completely decoupled so that the Helmholtz free energy of this reference system is given by:

$$F^{(0)} = F_i + F_e$$

The ionic contribution is calculated from classical statistical mechanics, using the pair distribution functions obtained in §I(4). An interesting property of the HNC closure, beside the fact that it is especially adapted to coulombic systems, is that it allows a direct calculation of the excess chemical potentials $\mu_i$, from the partial pair correlation functions [9]. Hence the excesses (i.e. non ideal) free enthalpy per ion follows directly from:

$$\frac{G_i^{ex}}{NkT} = \sum_{\alpha=1}^{Z} x_\alpha \mu_\alpha^{ex}$$

The further contributions to the free energy are calculated using the standard coupling constant integration:
\[ F = F(\lambda = 1) = F(\lambda = 0) + \int_0^1 \langle \mathcal{V}_{ie} \rangle_\lambda d\lambda \]  \hspace{1cm} \text{(13)}

where \( F(\lambda = 0) = F_i + F_c \) is the free energy of the reference system, whereas \( \langle \cdot \rangle_\lambda \) denotes the canonical average taken over the perturbated Hamiltonian. To first order in the coupling, the free energy is:

\[ F^{(1)} = F_i + F_e + \langle \mathcal{V}_{ie} \rangle_0 \]  \hspace{1cm} \text{(14)}

with

\[ \langle \mathcal{V}_{ie} \rangle_0 = \frac{3e^2}{2a^3} \bar{Z} \left[ N_1 Z_1 r_{1e}^2 + N_2 Z_2 r_{2e}^2 \left( 1 - \frac{2}{3} \xi \right) \right] \]  \hspace{1cm} \text{(15)}

The second order ion-electron contribution is calculated in the linear response approximation for the induced electron density \( \rho_{ie0} \), which yields:

\[ F_2 = \frac{1}{2} \sum_x \sum_{\beta} (N_x N_\beta)^{1/2} \left[ \frac{4}{(2\pi)^3} \int \frac{k^2}{4\pi^2} \bar{v}_{\alpha e}(k) \bar{v}_{\beta e}(k) S_{\alpha \beta}(0) d^3 k \right] \]  \hspace{1cm} \text{(16)}

the \( S_{\alpha \beta}(k) \) denote the partial structure factors of the unperturbed ionic fluid calculated in §I. For the dielectric function \( \varepsilon_0(k) \) we have chosen the zero-temperature form proposed by Ichimaru and Utsumi (11), which is well adapted to the highly correlated regime \( (r_s >> 1) \).

By truncating the perturbation expansion of the free energy after the second order, we restrict ourselves to linear screening in the description of the ion-electron coupling. This is a priori inapplicable in the regime of low metallic concentrations. However, since the weight of the electronic contribution to the thermodynamics of a metal-salt solution decreases with decreasing metal concentration \( x \), we have used the results of second order perturbation theory throughout the entire range of concentration.

In that case the total free energy finally reads:

\[ F^{(2)} = F_i + F_e + U_o + F_2 \]  \hspace{1cm} \text{(17)}

All other thermodynamic properties of the system can be derived from the free energy expression (17), by taking the appropriate derivatives with respect to the thermodynamic variables \( \Omega, T \) and \( x \). The excess Gibbs free energy of mixing is defined in the usual way as
\[ \Delta G_m(P,T,x) = G_m(P,T,x) - x G_m(P,T,x=1) - (1-x) G_m(P,T,x=0) \]  

where \( G_m(T,P,x) = F_m - \left( \frac{\partial F_m}{\partial x} \right) \). \( \Omega \) is the molar free energy of the mixture at the concentration \( x \). In practice, for fixed values of \( T \) and \( x \), the molar volume \( \Omega \) is varied to yield a prescribed value of the total pressure \( P \). All the results presented here are for \( P=0 \). The molar volumes at zero pressure calculated from the second order perturbation theory are listed in tables for several values of the concentration, together with the various contributions to the equation of state, for the system \( K_xKCl_{1-x} \) with \( \xi=0 \).

| x  | \( \Omega \) / cm\(^3\)mol\(^{-1}\) | \( r_3 \) | \( \beta P_1 / \rho \) | \( \beta P_2 / \rho \) | \( \beta P_1^{(2)} / \rho \) | \( \beta P_2^{(2)} / \rho \) |
|----|---------------------------------|---------|----------------|----------------|----------------|----------------|
| 1  | 37.045                          | 4.627   | -14.608        | -0.920         | 19.665         | -4.135         |
| 0.8| 35.186                          | 4.790   | -5.385         | -0.796         | 10.734         | -4.550         |
| 0.6| 32.072                          | 5.229   | -0.869         | -0.756         | 4.437          | -3.807         |
| 0.4| 39.275                          | 6.404   | 0.437          | -0.633         | 0.850          | -1.786         |
| 0.2| 53.203                          | 8.928   | 0.895          | -0.304         | -0.135         | -0.445         |
| 0.1| 62.767                          | 12.028  | 0.361          | -0.122         | -0.133         | -0.107         |
| 0  | 78.901                          |         | 0              | 0              | 0              | 0              |

TABLE 1

Molar Volumes and Various Contributions to the EOS at Zero Pressure for \( K_xKCl_{1-x} \) with \( \xi=0 \), at \( T=1250 K \). \( r_3 \) is Defined by Eqn. [10]. The Subscripts and Superscripts i.e. (1), (2) Denote Respectively Ions, Electrons, First and Second Order.

For the pure metal, the calculated molar volume is very sensitive to the second order term in pressure, due to the fact that the zeroth and first order contributions are of opposite signs. The calculated molar volume (which is independent of \( \xi \) at \( x=1 \)) is considerably smaller than the experimental value (68 cm /mole at \( T=1250 K \)). This defect may be attributed to a poor convergence of the perturbation series for the pressure in the high temperature range of expanded liquid metals (11).

For the pure salt, the calculated molar volume is larger than its experimental value for KCl(51.20cm /mole at \( T=1250 K \)). But we have checked that this discrepancy is essentially due to our neglect of Van der Waals interactions in the ionic potential model of eqns. [3]-[4].

The excess molar volume of mixing \( \Delta \Omega_m \) is defined as:
The most striking result of our calculation is its prediction of a large negative excess volume at intermediate concentrations, as shown on figure 2. Although the large absolute values of these excess volumes may be attributed to the crudeness of our model (especially the density independence of the pseudopotentials), we believe the sign of the excess volume is real. This is to be checked by experiments. Let us note too that the results are sensitive to the value assumed for \( \xi \).

III. MISCELLIBILITY GAP - CRITICAL BEHAVIOR

The various contributions to \( \Delta G \) are plotted in figure 3 as a function of the molar fraction \( x \) for a typical state of K,KCL. To zeroth order, when \( \Delta G \) is just the sum of independent ionic and electronic contributions, \( \Delta G \) is a convex function of \( x \) so that the solution would be thermodynamically unstable at all concentrations. But when the first and second order corrections due to the electron-ion coupling are added, \( \Delta G \) becomes concave, signaling that the solution is going to stabilize. This behaviour contrasts with the case of binary ionic mixtures (BIM) or metallic alloys where the ionic contribution always tends to stabilize the mixture (12,13).

As figure 4 shows for one value of \( \xi \), as \( \xi \) takes nonzero values, \( \Delta G \) builds up a convex portion on the salt-rich side, signaling phase separation. The concentrations of the coexisting liquid phases are determined by the usual double tangent construction. The critical coordinates, \( T_c \) and \( x_c \), are sensitive to \( \xi \) and are compared to the experimental values in the case of K,KCL in table 2. While the calculated critical temperature can be brought into agreement by an adequate choice of \( \xi \), the corresponding critical concentration \( x_c \) is too small. This is probably a consequence of the inadequacy of linear screening theory (and hence pseudo-potential approach) on the salt rich side of the phase diagram.

Figure 5 shows the results we get for K-KCl and Rb-RbBr for different values of \( \xi \).

| \( \xi \) | 0.01 | 0.05 | 0.2 | 0.333 | Experiment (15) |
|---|---|---|---|---|---|
| \( T_c/K \) | 1250 | 1650 | 2300 | 2500 | 1073 |
| \( x_c \) | 0.25 | 0.25 | 0.35 | 0.40 | 0.35 |

Table 2

Critical Coordinates for \( K_xKCl_{1-x} \) Calculated for Several Values of \( \xi \).
The demixing phenomena can be explained in terms of screening lengths. The metal-salt solutions are characterized by a competition between a Debye-Hückel type screening between the ions and a Thomas-Fermi type screening due to the rearrangement of the electronic background around each charge. These two different kinds of screening are characterized by two screening lengths or, equivalently, two dielectric functions. The electronic screening length is:

\[ \lambda_e^2 = \frac{1}{4\pi e^2} \left( \frac{\partial \nu_0}{\partial \rho_0} + \frac{\partial \nu_{\text{ie}}}{\partial \rho_2} \right) = \frac{1}{\kappa^2} \lim_{K \to 0} \varepsilon_e(K)^{-1} \]  

[20]

where \( \nu_0 \) is the chemical potential of the continuous electron gas, whereas \( \nu_{\text{ie}} = \frac{\partial (\xi^4/\alpha)}{\partial \rho_0} \) denotes the bound electrons contribution to the total electrochemical potential. Using the Nozieres-Pines (14) approximation for the correlation energy of an electron fluid at zero temperature, we obtain the following analytical expression for \( \lambda_e^2 \):

\[ \lambda_e^2 = \frac{Z_2 M_1 r_s^2 - Z_2 M_2 r_s^2}{M_4 Z_2 - M_2 Z_4} + \left( 0.409 r_s - 0.068 r_s^2 - 0.0017 r_s^3 \right) r_s^2 \]  

[21]

where \( r_s = r \left( 1 - \frac{\alpha}{2} \right)^{1/2} \) is the modified radius of the pseudopotential [8]. The term \( 0.409 r_s^2 \) is the Thomas-Fermi screening length squared, which becomes exact in the limit of weak coupling for the electron gas \( (r_s \to 0) \). The first term of eqn [21] exposes the electrostrictive behavior in the response of the system, because of the finite size of the ions in the ion-electron interaction. Let us note that in the metal-salt solutions, because of the strong variation of \( r_s \) along the phase diagram, \( \lambda_e^2 \) decreases quickly from metallic values to zero. This phenomenon is usually associated with the appearance of a local order (15). The screening length loses its significance in such situations. This is really different for BIM or binary alloys where the electronic screening length is always larger than the ionic one so that the screening effect is dominated by the ions.

For the ions the ionic screening length \( \lambda_i^2 \) can be related to the ionic correlation length, \( \lambda_c^2 \) through the equation:

\[ \lambda_i^2 = \frac{\chi_0}{\chi_i} \beta \frac{\partial^2 \delta_i}{\partial \mu_i^2} \left|_{\mu_i = \mu_p} \right. \lambda_c^2 = \frac{1}{\kappa^2} \lim_{K \to 0} \varepsilon_i(K)^{-1} \]  

[22]
Here $\chi_i$ and $\sigma_i$ denote respectively, the compressibility and the free enthalpy density for the ions whereas $\chi_0=\beta/\rho$ designs the compressibility of the perfect gas. $\lambda_c$ can be shown to be equal to:

$$
\lambda_c = \frac{S_{cc}(0)}{4\p\beta^2 Z^2} = \left\{ \frac{4\p\beta^2 Z^2}{\beta \frac{\partial^2}{\partial x_i^2} T_p} + \frac{\chi_0}{\chi_i} \delta^2 \right\}
$$

[23]

where $S_{cc}(0)$ is the concentration-concentration structure factor at zero wave-vector which diverges at the critical point and $\delta'$ is the expansion coefficient ($\delta' = 1/\rho(\partial \rho/\partial x_1)_{p,T}$).

VI. CONCLUSION

We have shown that our really simple model reproduces qualitatively and at least semiquantitatively the structure and the miscibility gap observed in metal-salt solutions. Moreover, we have characterized this phenomenon through two screening lengths, typical of two different screening phenomena, and a correlation length, of which the scalar value let us expect that the demixing critical behaviour of metal-salt solutions is probably Ising like.

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Comparison Between the Structure Factors Obtained from Neutron Diffraction (θ) (dots) and from the Model Hamiltonian [3].
Figure 2 - Relative Excess Molar Volume versus x for a K_{x}KCl_{1-x} Mixture at Zero Pressure.

Figure 3 - Various Contributions to the Molar Gibbs Versus Molar Fraction x, Full Curve: Ionic Contribution; Dashes: Ionic and Electronic Contributions; Long Dashes: First Order Perturbation Theory; Dash-dotted Curve: Second Order Perturbation Theory.
Figure 4 - Molar Gibbs Excess Free Energy Versus Molar Fraction X for a $K_x KCl_{1-x}$ Mixture, for a Non-Zero Value of $\xi$.

Figure 5 - Phase Diagrams of $K_x KCl_{1-x}$ and $Rb_x RbBr_{1-x}$ for three different values of $\xi$. 

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