Phase Densities of Molten Binary Mixtures of Alkali Halogenides with Limited Mutual Solubility

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The densities of binary mixtures of LiF with CsCl, KBr, RbBr, CsBr, KI, RbI and CsI have been investigated at 1093 – 1253 K. For the system LiF with KBr the dependence of the density on the temperature was measured up to the critical point, where the system became single-phased, and the critical behaviour was evaluated. The critical exponent of the order parameter, which was found from the density measurements, is close to 0.5.

Key words: Immiscibility Demixing; Ionic Melts; Density; Critical Behaviour.

1. Introduction

This study pioneers investigations of the physicochemical properties of binary mixtures of LiF with CsCl, KBr, RbBr, CsBr, KI, RbI and CsI. These systems were chosen because they are some of the few demixing melts of inorganic salts known to date [1]. A specific feature of the mixtures of alkali halogenides is that the interaction of their components may be viewed as purely Coulombic. Therefore the immiscibility of these melts with ions of different dimensions can be described by the Debye-Hückel and mean-spherical approximations [2]. It was possible to reveal the dependence of the critical temperature on the electrolyte asymmetry, establish the character of the dispersion of the critical fluctuations of the density and concentration in the phase contact zone, and predict the shift of the immiscibility gap towards the component with the smaller ions and charges.

Experimental studies on such systems are scarce. For instance, data on the properties of immiscible ionic systems, except phase diagrams [3 – 5], are not available. Such properties as the density, the interfacial tension at the boundary of immiscible melts, the potential difference between the phases have little been studied so far. The interfacial tension was measured only in the “sodium borosilicate-silver chloride” system, where the interparticle bonds are largely covalent [6]. The lack of knowledge of the physicochemical characteristics of the simplest immiscible ionic melts considerably retards the further advancement of our ideas about the origin of immiscibility.

The density can be used to calculate other parameters of a liquid system, such as the viscosity, the molar volume, the surface tension. Densities of molten individual salts and their mixtures are known well enough [7]. They served as the basis for the development of model representations about the structure of ionic melts and the redistribution of the particle binding energy caused by mixing of salts. A significant augmentation of these data might be information about the density of two-phase salt mixtures at thermodynamic equilibrium. Also, experimental data on phase densities in these systems may prove to be very informative for the theoretical description of immiscibility, since the difference of densities determines the ordering parameter of demixing-type phase transitions.

This study had several goals: to develop a method for the determination of phase densities in immiscible melts; to measure densities of coexisting phases in the seven binary systems already mentioned over a wide temperature interval; to determine the temperature dependence of the difference of phase densities; and to estimate the parameters of the critical behaviour of systems, in which the critical temperature can be reached.

2. Experimental

The Archimedean method, described in [8, 9], was chosen for measurements of the density. In this method, the difference in the weight of a metal bob

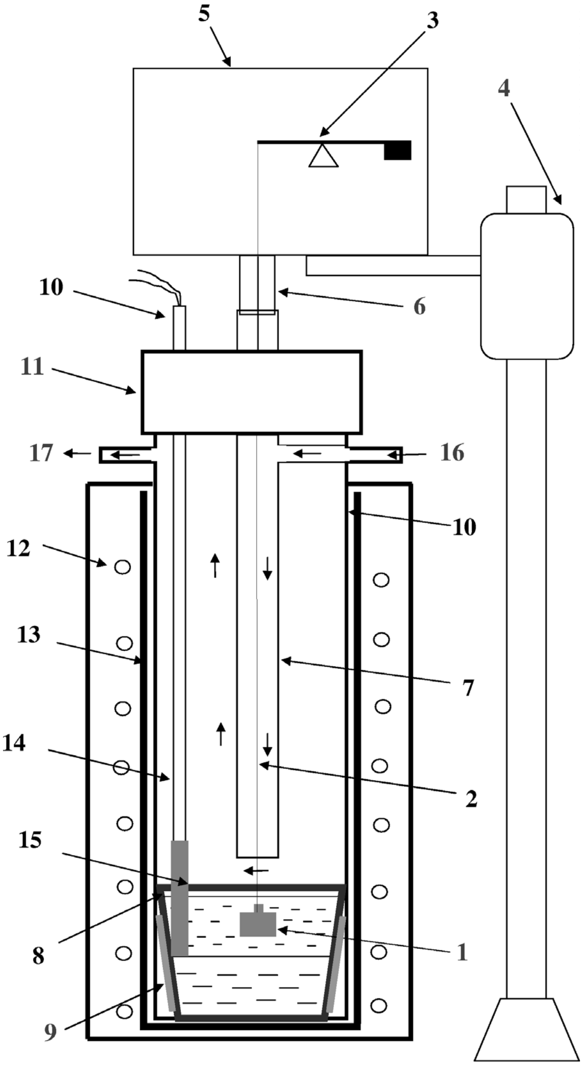

Fig. 1. Apparatus for density measurements.

suspended in air and immersed in a liquid phase (Δm) is determined. The ratio between this difference and the volume of the bob (V) gives the liquid density at a given temperature. The main difficulties encountered in the Archimedean method arise from the necessity to take into account the flow of liquid onto the suspension wire of the bob under the action of surface tension; the condensation of salt vapors on the suspension wire at high experimental temperatures; and the thermal expansion of the bob. In the case of the systems under consideration, additional difficulties were due to the corrosiveness of the lithium-fluoride-containing electrolyte. This circumstance limited the choice of structural materials of the cell. A considerable requirement was also that the temperature of the immiscible salts had to be maintained and measured as accurately as possible. This requirement was necessary for the evaluation of the state of the system near the critical temperature.

The setup for the density measurements is shown in Figure 1. The platinum bob (1), about 1 cm in diameter, was suspended by a thin platinum wire (2) (0.1 mm thick) on one of the beams of a Sartorius microbalance (3), which was mounted on the cathetometer (4). This arrangement allowed a smooth movement of the bob and provided accurate measurements of its immersion depth in the melt.

The measuring unit of the balance was totally enclosed in the stainless-steel cap (5). The vacuum-tight section (6) communicated the balance casing and the measuring cell, providing the same atmosphere in all parts of the setup. To preclude condensation of the salt on the platinum wire, it was placed in the quartz tube (7) (1.2 cm in diameter). Purified Ar was blown at a small rate through the tube. The electrolyte was placed in the glassy-carbon crucible (8), which was wrapped in the platinum plate (9) for uniform heating of the crucible. The crucible was placed in the quartz tube (10), which was sealed with the rubber plug (11). Molybdenum screens protected the plug from high temperatures. The cell was installed in the furnace (12), whose heat was adjusted with a Proterm heat controller, which maintained the temperature within 0.1 °C. The cell and the furnace were separated by the stainless-steel tube (13), which ensured a uniform distribution of the temperature over the cell volume. The temperature was measured using a Pt/PtRh thermocouple (14), which was immersed to the center of the melt near the interface between the demixed phases. A part of the thermocouple, which contacted the melt, was protected from the corrosive electrolyte with the platinum casing (15). An E-24 digital-to-analog converter controlled the temperature within 0.5 °C. The pipes were used for the gas (Ar) input (16) and evacuation (17) of the cell.

The salts were prepared by the following methods. Lithium fluoride was dried in a vacuum at 673 K for 4 h, slowly heated to 50 K above the melting point (1118 K), cooled and immediately filled into the cell. The other salts were dried, melted under an argon atmosphere and then refined by six-fold zone melting in a flow of purified argon. The salts were kept in sealed vessels made of dark glass.

Before each experiment the system was evacuated and then filled with argon, which was passed through

Table 1. Coefficients a and b of $\rho(\Delta\rho) = a - bT$ approximating the temperature dependences of the phase densities.

		Light phase		Heavy phase		$2\Delta\rho$	
System	$2\Delta T$, K	a	$b \cdot 10^4$	a	$b \cdot 10^4$	a	$b \cdot 10^4$
75%LiF-25%CsCl	1130 – 1310	2.850	6.918	4.696	19.697	1.846	12.778
80%LiF-20%CsBr	1120 – 1260	2.772	7.433	4.366	14.045	1.357	4.555
80%LiF-20%CsI	1115 – 1310	2.230	3.549	4.563	15.011	2.334	11.465
80%LiF-20%RbBr	1160 – 1310	2.293	3.266	4.539	17.984	2.245	14.718
80%LiF-20%RbI	1165 – 1315	1.772	−0.257	4.133	13.222	2.361	13.479
76%LiF-%KBr	1130 – 1330	2.039	1.883	2.907	8.034	0.863	6.151
75%LiF-25%KI	1115 – 1340	1.772	−0.231	3.363	9.765	1.591	9.997

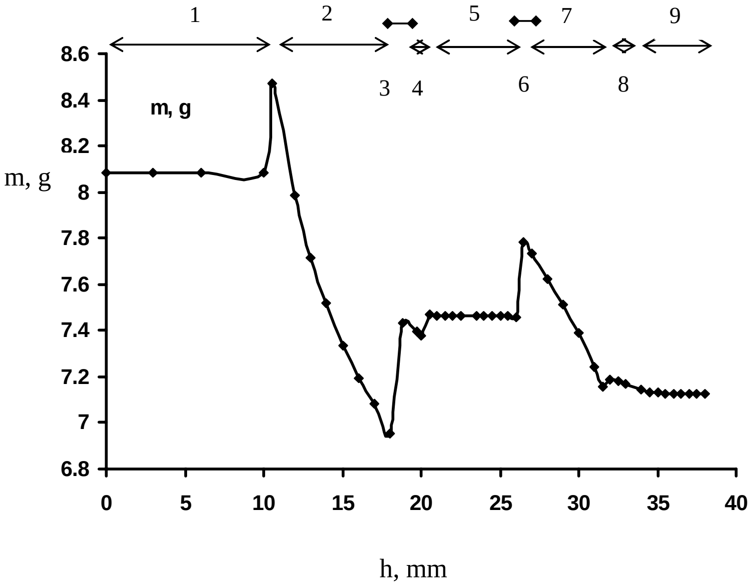

Fig. 2. Dependence of the weight m of the Pt bob on the depth h of immersion into the 20%CsI-80%LiF peeling melt at 956 K.

zirconium chips heated to 800 K to remove oxygen impurities.

To determine the volume of the platinum bob, it was weighed in distilled water at 298 K and then in pure molten CsCl and NaCl at several temperatures. The Δm values and known densities of the liquids (ρ_{liq}) [7] were used to calculate the volume by the formula $V = \Delta m/\rho_{\text{liq}}$.

This calibration automatically took into account the effect of the temperature and the pulling force of the surface tension. The densities of salts, which were determined using these values of the bob volume at different temperatures, agreed well with reference density values.

3. Results and Discussion

The directly measured experimental values represent dependences of the weight m of the bob on its immersion depth h in the molten medium. A typical dependence is shown in Figure 2. Several sections may be distinguished: 1. The mass of the sample in the gaseous phase does not change until the sample touches the melt, at which moment the balance reading increases abruptly. 2. The mass of the sample, which is partially immersed in the upper (2) or lower (7) liquid phase, decreases due to the buoyancy force. 3. The mass increases because the molten upper (3) and lower (8) phases flow onto the top of the bob. 4. The mass decreases because the upper projecting portion of the bob (Fig. 1) smoothly submerges into the liquid phase. 5. The mass remains unchanged; this is an indication that the sample is fully immersed in the upper (5) or lower (9) phase. 6. The mass increases under the influence of the interfacial tension on the interface of the liquid phases. Densities of the upper and lower phases of the immiscible systems were calculated using the mass values measured in sections (5) and (9) and the bob volume at the corresponding temperature.

Temperature dependences of the phase densities were measured in series of experiments (3 – 4 parallel runs for each salt) with the following systems: 80% LiF + 20% CsI, 70% LiF + 30% CsBr, 65% LiF + 35% CsBr, 80% LiF + 20% CsCl, 75% LiF + 25% CsCl,

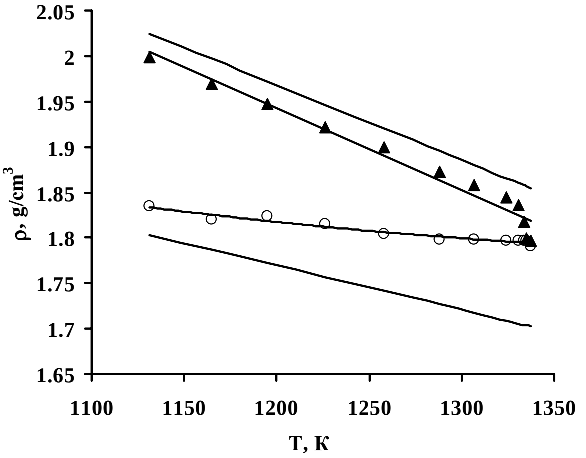

Fig. 3. Temperature dependences of density in the system Li,K-F,Br in pure KBr and LiF. 1, Pure LiF; 2, upper phase; 3, lower phase; 4, pure KBr.

70% LiF + 30% CsCl, 80% LiF + 20% RbI, 80% LiF + 20% RbBr, 80% LiF + 20% KI, 70% LiF + 30% KBr, 75% LiF + 25% KBr, and 76% LiF + 24% KBr. Table 1 contains coefficients of equations approximating the temperature dependences of the phase densities.

A typical temperature dependence of the densities of coexisting phases is shown in Fig. 3 (76% LiF + 24% KBr was taken as an example) along with the densities of individual melts of lithium fluoride (line 1, Fig. 3) and potassium bromide (line 4, Fig. 3) at different temperatures [7]. The bottom line (2, Fig. 3) corresponds to the density of the light (lower) phase enriched with lithium fluoride, while the top line (3, Fig. 3) characterizes the density of the heavy (upper) phase in a two-phase system for all the cases under consideration. It is seen from Fig. 3 that the densities of the upper and lower phases decrease with growing temperature. The density of the heavy phase always drops more abruptly than the density of the light phase as the temperature rises. This fact suggests indirectly that the heavy component of the system dissolves less in the light component and the light halogenide dissolves better in the heavy halogenide when the change of the temperature is the same. The shift of the immiscibility gap towards the component with the smaller ion is probably due to the larger screening power of a small-radius ion and is confirmed by results of both experimental [3] and theoretical [2] studies. Thus, the densities of the demixed phases become closer to one another as the temperature rises. Temperature dependences of the density differential between the lower and upper phases in all the systems at hand are shown in Fig. 4. The experimental setup, which was used for density measurements, allowed achieving the critical temperature only for the 70 (75, 76)% LiF + 30 (25, 24)% KBr system. The temperature, at which the phases mix, is different for different compositions. For example, it is 1251 K for 70% LiF + 30% KBr, 1295 K for 75% LiF + 25% KBr, and 1333 K for 76% LiF + 24% KBr melts. Thus, the composition of the system of 76% LiF + 24% KBr is the most close to the critical composition.

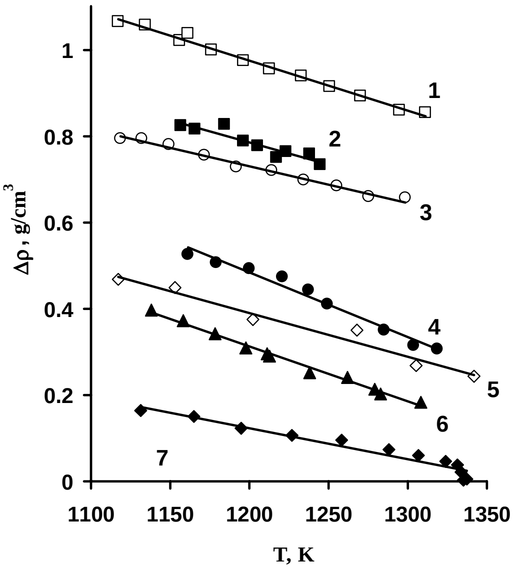

Fig. 4. Temperature dependence of the density mismatch for: 1, CsI-LiF; 2, CsBr-LiF; 3, RbI-LiF; 4, RbBr-LiF; 5, KI-LiF; 6, CsCl-LiF; 7, KBr-LiF.

According to Sinistri et al. [3], our temperature interval should include critical temperatures (the upper boundary of immiscibility gaps) of the LiF-CsCl (T_c = 1185 K) and LiF-RbBr (T_c = 1323 K) systems. Sinistri reported the critical temperature of the 70% LiF + 30% KBr mixture equal to T_c = 1223 K, while in our experiments it was observed at 1333 K for 76% LiF + 24% KBr. This discrepancy is probably due to specific features of the visual method used by Sinistri for the determination of the demixing start point, which is difficult to locate with a sufficient accuracy at high temperatures. The compositions, which are given in [3] as critical ones for observation of the immiscibility gap vertex, probably need to be refined too.

The difficulties involved in visual determination of the phase transition temperature may be seen from Fig. 5, which presents dependences of the mass of the sample on the immersion depth in the Li,Rb||F,Br sys-

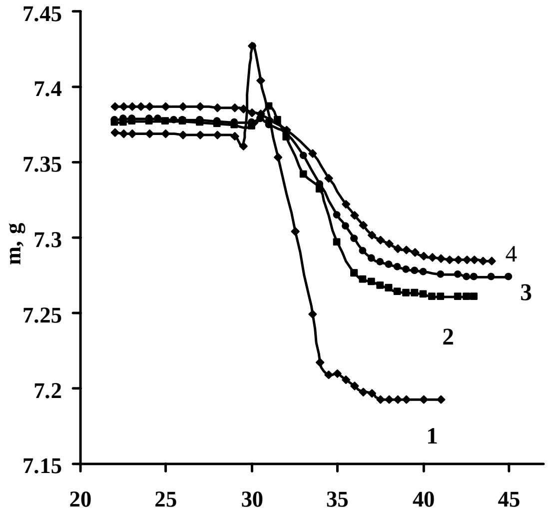

Fig. 5. Weight changing of Pt bob with the depth of immersion (sections 5 – 9, Fig. 2) for the system Li,Rb-F,Br at: 1, 1161 K; 2, 1285 K; 3, 1304 K; 4, 1319 K.

tem at different temperatures. The peak of the mass variation (which is due to the interfacial tension) – at that moment the end-wall of the bob touches the interface – decreases with growing temperature and becomes imperceptible at 1319 K. Vanishing of a clear-cut interface at this temperature probably led the researchers [3] to take this temperature (1323 K) as the critical point. A similar correlation between temperatures of vanishing (smoothing) of the interfacial tension peak T_γ, which was determined by us, and critical temperatures reported in [3] shows up also in the Li,Cs||F,Cl ($T_\gamma = 1173$ K; $T_c = 1185$ K [3]) and Li,K||F,Br ($T_\gamma = 1218$ K; $T_c = 1223$ K [3]) systems. Smearing of the boundary between liquid phases is especially pronounced upon approaching to critical temperatures.

The working temperature interval used in this study was sufficient for the determination of the upper critical point for the Li,K||F,Br system and, therefore, an attempt was made to evaluate the behaviour of the system near the full miscibility temperature. Figure 6 presents logarithm of the ordering parameter η versus the reduced temperature $\tau = |T - T_c|/T_c$ for three compositions studied: 76% LiF + 24% KBr (circles), 25% KBr + 75% LiF (triangles), and 30% KBr + 70% LiF (squares). In this case, the ordering parameter is calculated as $\eta = (\rho_1 - \rho_2)/\rho_c$, where ρ_1 and ρ_2 denote the densities of the coexisting heavy and light liquid phases, and ρ_c is the density at the critical point.

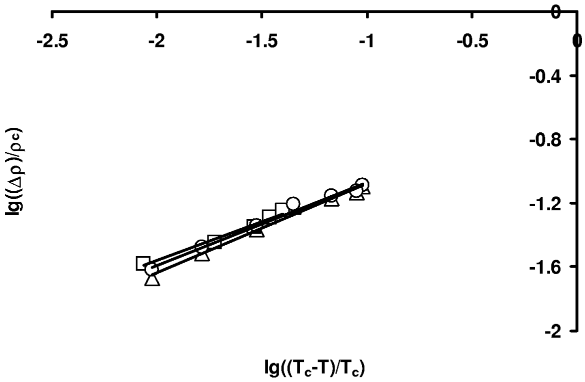

Fig. 6. Logarithmic dependence of the order parameter on the reduced temperature. Squares, 30% KBr; triangles, 25% KBr; circles, 24% KBr.

The experimental curves proved to be described well by the empirical equation $\eta \cong \tau^\beta$. The critical index of the ordering parameter equals 0.516, 0.559 and 0.4907 for the first, second and third compositions, respectively. It may be taken equal to 0.5 in first approximation, i. e. of the same order as the characteristic value for immiscible liquids near the critical temperature [10]. The spread of the experimental values of the critical index may be related to the measurement error of the critical point. It is necessary, specifically, to locate more precisely the immiscibility gap maximum with respect to the composition axis. The working temperature interval should be expanded in the future to reach critical points for other ionic systems having limited solubility.

4. Conclusion

Densities of coexisting phases in molten limited solubility ionic systems of alkali halogenides (KBr, KI, RbBr, RbI, CsCl, CsBr, CsI) with lithium fluoride were measured over a wide temperature interval using the method of hydrostatic weighing. It was found that the densities of both the upper and lower phases decreased with growing temperature. The decrease in the density of the heavy phase was more pronounced than that of the light phase at all times. The difference of the phase densities diminished linearly with the temperature in all systems. This regularity was observed up to the critical point of miscibility in the molten KBr-LiF mixture as an example. The critical index of the ordering parameter, which was calculated from these data, proved to be about 1/2.

The behaviour of salt melts similar to the melts used in this study was not analyzed anywhere under critical conditions, except the aforementioned paper by Sinistri et al. However, there is a wealth of information about physicochemical properties of ionic fluid mixtures, most of which are salt solutions with organic ions in polar media with a considerable dielectric constant [11 – 14]. The same mixtures were the subject of most theoretical studies, whose results are summarized in [15, 16]. Two opinions on the type of liquid-liquid immiscibilities have been formed today. As is known, it is determined by the exponent of the order parameter β in the vicinity of the critical point. In this respect, ionic systems are divided into two classes. The first class is characterized by the mean-field behaviour ($\beta = 0.5$), whereas the Ising-like criticality ($\beta = 0.33$), which is typical for molecular systems, is observed in the second class. It was found that one type of criticality was replaced by the other type in some systems. Probably, the key points in understanding the reasons for the specific type of the criticality are three experimental facts [11 – 14]: the behaviour of solutions of strong electrolytes (1) in solvents having a small dielectric constant (2) approaches the mean-field type of the criticality with distance from the critical point (3). For this reason, the theory, which is based predominantly on the Coulomb interparticle interaction, predicts the classical behaviour of the systems [15], whereas the Ising criticality is formed if short range forces are taken into account [16].

The halide melts, which are analyzed in this study, undoubtedly are far by their nature from ionic fluid mixtures discussed in the literature. The solvent having a large dielectric constant is absent between particles, and long range Coulomb forces prevail. Therefore they can be quite reasonably simulated as charged hard spheres having an arbitrary diameter and the Coulomb interaction potential [16 – 18]. This determines their mean-field type of the criticality observed in the experiment. Furthermore, if the behaviour of these melts is described in terms of the Debye-Hückel theory, which takes into account the excluded volume effect, it is possible to predict with a good approximation not only values of main critical parameters of liquid alkali halides [18, 19], but also the configuration of the immiscibility gap depending on dimensional differences of ions [3].

The possibility of transition from the mean-field type of the criticality to the Ising criticality in such melts is open to question so far. The answer can be found in experiments by improving the accuracy of measurements near the critical point (which is a difficult task for experimentalists) and the use of a variety of research methods. We think the Debye-Hückel theory has a reserve if the equation of state of molten halides of alkali metals correctly allows for the role of large ionic complexes and neutral dimers [16]. Most probably, their concentration in the liquid phase becomes considerable near the critical point if one considers the fact that the vapor phase over these melts consists mostly of neutral molecules [19]. In this case, properties of the system are increasingly determined by short range ion-dipole and intermolecular forces, which are responsible, most likely, for the Ising behaviour.

Acknowledgements

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