Contents lists available at SciVerse ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Densities of a dissolving mixture of molten (AgI + NaCl)

V.P. Stepanov *, N.P. Kulik, K.G. Peshkina

Institute of High-Temperature Electrochemistry, Russian Academy of Sciences, Ural Division, Akademicheskaya str. 20, Yekaterinburg 620990, Russia

ABSTRACT

The densities of a molten mixture of (0.5 AgI + 0.5 NaCl) were measured along the saturation line over a wide temperature range by the hydrostatic weight method to establish the peculiarities of the mixing of salts with different chemical bonds. We showed that the difference between the magnitudes of the densities for the coexisting phases decreases with increasing temperature and becomes equal to zero at 1063.5 K. This temperature corresponds to the critical phase transition point, T_c. The temperature dependence of the difference in densities, $\Delta\rho$, is described by equation $\Delta\rho/\rho_c \approx \left(\frac{T_c-T}{T_c}\right)^\beta$, where ρ_c is the density at T_c. The index $\beta = 0.476$ occurs at a lower value than that found for alkali halide melts ($\beta = 0.52$) where long-range Coulombic forces between ions prevail.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

The immiscibility phenomenon in ionic condensed systems and its numerous physical and chemical aspects has been of great importance for both fundamental and practical purposes. The presence of an electrical potential drop through the interface between two immiscible liquids [1] must have a specific influence on the kinetics of extraction and the chemical reactions occurring at this interface. A great number of questions have been raised regarding this interface, including the cause and regularity of the segregation, the characteristics of the phases on the saturation line and the role of charge fluctuations in the liquid–liquid phase transitions of these systems.

Much work has been performed studying and analysing ionic liquids, which constitute solutions of low melting salts with large organic cations (imidazolium, pyridinium, phosphonium) and inorganic anions (Cl^-, BF_4^- and so on) in a dielectric continuum (mostly water, alcohols) with a considerable dielectric constant [2–26]. A coincident interpretation of the results of these investigations is complicated by the complexity of the properties of ionic liquids, such as their nanoheterogenity, high viscosity, hydrogen bonding, low ion dissociation, etc. [18,27,28]. Nonetheless, the scrupulous measurements of the coexistence curves, light scattering, turbidity and electrical conductivity for these systems have provided the opportunity for establishing peculiarities in the behavior of ionic liquids in the de-mixing region. It has been shown that the critical solution temperature increases and that the biphasic region becomes larger when the chain length of the alcohol increases. On

the contrary, the critical temperature decreases and the de-mixing field narrows with increasing size of the organic cation. The reductions in the critical temperatures have been found to depend on the dielectric constant of the solvent. It is of consequence that most of the systems studied have shown Ising-like behavior.

Our group has investigated discrepancies in the segregation of reciprocal ternary mixtures of alkali halides, where one of the components is a salt with relatively small ionic radii (e.g., lithium fluoride) and the second component has larger ionic radii (e.g., potassium bromide, cesium chloride, etc.). Above the melting point, these salts essentially dissociate entirely. A solvent with a large dielectric constant is absent in this case, and the long-range Coulombic forces between the particles prevail. Therefore, they can be reasonably simulated as charged hard spheres having an arbitrary diameter and a Coulomb interaction potential [29]. It turned out that there is a limit of the ratio of the cation and anion radii when their composition becomes unstable. As a result, mixtures of such components divide into two liquid phases below the critical temperature. The increasing differences in ionic size are accompanied by an increase in the critical temperature and the displacement of the dome immiscibility to the component with the smallest ionic radius. Experimental studies on the density [30], sound velocity [31], compressibility [32], electrical conductivity [33,34] at the saturation line and of the interfacial tension [35] for these molten salts have shown that the difference between the magnitudes of the coexisting phase properties, Δ, increased with the radius of the halide anion or the alkali cation at the same temperature. Temperature growth led to decreases in these differences along the saturation line for mixtures up to zero at the critical mixing point, T_c. In the vicinity of the critical point, the temperature dependence of the differences for each property can be described

* Corresponding author. Tel.: +7 343 3740055.
E-mail address: v.stepanov@ihte.uran.ru (V.P. Stepanov).

TABLE 1
Provenance and mass fraction purity of the materials studied.

Chemical name	Chem abstracts number	Provenance	Initial mass fraction purity
Silver iodide [a] AgI	7783-96-2	Russian chemical	0.99
Sodium chloride [a] NaCl	7647-14-5	Russian chemical	0.995
Argon Ar	7440-37-1	Russian chemical	0.9999

[a] Dried in vacuum melted under argon, zone-refined in a flow of argon.

by the universal equation $\Delta \approx (T_c - T)^k$ with van der Waals exponents.

To determine if the nature of the chemical bond influences the behavior of molten systems in the two-phase region, it is necessary to investigate the mixtures without a molecular solvent, which may contain components that contribute to polar or covalent chemical bonds with the ions. In this respect, a molten mixture of (AgI + NaCl) in the region of the upper critical point [36] of mixing is of interest. It has been shown that the structure factors of molten silver halides are different from those of molten alkali halides [37–39]. The main features of the total structure factors of the silver halides observed here are explained well with the assumption of essential ion polarization and sp^3 hybridization in the liquid silver halides. In this paper, we provide density measurements of the dissolved equimolar mixture of (AgI + NaCl) (this composition corresponds to the top of the miscibility gap [36]) over an extended temperature range in the two-phase region to address any discrepancies in the liquid/liquid phase transition of the silver halide.

2. Experimental

2.1. Materials

Particular attention was paid to eliminate any impurities that could arise from reactions of the salts with atmospheric oxygen and moisture. The salts were prepared in the following fashion. Silver iodide (mass fraction purity 0.99) and sodium chloride (mass fraction purity 0.995) were dried in a vacuum at $T = 673$ K for 4 h, and slowly brought to a temperature 50 K above their melting points and cooled in an argon atmosphere. The smelted salts were then subjected to zone purification in a flow of argon three times. Regarding the procedure of the zone fusion more detailed information is given in our former study [40]. The measured melting points of the salts after purification (1074 ± 0.5 K for NaCl and 832 ± 0.5 K for AgI) indicate the high purity of the samples and strongly agree with the reference data [41]. The salts were stored in hermetically sealed vessels. The provenance and purity values are listed in Table 1.

2.2. Measuring procedure

The Archimedean displacement method was used to measure the densities of our samples because it is the simplest method to use for high temperature applications and allows for high accuracy measurements. Our experimental setup was described in detail previously [30]. The method is based on determining the difference between the mass, Δm, of a solid bob hanging in air and submersed in a liquid phase. The ratio of this difference to the volume of the bob at a given temperature yields the magnitude of the liquid density, ρ. The primary complications associated with this method include allowing for the effects of an influx of liquid across the thread on which the bob is suspended under the action of surface tension forces, the condensation of salt vapour on the thread at high temperatures during the experiment, and the thermal expansion of the bob. During the experiments, the temperature was maintained and measured in the stratifying layers as accurately as possible. This requirement was necessary in order to have sufficient grounds

for determining the system's state in the vicinity of the critical temperature. As a result, errors were reduced as much as possible by the careful design of the procedures for measuring the density in two-phase liquid systems at high temperatures [30]. The experimental setup was built on the base of a Sartorius microbalance whose protective housing had a gas space common with the measuring cell. The bob was a platinum cylinder that was suspended on the stirrup of the balance via a thin platinum wire. The electrolyte was placed in a quartz test tube in a platinum crucible. Between the test tube and the furnace heating element, we placed a beaker of stainless steel, which ensured a uniform distribution of temperature over the volume of the cell. The temperature was maintained automatically to within an accuracy of 0.5 K and measured by a platinum/platinum–rhodium thermocouple immersed in the middle of the melt near the interface between the stratified phases. The portion of the thermocouple that was in contact with the melt was protected from the electrolyte by a platinum casing.

The volume of the platinum cylinder was determined by weighing it in pure molten cesium and sodium chloride at several temperatures. The Δm values obtained and the known densities, ρ, of the liquids [42] were used to determine the volume according to the formula: $V = \Delta m / \rho$. A calibration procedure of this type automatically accounts for the effects of temperature and surface tension. The values obtained for the volume of the bob at different temperatures were used as a basis for determining the densities of known salts and showed good coincidence with reference data. The accuracy of the observed densities was evaluated within 0.5%.

Prior to each experiment, the system was evacuated and filled with pure argon to a pressure of 1 atm. Measurements were performed no sooner than 30 min after the temperature was changed, when the density in each phase was assumed constant at certain points of the melts at each stationary temperature, which was evidence that the system had reached thermodynamic equilibrium. The temperature dependence of the density was analysed within both the rising and falling regimes. Irrespective of the temperature regime, the density values at each temperature coincided within 0.1%.

3. Results and discussion

The temperature dependencies of density in mutually saturated (AgI + NaCl) coexisting phases and in the region of complete miscibility of the components are listed in table 2 and illustrated in figure 1. The upper line of the two phases system corresponds to the density of the heavy phase enriched in silver iodide, and the lower line characterizes the density in the sodium chloride predominate phase. The system is biphasic between the melting point and 1063.5 K. The density of the coexisting phases converges when the temperature increases. The temperature coefficient of the reduced density difference is lower than that for the alkali halide melts.

Polytherms of the density for the pure component melts are shown by thin lines [41,42]. An analysis of these primary experimental data reveals certain special features in the behavior of these stratifying melts. We see that the densities in both phases have