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## Interfacial segregation and the wetting transition in fluid metal–salt systems

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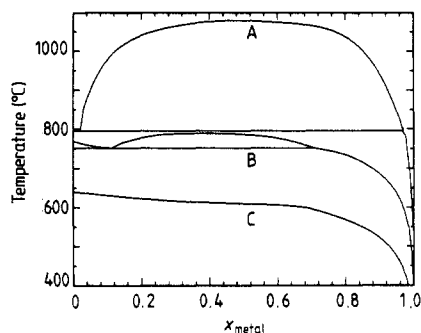
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**Abstract.** We report the first systematic study of the wetting behaviour in fluid alkali metal–alkali halide systems on the metal-rich side of the phase diagram. To this end the interface of fluid sample–inert substrate (sapphire) has been probed by ellipsometry. Of particular interest is the influence of differences of the bulk phase diagram on the wetting characteristics. If the bulk fluid phase exhibits homogeneous miscibility like Cs–CsCl the optical reflectivity changes continuously with composition consistent with metallic Drude type behaviour. However, in systems with a critical and a triple point like K–KCl and Na–NaCl a wetting transition is observed. This occurs in metal-rich solutions approaching the triple point along the phase boundary. In K–KCl a salt-rich wetting film of  $\approx 100$  nm thickness and composition corresponding to  $K_{0.1}KCl_{0.9}$  has been determined. This is the film thickness in thermal equilibrium as has been found by vigorous ultrasonic stirring.

### 1. Introduction

Wetting phenomena play an important role in different areas of physics and chemistry. A renewed interest in this field has been stimulated by the prediction of wetting transitions at fluid interfaces induced, for example, by a bulk critical point (Cahn 1977, Ebner and Saam 1977), or a bulk triple point (Pandit and Fisher 1983). In recent years a large number of theoretical studies on this subject has been published—for a recent review see for example Dietrich (1988) or Shick (1989). On the experimental side only a few systems have been investigated so far and these are all characterized by weak van der Waals type interactions (see e.g. Dietrich 1988).

In contrast to these, metal–molten salt (MMX) solutions are characterized by a screened Coulomb type interaction. These fluids exhibit some peculiarities which make them particularly attractive for the investigation of the wetting phenomena described above. First, a transition from metallic to non-metallic (ionic) states occurs with varying composition. As a consequence the intermolecular interactions of the metal-rich and salt-rich phases, respectively, differ distinctly which leads to extreme differences in the electronic properties such as the optical constants. This is advantageous to the experimental study of the wetting transitions by techniques such as ellipsometry. For the experimental understanding of the above phenomena a second advantage of MMX solutions is the following: within the same class of systems the phase diagram varies from complete miscibility to liquid–liquid demixing with an upper critical consolute point and a monotectic triplet point on the metal-rich side of the phase diagram. This is demonstrated in figure 1 for the example of alkali metal–alkali halide solutions. A mis-



**Figure 1.** Phase diagrams of liquid A,  $\text{Na}_x\text{NaCl}_{1-x}$ ; B,  $\text{K}_x\text{KCl}_{1-x}$ ; and C,  $\text{Cs}_x\text{CsCl}_{1-x}$  solutions according to Bredig (1964).

cibility gap is pronounced in Na–NaCl, is reduced in K–KCl and does not exist in Cs–CsCl.

In a previous paper we reported a wetting transition which we had observed in K–KCl near 500 °C approaching the triplet point along the phase boundary (Nattland and Freyland 1988). Extending this work to the systems shown in figure 1, in the present paper we focus attention on the influence of the bulk phase behaviour on the wetting characteristics in these solutions.

## 2. Experimental procedure

In order to study the fluid sample–sapphire interface, ellipsometric measurements have been performed with the polarizer–compensator–sample–analyser (PCSA) arrangement (see e.g. Azzam and Bashara 1987). Reflection of parallel (p) and vertical (s) polarized light has been measured at an angle of incidence of 70°. The ellipsometric angles  $\psi$  and  $\Delta$  have been determined by the method of null ellipsometry which yields the reflectivity ratio  $r_p/r_s$  according to  $r_p/r_s = \tan \psi \exp(j\Delta)$ .

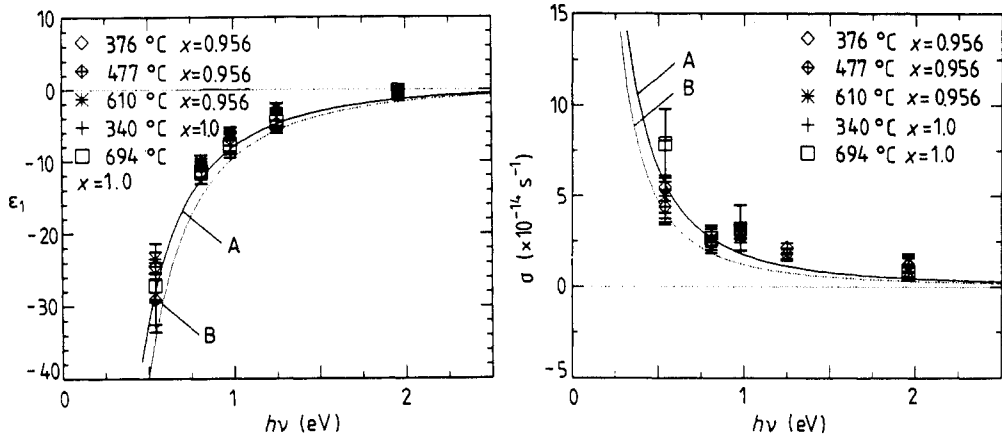
From this the optical constants  $\epsilon_1$  and  $\epsilon_2$ , i.e. the real and imaginary part of the dielectric function of the fluid interface, have been calculated with the aid of the Fresnel equations. For details of the experimental technique and of the necessary calibrations and corrections reference is given to a recent paper by Nattland and Freyland (1989) and to the diploma thesis of Juchem (1989).

Measurements have been performed at temperatures up to about 750 °C at various bulk compositions of metal-rich solutions of Cs–CsCl, K–KCl and Na–NaCl. Results have been obtained both on heating along the phase boundary and at  $(T, x)$  values in the homogeneous one-phase region. The optical reflection has been measured at several—on average six—wavelengths in the range  $632 \leq \lambda \leq 2316$  nm; different wavelengths both from lasers and a Xe arc lamp have been used. In order to obtain insight into the thermodynamic equilibrium state of the intruded wetting film we rigorously stirred the fluid sample using an ultrasonic device which was directly connected to the sapphire cell. The efficiency of the ultrasonic stirring was recorded simultaneously with the reflection measurements from the vibration of the reflected beam with the ultrasonic frequency. For this purpose a part of the reflected beam was deflected by a semi-transparent mirror. For further details see Juchem (1989).

## 3. Results and discussion

### 3.1. $\text{Cs}_x\text{CsCl}_{1-x}$ solutions

This system exhibits a continuous phase line between metal-rich solutions and pure

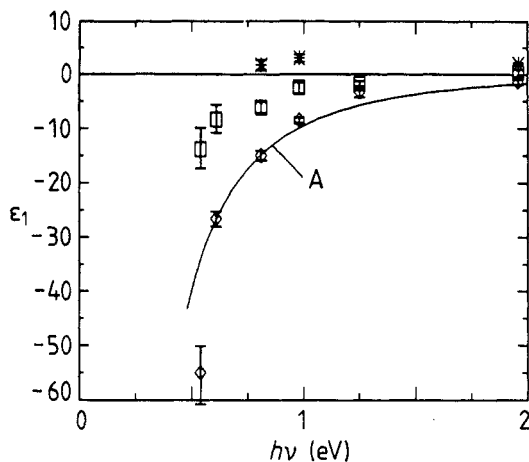


**Figure 2.** Real part of the dielectric function  $\varepsilon_1(\omega)$  and optical conductivity  $\sigma(\omega)$  of pure Cs (340 °C and 694 °C) and  $\text{Cs}_{0.96}\text{CsCl}_{0.04}$  (376 °C, 477 °C, and 610 °C) as determined from ellipsometric measurements at various wavelengths. The Drude curves of pure Cs at 300 and 700 °C are plotted for comparison. Curves A, 700 °C NFE; curves B, 300 °C NFE.

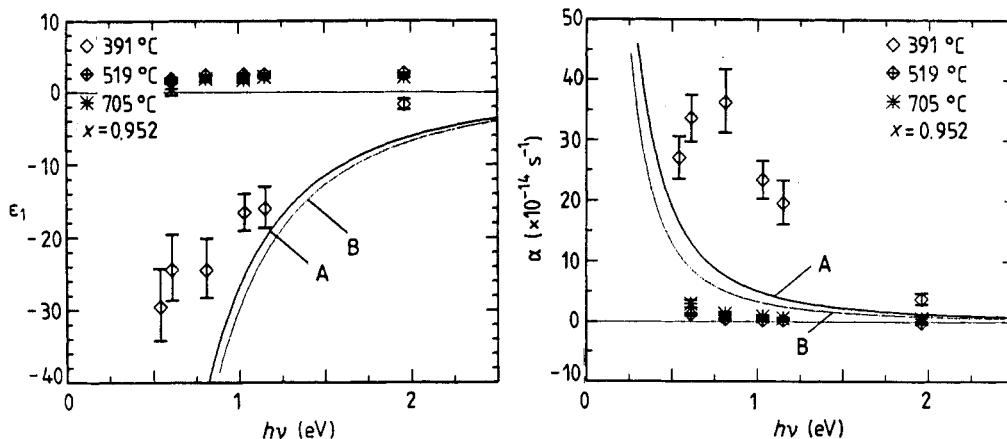
molten salt. No monotectic triple or critical point intervenes, so we do not expect an abrupt change of the optical reflection or strong deviations from metallic behaviour at the fluid interface if we add more and more salt to the liquid metal. This is exactly what we observe in fluid  $\text{Cs}_x\text{CsCl}_{1-x}$  for compositions  $1 \geq x \geq 0.87$  and temperatures up to 970 K. This is presented in figure 2 where results of pure Cs are compared with data for a sample of  $\text{Cs}_{0.96}\text{CsCl}_{0.04}$ . The real part of  $\varepsilon$ ,  $\varepsilon_1$ , and the optical conductivity,  $\sigma(\omega) = \varepsilon_2\omega(4\pi)^{-1}$  at various temperatures are plotted. The full curves correspond to calculations of  $\varepsilon_1$  and  $\sigma(\omega)$  of pure Cs for two temperatures of 300 and 700 °C according to the Drude model taking into account the DC conductivity and the number density at corresponding temperatures (see e.g. Ashcroft and Mermin 1976). In a first approximation the Drude model describes the main features of the experimental results, i.e. nearly free electron behaviour prevails. There is a slight deviation in  $\sigma(\omega)$  around 1 eV. This may indicate s–d transitions similar to the solid state (see also Ashcroft and Mermin (1976)). Increasing the concentration of salt up to  $\text{Cs}_{0.87}\text{CsCl}_{0.13}$ ,  $\varepsilon_1$  still remains consistent with the Drude model if one allows a variation of the effective mass up to  $\approx 2 m_e$ . A similar change of the effective mass has been found in expanded liquid Rb (Nattland *et al* 1986). In summary we may conclude that in the  $\text{Cs}_x\text{CsCl}_{1-x}$  system the fluid interface remains metallic up to relatively high additions of salt of the order of 10% in the bulk phase.

### 3.2. $\text{K}_x\text{KCl}_{1-x}$ and $\text{Na}_x\text{NaCl}_{1-x}$ solutions

As mentioned already, in  $\text{K}_x\text{KCl}_{1-x}$  we observe a discontinuous change in the optical reflectivity along the phase boundary for  $T \geq 500$  °C and a metal mole fraction of  $x_K \leq 0.99$ . At higher temperatures and lower metal concentrations clear deviations from a simple metallic picture occur. To demonstrate this we have evaluated the reflectivity coefficients measured by ellipsometry assuming that only one interface exists separating the fluid phase from the inert sapphire phase. The optical constants obtained using this



**Figure 3.** Real part of the dielectric function  $\epsilon_1(\omega)$  of pure K (710 °C);  $K_{0.96}KCl_{0.04}$  (754 °C); and  $K_{0.91}KCl_{0.09}$  (726 °C) as determined by ellipsometry. For comparison the Drude curve of pure K is plotted at 700 °C.  $\diamond$ , 710 °C,  $x = 1.0$ ; \*, 754 °C,  $x = 0.958$ ;  $\square$ , 726 °C,  $x = 0.913$ . Curve A,  $m_e/m_0 = 1.1$ , 700 °C.



**Figure 4.** Real part of the dielectric function  $\epsilon_1(\omega)$  and optical conductivity  $\sigma(\omega)$  of  $Na_xNaCl_{1-x}$  as determined for three temperatures along the phase boundary. The two full curves correspond to pure Na at 300 °C and 700 °C using the nearly free electron model (NFE): curves A, 700 °C; curves B, 300 °C.

pseudobinary phase model are given in figure 3 for the example of  $\epsilon_1$  of  $K_xKCl_{1-x}$  at three compositions  $x_K = 1, 0.96$  and  $0.91$  and temperatures near 750 °C, i.e. in the homogeneous one-phase region, near the monotectic temperature. For comparison the Drude calculation of pure K is plotted for 700 °C. It is obvious that a two-phase model fails to explain the measured optical constants within a metallic type picture as should be appropriate for the bulk phase in this concentration range. This effect is even more pronounced in  $Na_xNaCl_{1-x}$  as is seen in figure 4. Here results of  $\epsilon_1$  and  $\sigma(\omega)$ —assuming a two-phase model—are shown for three temperatures measured along the phase boundary. Clearly non-metallic characteristics are observed ( $\epsilon_1 > 0$ ) although the bulk composition at saturation is definitely metallic ( $x_{Na} \geq 0.99$ ). So we have to conclude that a two-phase model is not consistent with the measured reflectivities. For this reason we applied a three-phase model with two separating interfaces to explain the data. We have

to assume that a salt-rich wetting film intrudes between the bulk metallic fluid and the sapphire. The optical constants of the sapphire are known whereas those of the bulk metal with  $x_M \geq 0.95$  are well approximated by the Drude model (see the  $Cs_xCsCl_{1-x}$  data). Under these conditions the composition of the wetting film and its thickness may be determined from two measurements at different angles of incidence. In this way we determined a composition of the wetting film in  $K_xKCl_{1-x}$  which corresponds roughly to  $K_{0.1}KCl_{0.9}$ . The film thickness is roughly 100 nm. Concerning the nature of the wetting phase different possibilities have to be envisaged. If triple point wetting corresponding to the Pandit–Fisher scenario prevails the wetting phase may be the salt-rich fluid. On the other hand we know that the phase diagrams as depicted in figure 1 cannot be correct. On the salt-rich end a solid phase of salt with dissolved metal—the well known F centres in alkali halides—of unknown phase width must exist. So far this has not been measured in detail and therefore is not given in figure 1.

#### 4. Conclusions

In MMX solutions a wetting transition from low to high adsorption occurs if the bulk phase diagram exhibits phase separation with a corresponding critical and triple point. The wetting transition sets in at temperatures well below the triple and critical point temperatures and at salt concentrations around 1 mol% or more on the phase boundary. The larger the miscibility gap the more pronounced is the effect. In  $Cs_xCsCl_{1-x}$  where a homogeneous miscibility exists the fluid interface changes continuously but remains metallic up to a bulk composition of  $x_{Cs} \geq 0.9$ .

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