Macroscopic Adsorption and Wetting Transition at the Fluid-Solid Interface of K_xKCl_{1-x} Solutions

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We have studied the wetting behavior of K_xKCl_{1-x} solutions at a fluid-solid interface by optical reflectivity and ellipsometric measurements as a function of temperature and composition. In metal-rich solutions a wetting transition is observed along the phase boundary near 480 °C. Analysis by the Drude slab model yields that the intruding wetting film corresponds to roughly $K_{0.1}KCl_{0.9}$ and has a thickness of the order of 200 nm for conditions well away from the critical point.

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Wetting phenomena in fluid systems have excited considerable interest during the last few years stimulated, in particular, by the seminal paper of Cahn[1] in 1977. Cahn considered binary fluid mixtures with a critical demixing point and predicted a surface phase transition from low to high adsorption at fluid-solid or fluid-vapor interfaces as the critical point is approached. Meanwhile a vast number of theoretical studies have appeared and a wealth of wetting transitions have been investigated.[2] So, for example, wetting transitions on a substrate may also be influenced by a bulk triple point as has been stressed first by Pandit and Fisher.[3]

In the various model calculations distinct interatomic interactions have been investigated which may lead to clear differences in the wetting behavior.[2] Both short-range exponentially decaying and long-range power-law potentials have been considered. Experimentally, interfacial wetting in binary liquid mixtures so far has been studied only for five systems.[2] These are all characterized by dispersive or van der Waals type adsorbate-adsorbate interactions. In the majority of these experiments ellipsometry has been used to probe interfacial adsorption and to determine the wetting film thickness.[4]

In this Letter we report the first observation of a wetting transition and macroscopic surface segregation at the fluid-solid interface in a system with screened Coulomb interaction, the metal-molten-salt solution K_xKCl_{1-x}. This mixture has an upper critical point of $T_c = 790\,°C$, $x_c = 0.40$, and a monotectic triple point of $T_m = 751\,°C$[5] and $x_m = 0.7$ (see Fig. 1). The most striking characteristic of the bulk liquid is a continuous transformation from metallic to nonmetallic states with varying composition above T_c. As a result of this metal-nonmetal transition, the optical constants change extremely going from the metal-rich to the salt-rich end of the phase diagram. In addition, the salt-rich solutions exhibit distinct F-center absorption bands in the visible-infrared region.[6]

As a result of these peculiarities, interfacial phenomena in these solutions may lead to relatively pronounced changes of their optical features. Two different methods have been used to determine the properties of the fluid-sapphire interface: reflectivity measurements at normal incidence and ellipsometry at an angle of incidence of $\phi = 70°$. With increasing temperature along the phase boundary on the metal-rich side a marked change of reflectivity is observed in both experiments near 480 °C, an indication of a wetting transition. Above this temperature a salt-rich film is adsorbed at the sapphire which has a composition of roughly $K_{0.1}KCl_{0.9}$ and a macroscopic thickness of $\simeq 200$ nm, e.g. at 770 °C. To our knowledge this is the first time that a wetting transition with this magnitude of the film thickness has been observed in a fluid system with screened Coulomb interactions.

The sample cell employed in the ellipsometric measurements is drawn schematically in Fig. 2. The surface of interest is the base of a sapphire prism in contact with the fluid sample. For corrosion reasons sapphire has to be used. The sample is contained in a cavity inside a second circular sapphire plate. The two sapphires are fixed inside a metal frame and vacuum-tight sealing of the sample up to high temperatures is achieved by compression of thin Ta wire rings between the respective sapphire surfaces. The cell is mounted inside a vacuum

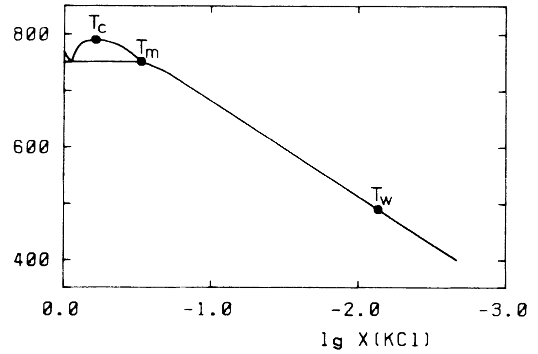

FIG. 1. Phase diagram of K-KCl; to expand the metal-rich end the salt mole fraction x(KCl) is given on a logarithmic scale (see Ref. 5).

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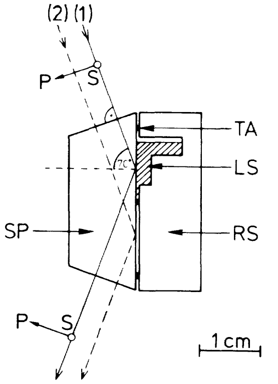

FIG. 2. Schematic drawing of the vertical cross section of the sample cell. (1), (2), Polarized light reflected at sapphire-sample and sapphire-vacuum interface, respectively; SP, sapphire prism; RS, reservoir sapphire with sample compartment; LS, liquid sample; TA, 50-μm-thick tantalum sealing wires.

furnace which can be moved with high precision in the vertical and horizontal directions relative to the aligned optical beam. In this way the change of the polarization state at the sapphire-sample and sapphire-vacuum interfaces [beam (1) and (2), respectively, in Fig. 2] have been measured at various positions at the same constant temperature. This internal calibration was necessary to correct for birefringence and stress birefringence of the sapphire. An ellipsometer has been constructed to measure the reflectivity ratio ρ,

$$\rho = r_p / r_s = \tan\psi \exp(j\Delta),$$

of p- and s-polarized light from a laser or a Xe-arc lamp. The polarizer-compensator-sample-analyzer (PCSA) ellipsometer arrangement was chosen.[7] The ellipsometric angles ψ (azimuth) and Δ (phase shift) have been determined by the method of null ellipsometry.[7] In order to minimize phase-shift errors due to the sapphire birefringence, accurate temperature control to better than ±0.1 °C was necessary. Further details of this high-temperature ellipsometer will be published elsewhere.[8]

All sample preparations, assembling, and sealing of the cell have been performed in an argon-filled stainless-steel glove box. The level of O_2 and H_2O impurities was below 2 ppm. In order to getter O_2 impurities dissolved in the alkali metal a small Ti sponge was placed inside the sample compartment opposite to the prism base. This technique has proven successful in previous reflectivity measurements of pure liquid alkali metals.[9] For the experiments at normal incidence a cell similar to that of Fig. 2 has been used. The reflectance has been recorded with a Cary model 17H spectrometer as described previously.[9].

Figure 3 presents typical reflectivity results for temperatures and compositions along the coexistence curve of the metal-rich phase region. In Fig. 3(a) the detector output of the intensity of polarized light reflected at the sapphire–liquid-sample interface is shown as a function of temperature. This measurement has been obtained on heating of a sample of nominal composition $K_{0.53}KCl_{0.47}$. The harmonic behavior of the intensity with temperature at constant polarizer and analyzer settings reflects the contribution of the sapphire birefringence to Δ which has a linear temperature dependence.[8,10] However, near 480 °C a clear break in the harmonic oscillations occurs which indicates a marked change of the optical behavior of the fluid-sapphire interface. In Fig. 3(b) the normal reflectance at a constant wavelength of 885 nm is plotted as a function of the salt mole fraction along the coexistence curve. Reflectance spectra at various wavelengths in the visible range show similar behavior. In all cases a hysteresis occurs between heating and cooling cycles. The clear kink in the plot of Fig. 3(b) corresponds to a saturation temperature of 480 °C. These separate observations in the ellipsometric and reflectance measurements demonstrate that near 480 °C the optical constants of the fluid interface change drastically. In this connection we may add that the optical reflectance spec-

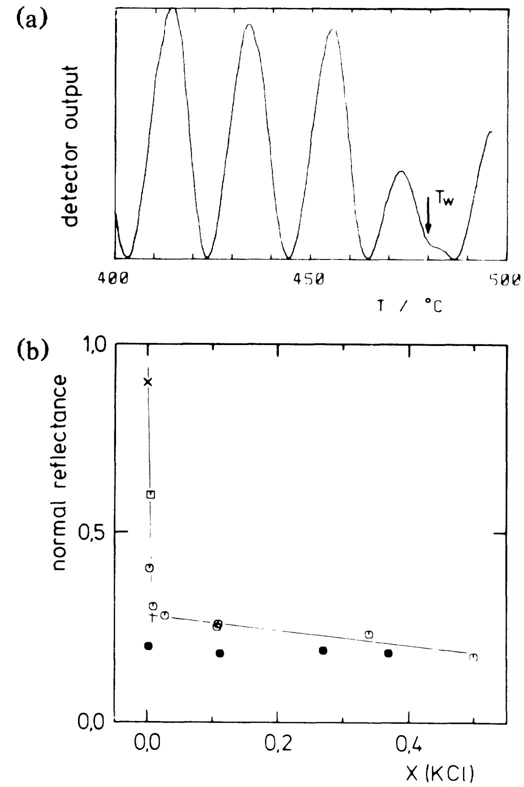

FIG. 3. (a) Original recorder plot of the intensity of polarized light ($\lambda = 633$ nm) reflected at the sapphire–liquid-sample interface vs temperature (see text). (b) Normal reflectance at constant wavelength ($\lambda = 885$ nm) of K-KCl solutions as a function of salt mole fraction x(KCl) along the coexistence curve. (Open symbols, heating; filled symbols, cooling.)

tra of metal-rich Rb_xRbCl_{1-x} solutions exhibit similar behavior.[9]

At this point it is interesting to note that up to $\simeq 350\,°C$ the ellipsometric data, evaluated with the Fresnel equations valid for the simple sapphire-fluid interface, yield values of the optical constants of the liquid consistent with those of pure potassium.[8] This is not surprising as the equilibrium concentration of dissolved KCl at this temperature is well below 1% and approaches 1% near 520 °C (see Fig. 1). However, above 480 °C the same evaluation leads to completely unphysical results.

If the abrupt change of reflectivity at this temperature signals a wetting transition then a salt-rich film of macroscopic thickness should attach to the sapphire for $T \geqq T_w = 480\,°C$ and conditions near the phase boundary. This has been predicted for both first- and second-order wetting transitions.[2] Therefore we have tried a simple Drude slab model to interpret the ellipsometric and reflectance data for $T > T_w$. We assume that the film has a homogeneous composition and uniform thickness. The light beam undergoes multiple reflection at the sapphire-film and film-bulk-liquid interfaces where the bulk liquid is highly concentrated in metal so that its optical constants may be approximated by those of pure potassium (see above). With these assumptions and the known refractive index of sapphire we are left with the following interesting quantities: refractive index n and adsorption coefficient k of the film and its thickness t. These we have determined from fits of the corresponding ellipsometric equations for the slab model—see Ref. 7, p. 283—to the experimental ψ and Δ values measured at $\phi = 70°$ and to the reflectance data at normal incidence. Figure 4 presents a typical result of n and k determined at five different wavelengths for a sample measured at 770 °C and bulk composition of $K_{0.96}KCl_{0.04}$. The optical constants determined for two compositions in the bulk salt-rich phase at comparable temperature[8] are included in Fig. 4. The trend in the k and n values of the film is comparable with the corresponding results measured for a bulk composition $K_{0.11}KCl_{0.89}$. From this comparison it is evident that the film composition corresponds to roughly $K_{0.1}KCl_{0.9}$, i.e., near the salt-rich eutectic composition.[5] The F-band absorption characteristic of the salt-rich phase region is visible in the film data. The film thickness consistent with these n and k values we find to be equal to $t \simeq 200$ nm, i.e., of macroscopic magnitude. Similar results of n, k, and t for the wetting film have been obtained at other compositions and temperatures on the bulk metal-rich side for $T > T_w$.[8]

We are aware that the slab model together with the foregoing assumptions presents a gross simplification of the problem. However, as T_w is far below T_c, this evaluation is possible. It gives a first insight into the magnitude of the composition and thickness of the wetting layer. The most striking results are the relatively large film thickness and the strong difference between T_c and T_w. To what extent this is related with the screened Coulomb interaction and the metal-nonmetal transition in these solutions is an open theoretical problem. Stronger metallic interactions may play an important role. This suggestion is supported by a recent study of undercooling in emulsified liquid-alloy droplets,[11] which is of some technological interest. The microstructure of quenched solidified droplets reveals a surface coating enriched in one alloy component with a thickness of the order of 1 μm. Finally, possible deviations from thermal equilibrium and temperature gradients—below 1 K mm^{-1} in our samples—may have a strong influence on the wetting behavior of the fluid-solid interface. This has been discussed in detail by Wu, Schlossman, and Franck[12] who have studied the role of stirring on the steady-state thickness of the wetting layer. However, these effects are difficult to control in the high-temperature systems investigated here.

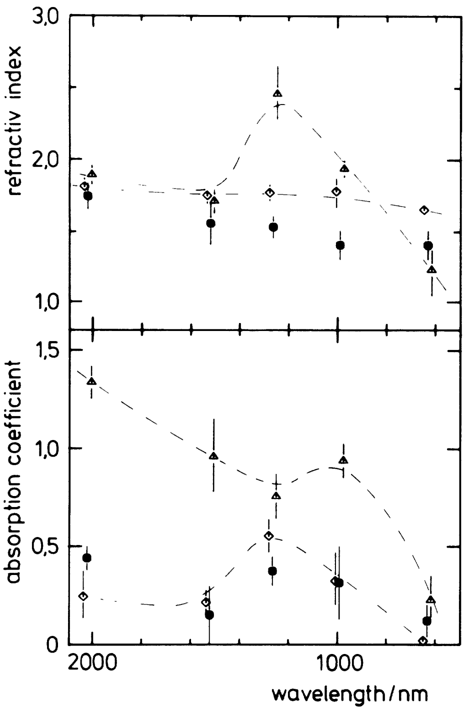

FIG. 4. Refractive index n and absorption coefficient k of liquid K_xKCl_{1-x} solutions at different wavelengths. Open symbols refer to measurements on bulk salt-rich samples (triangles, $x = 0.25$, lozenges, $x = 0.11$), whereas filled circles present the corresponding optical constants determined for wetting film.

In summary, we have measured the optical reflectivity by two different methods at the fluid-solid interface of K_xKCl_{1-x} solutions. Pronounced changes in the optical properties of the fluid interface strongly indicate that a wetting transition occurs in metal-rich solutions at a temperature well below the critical point. For the intruding salt-rich wetting film a macroscopic thickness of the order of 200 nm is found. The hysteretic behavior of the reflectivity results is indicative of a first-order wetting transition. As expected from theory, no wetting transition is observed on the salt-rich side of the phase diagram.

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