ADDITION OF MOLTEN SALT IN MOLTEN METAL. STRUCTURE AND DYNAMICS

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Abstract

A partial structure factor analysis (based on the chlorine isotopic substitution method in neutron scattering experiments) of the solutions K\textsubscript{x}(KCl)\textsubscript{1-x} with x = 0.8 and 0.6 shows how strongly the hot liquid metal can be structured by the introduction of salt. The measurement of the structure factor of pure liquid potassium up to 700°C is used in the discussion. Extended sound modes measured in the metallic regime were similar to the ones observed in pure metal. With the addition of salt, strong damping effects are observed and related to the structuring effect created by the salt.

The addition of salt in a liquid alkali metal generates, over a concentration range which depends on the metal, a non-stability domain (miscibility gap) together with a strong scattering regime for conduction. Near the pure salt limit of the phase diagram, the short range order is related to full ionic bonding, the excess electron becoming localized or solvated because of fluctuations of the Coulombic potential assisted by local structure rearrangements (1) (2). On the metal rich side, although thermodynamics (3) predict a significant restructuring of the hot liquid metal by the halogen ions, analysis of conductivity or excess magnetic susceptibility data (4) indicated nearly free electron behaviour down to a very large fraction of salt (x ≈ 0.5).

Theoretical models based on a single electron screening theory (5) can reproduce the stability conditions and take into account the screening length with a continuous fluid of electrons interacting with finite sized ions. They do not consider the restructuring of the metal atoms by the halogen ions, so that the dielectric behaviour cannot be well represented.
In this paper we want to demonstrate how the restructuring of the metal atoms by negative ions can be described as a local structure with short range order and additional strong interactions leading to medium range order. If these structural effects exist in the system, then the dynamics should be strongly affected. The existence of collective excitations in liquids, as a result of the solid state collective modes, is now well established (6) (7). In charged liquids, the appropriate dynamical variables (linked to mass and charge fluctuations) must vary in some wavenumber ranges related to the interactions existing in the system. It is therefore interesting to measure the collective modes because they point to wavenumber and energy domains where collisional processes can be involved and influence the transport properties. This could, in our case, help indirectly to specify the behaviour of the electron.

After a detailed description of the microscopic structure of the metal-molten salt solutions in the metal rich and strong scattering regime, we shall present below an analysis of the effect of salt addition on the low energy excitations connected to the density response function of liquid alkali metals.

I. Structural modifications induced in hot alkali metal by addition of salt

The structural information were obtained from neutron scattering measurements. We shall not describe here the analysis of the data, which will be presented in a specialized paper (8). We only point out the extreme difficulty in measuring low scatterers like potassium. Moreover, at high temperature, the weakness of the interference signal makes it even more difficult to separate it from the diffusion of the sample environment (furnace, container) or from contributions due to small amounts of impurities such as hydrogen. The measurement of the temperature dependence of the structure factor of liquid potassium allowed us, owing to the relative simplicity of its analysis, to crosscheck the validity of our data treatment. It also provides useful information for the discussion of the metal partial structure factor in the metal-molten salt mixture.

a) The pure metal structure

The structure factor of liquid K is known, not too far from the melting point (9). We have measured its temperature dependence, which is related to the density variation and to the number fluctuations at the \( Q = 0 \) limit (\( Q = (4\pi/\lambda) \sin \Theta \), where \( \lambda \) is the neutron wavelength and \( 2\Theta \) is the scattering angle). Comparison between experimental data and recent theoretical calculation is excellent (10). The calculation of the structure factor \( S(Q) \) at a given density is made with an effective potential and a self-consistent integral equation (HMSA). This gives better results than the OCP model. The data are presented in figure 1.
b) Structure of the solutions in the metallic conduction regime

\[ \sigma > 5 \times 10^{-3} \ \Omega^{-1} \ cm^{-1} \]

The determination of the microscopic structure allows us to obtain the local and the medium range order. Neutron scattering, using isotopic substitution, is the only technique able to give this type of information on a large momentum transfer range with possible extrapolation to the thermodynamic limit \( (Q \to 0) \). Recent improvements of the high flux reactor instruments (ILL Grenoble) have been described (11). They permit us to analyse the structure, i.e. one of the most difficult binary mixtures studied up to now. Figures 2a and 2b give the three total structure factors obtained by varying the chlorine isotopic composition at a fixed salt concentration. The low statistical accuracy obtained with the \(^{37}\)Cl sample comes from a corresponding relatively low counting time. These structure factors are typical of \( \text{K}_x(\text{KCl})_{1-x} \) mixtures. The curves are more or less structured according to the scattering length of the chlorine isotope as compared to that of the alkali metal. The large diffusion at low momentum transfer is due to fluctuations existing in the vicinity of the phase separation region.

In figures 3a and 3b, we give the partial structure factors extracted from the resolution of the linear system of equations formed by the above total structure factors. These partial structure factors are worth a few comments.

For the composition \( \text{K}_0.8(\text{KCl})_{0.2} \), the potassium partial structure factor is not very different from that of the pure metal given for comparison, except at low momentum transfer. There is a correlation between the potassium and the chlorine partials, which have similar peak positions but different peak intensities. The ClK partial exhibits the enhanced stability of the unlike atom interaction at a momentum transfer value slightly smaller than in the case of pure molten salt \( \text{K}_N \). Medium range order effects are apparent in all partials at low momentum transfer. This produces a hump at about 1 Å⁻¹ in the ClK partial.

The partial structure factors were also obtained for a higher addition of salt into the metal, \( \text{K}_0.6(\text{KCl})_{0.4} \). The temperature was kept equivalent for the two concentrations \( ((T_{\text{exp}} - T_{\text{m.p}})/T_{\text{m.p}} = 1.1) \). We see very significant differences between the partials at 80% and 60% metal concentration: enhancement of structure of the partials at large Q values, symmetric pattern for the like-ion partials, strong structuring of the KK partial at large Q, accompanied by a significant decrease of the first peak intensity. At Q values around 1 Å⁻¹ a strong hump is now obtained in the ClK partial but we shall not comment on it. The low Q part of this diagram is still investigated for possible systematic errors. At large Q values, we have not yet quantified with accuracy the nearest neighbour coordination number between unlike ions,
corresponding to the characteristic wavenumber $k_n$; nevertheless a rough analysis gives a value of 4. This fourfold coordination seems favourable in monovalent ionic systems in which Coulombic forces are involved (2). A model for electron localization with the assistance of neighbouring $K^+$ ion relaxation gives a coordination of four (1). In compounds where a partial covalent contribution to the binding exists, a low coordination is favoured (2), which could in turn favour a high cationic mobility. Further work is being done in order to prove if small additions (< 10%) of molten salt into a hot alkali metal could stabilize the fourfold coordination at the same time as the metallic interaction between $K$ atoms decreases. Of course, such a structural effect in a metallic liquid must influence its dynamics, in particular, the collective particle motions.

II. Preliminaries on the dynamics of a hot alkali liquid perturbed by dissolution of salt

Neutron scattering experiments allow us to measure the coherent dynamic structure factor $S_{\text{coh}}(Q, \omega)$ related to collective particle motions in the system. The description of collective fluctuations in a liquid is well analysed by the linearized hydrodynamics as long as the wavelength of the fluctuation is much greater than the atomic size. This is the case for light scattering experiments where we can investigate heat and sound modes. For neutron scattering the wavelength of the radiation becomes of the order of the interatomic distances and the concept of extended modes is introduced (15). Neutron scattering experiments on molten Rb at temperatures slightly above the melting point, show the existence of such extended sound modes for $Q$ values up to $Q \approx 1$ ($a$, being the mean free path between collisions). The data are well represented by three Lorentzian lines corresponding to Rayleigh and Brillouin scattering or heat and sound modes, respectively. In figure 4, the sound mode of liquid rubidium shows a maximum at a $Q$ value corresponding to half of that of the maximum in the structure factor (16). In ionic liquids, it has been proven useful to introduce the mass density and charge density fluctuation variables (2). $S_{\text{MW}}(Q, \omega)$ is, at low $Q$ and $\omega$, isomorphous to the hydrodynamic structure factor of a monatomic liquid.

We also present in figure 4 some experimental results on a solution of Rb$_{0.9}$(RbCl)$_{0.1}$, which is, in first approximation, of purely metallic character, and on Rb$_{0.8}$(RbBr)$_{0.2}$ sample, which should have the same structural properties as K$_{0.8}$ (KCl)$_{0.2}$. Details on the experiment and its analysis are published separately (17).

The dispersion of the mass density as a function of momentum transfer given in figure 4 for the M-MX solutions is obtained from the side peak positions in the inelastic scattering spectra measured on a triple axis spectrometer. The positions obtained on the energy loss and on the energy gain side are represented
separately. In the hydrodynamics regime, these positions at ± ω_0 are related to the adiabatic sound velocity. Therefore the knowledge of the pure metal sound velocity allows us to draw the hydrodynamic regime limit in the case of the strongly metallic concentration.

No significant difference is detected in the dispersion law of Rb_0.9(RbCl)_0.1 as compared to pure Rb. This confirms the assumption that at this concentration, we remain in the metallic regime. And the sound velocity should not vary much from the pure metal one. At higher dilution of the metal, the results are not equivalent. Although the weakening of the signal renders the data analysis extremely difficult, some trends seem to be observed. A gap seems to occur at 1 Å⁻¹. A similar one is observed in argon (7). This might come from the coupling between collective acoustic motion and the structure of the liquid shown in the partial structure factors. Also interesting is the extrapolation to the hydrodynamic regime. From the shape of the dispersion law, one wonders if the isothermal sound velocity of this mixture does not become anomalous.

Further studies should be made on the damping of the collective modes which might turn out to be of general importance for the ionic and electrolytic liquids. Indeed, in a study of collective excitations in electrolytic glasses at very low water content, we detected (18) low frequency harmonic modes (up to 4 meV), in addition to the sound modes, and a damping of these modes occurs at the glass transition. The structured picture of the M-MX solutions in the strong scattering regime and its effect on collective motions are beginning to be deciphered.
REFERENCES

(1) G. Senatore, M. Parinello, M.P. Tosi, Phil. Mag. (1980) B41, 595
(2) M. Rovere, M.P. Tosi, Rep. Progr. Phys. (1986) 49, 1001
(3) H. Yokohama, O.J. Kleppa, J. Chem. Phys. (1982) 76, 5574
(4) N. Nicoloso, W. Freyland, Z. Phys. Chem. (1983) 135, 39
(5) G. Chabrier, J. Phys. C (1987) 20, 357
(6) J.R.D. Copley, J.M. Rove, Phys. Rev. Lett. (1973) 32, 49
(7) I.M. de Schepper, P. Verkerk, A.A. van Well, L.A. de Graaf, Phys. Rev. Lett. (1983) 50, 974
(8) J.F. Jal, P. Chieux, J. Dupuy, to be published
(9) M.B. Huijben, W. van der Lugt, Act. Cryst. (1975) A35, 431
(10) J.F. Jal, G. Kahl, P. Chieux, J. Dupuy, J.P. Hansen, to be published
(11) J. Dupuy, J.F. Jal, A. Aouizerat-Elarby, P. Chieux Trends in Physics (Ed. Javta, J. Pantoflietch) (Prague Europ. Phys. Soc., p. 394)
(12) M.A. Bredig (1964) in Molten Salt Chemistry, Ed. M. Blander, N.Y., Interscience, p. 367
(13) J.F. Jal, P. Chieux, J. Dupuy, J. de Physique (1980) 41, 657
(14) J.P. Boon, S. Yip, Molecular Hydrodynamics, Mc Graw-Hill, N.Y., (1980)
(15) L.M. de Schepper, E.C.D. Cohen, J. of Stat. Phys. (1982) 27, 223
(16) J.R.D. Copley, J.M. Rove, Phys. Rev. Lett. (1974) 32, 49
(17) C. Matthieu, J.F. Jal, J. Dupuy, J. Suck, P. Chieux, Liquid and Amorphous Metals (LAM6), Garmisch (1986) to appear in Z. Phys. Chem.
(18) J.F. Jal, A. Aouizerat-Elarby, J. Dupuy, J. Dianoux, to be published.
Figure 1: Structure factor of liquid potassium at several temperatures
Figure 2a: Total structure factor of the $K_{0.8}(KCl)_{0.2}$ solution for three chlorine isotopic compositions

$S(Q)\text{ vs } Q(\text{Å}^{-1})$
Figure 2b: Total structure factor of the $K_{0.6}(KCl)_{0.4}$ solution for three chlorine isotopic compositions.
Figure 3a: Partial structure factor for the K$_{0.8}$(KCl)$_{0.2}$ solution. The structure factor of pure potassium at 700°C (---) is drawn for comparison on the $S_{KK}$ partial.

The central line ($k_N$) of the triple hump characteristic of the pure ClK pattern is marked.
Figure 3b: Partial structure factors for the $K_{0.6}(KCl)_{0.4}$ solution.
Figure 4: Upper curve - The dispersion of the collective density fluctuations in pure liquid rubidium (ref. (16)). The arrow at low Q values is obtained from the sound velocity of the pure metal (hydrodynamic regime).

Central curve - The dispersion of the collective density fluctuations in Rb$_{0.9}$(RbCl)$_{0.1}$. Energy gain and energy loss are quoted separately. The arrow at low Q values is obtained from the sound velocity of the pure metal.

Lower curve - The dispersion of the collective density fluctuations in Rb$_{0.8}$(RbBr)$_{0.2}$. 

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