Densities of Molten Binary Fluoride Salts: (Li-K)F, (Li-Rb)F and (Li-Cs)F Systems

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Densities of molten binary fluoride salts have been measured by means of the Archimedean method. Molar volumes at 1123 K were calculated for each system and the isotherm of the molar volumes showed a slightly positive deviation from the additivity rule in (Li-Rb)F and (Li-Cs)F systems. It is shown that there exist linear relationships between the third power of the nearest ionic distance and molar volumes of pure salts at the melting point, and also between a temperature coefficient of molar volume and the reciprocal of an effective interionic force of unlike ions. The structure of alkali halide salts was discussed from the standpoint of an interionic force.

1 Introduction

The study of alkali halides is of fundamental importance in order to elucidate the ionic structure of molten salts since they are the simplest and consist of positive and negative, singly charged, spherical, ionic particles. Of all halide systems, research on molten fluorides which have the strongest interionic force between unlike ions is of extremely interest. However, molten fluorides are probably among the least studied halide systems. The main reason for the apparently limited interest in molten fluorides is due to the experimental difficulty because of the corrosive nature and toxicity.

Due to the strong interionic force the mixing properties of fluorides show large deviation from the additivity rule in isotherms of surface tension¹⁾ and electrical conductance²⁾. Kleppa *et al.* have shown that the deviation of molar volume of molten nitrates after mixing the contributing substances 1 and 2 is always positive and evidently zero in case of identical chemical compounds. The change of volume by mixing these substances will be proportional to the expression $V \sim [(d_1 - d_2)/(d_1 + d_2)]^{4/3}$. Hence the change of volume resulting from the mixing is not ideal but shows a positive deviation

increasing with growing difference of the cation radii.

In this study we measured the densities of binary alkali fluorides containing a Li ion which is the smallest radius among alkali cations and investigated the effect on molar volume by the addition of cations such as K⁺, Rb⁺ and Cs⁺, having varying sizes and charge densities.

2 Experimental

The density was measured on the basis of Archimedes' principle. The furnace assembly for the measurement is illustrated in Fig. 1. A platinum bob of 25 g in weight was connected with a thin platinum wire and suspended from the balance pan. When a Pt wire more than 0.02 cm in diameter was used to suspend the bob, the reading of a balance pan was unstable owing to the large surface tension of fluoride melts. After all a thin Pt-13% Rh wire of 0.01 cm in diameter was used to suspend the bob.

The density of the bob was calibrated by first weighing in air and then in water at a known temperature to evaluate its volume. The volume, V_0 , was calculated from the following equation.

$$V_0 = (W_a - W_w) / (d_w - d_a) + \pi \sigma_w a_0 / (g(d_w - d_a))$$

where W , d , t , σ and g are a weight of the bob, density, temperature, surface tension and gravitational constant, respectively and a_0 is a diameter of a thin wire ($a_0 = 0.01$ cm), the suffixes w and a refer to the measurement in the water and the air, respectively. The expansion

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Fig. 1 Apparatus for density determinations by the Archimedian method

- 1: Pt, 10% Rh suspension wire
- 2: Pt-Pt, Rh thermocouple
- 3: Furnace
- 4: Pt crucible; height 11cm O.D. 4.5 cm
- 5: Pt density bob
- 6: Nickel cover plate
- 7: Pt-Pt, Rh thermocouple

of the bob with increasing temperature was considered with the following equation.

$$V_m = V_0(1 + \beta(t_m - t_a))$$

where β is the coefficient of cubical expansion of platinum ($\beta = 0.3057 \times 10^{-4}$). By using these equations, the density of a melt, d_m , is written as

$$d_m = (W_a + d_a V_a - W_m) / V_m + \pi \sigma_m a_0 / (V_m g)$$

where the subscript m refers to a melt and σ_m is the surface tension of the sample⁴⁾.

In order to avoid absorption of atmospheric moisture, the salt was kept under dried argon gas in a glove box during the measurement. The temperature was measured with a Pt-Pt, Rh thermocouple, after it reached the desired point and remained constant for 15~20 minutes. The measurements were repeated for various temperatures with an interval of 15~20 K and covering a total range of about 120 K. In general, it was found more convenient to start with the highest desired temperature and bring it down during a density run.

The chemicals used, LiF and KF, were of reagent grade quality, and RbF and CsF were of 98% purity (Soegawa Chem. Ltd. Japan). The sample was weighed and prepared in a glove box thoroughly dried with P_2O_5 . After it was dried in a vacuum oven at about 470 K for a day, it was heated up to 50 K above a melting point. The melt was bubbled with dried argon gas for 30 minutes, and then outgassed for 30 minutes under vacuum.

3 Results

Figure 2 shows the values obtained for the densities of the pure fluorides together with previously published data. The observed values of density differ by a fair amount from one experimentalist to another. The experimental errors of our investigated results are below $\pm 1.0\%$ mainly due to the fluctuation of measured temperatures in a furnace. For LiF, KF and CsF the present results are in relatively close agreement with other published data. Regarding RbF our obtained values are higher than those of other investigators. The discrepancy between Jaeger's and our results is $\sim 1.4\%$.

Fig. 2 Density versus temperature for pure alkali fluoride melts

Fig. 3 Density versus temperature for LiF-KF mixture

The measurement has carried out under a stream of a dried argon gas into the glove box to avoid absorption of atmospheric moisture. The chemical of RbF satisfied the qualification chemically pure of 98%. Considering the low level of moisture in the glove box and a small amount of impurities in the chemical, we can not explain the discrepancy of RbF data.

In Figs. 3, 4 and 5 the densities of the fluoride mixtures containing LiF are plotted against a temperature. The experimental errors of mixtures are estimated to be less than $\pm 0.6\%$, since the measured temperatures were relatively low in comparison with pure salts. As may be seen from the figures the density of each system at a given temperature decreases with increasing concentration of LiF.

The density was also measured for the LiF-NaF-KF ternary eutectic, referred to as FLINAK, which has the composition 46.5 mol % LiF-11.5 mol % NaF-42.0 mol % KF and melts at 732 K⁵⁾. This melt is proposed for use as the coolant in a molten salt breeder reactor.

The data obtained are expressed as a linear

Fig. 4 Density versus temperature for LiF-RbF mixture

Fig. 5 Density versus temperature for LiF-CsF mixture

Table 1 Densities of Fluoride melts as a function of temperature
 $d/10^3 \text{ Kg m}^{-3} = A - B \times 10^{-3} T$

LiF mol %	A	B	Temperature range/K
LiF-KF system			
0	2.606 ± 0.017	0.6194 ± 0.011	1135–1222
20	2.537 ± 0.015	0.5657 ± 0.019	1049–1154
35	2.532 ± 0.005	0.5695 ± 0.006	928–1124
50	2.565 ± 0.001	0.6112 ± 0.002	769–1022
65	2.523 ± 0.002	0.5945 ± 0.003	924–1090
80	2.618 ± 0.010	0.6902 ± 0.013	1090–1139
100	2.453 ± 0.017	0.5612 ± 0.020	1128–1196
LiF-RbF system			
0	3.959 ± 0.004	0.945 ± 0.004	1087–1204
20	3.706 ± 0.009	0.833 ± 0.010	996–1191
35	3.660 ± 0.011	0.860 ± 0.014	931–1134
50	3.588 ± 0.006	0.913 ± 0.008	851–1144
65	3.210 ± 0.002	0.715 ± 0.003	970–1169
80	2.812 ± 0.002	0.576 ± 0.006	1059–1199
90	2.729 ± 0.002	0.609 ± 0.009	1103–1205
LiF-CsF system			
0	4.801 ± 0.007	1.220 ± 0.009	980–1072
20	4.677 ± 0.002	1.240 ± 0.003	881–1118
35	4.448 ± 0.004	1.158 ± 0.005	774–1076
50	4.229 ± 0.007	1.112 ± 0.012	830–986
65	3.668 ± 0.008	0.760 ± 0.012	938–1050
80	3.271 ± 0.009	0.633 ± 0.010	1043–1143
FLINAK (LiF-NaF-KF : 7-44-49 mol %)			
	2.553 ± 0.002	0.6041 ± 0.0034	742–1015

function of temperature in each case and are, therefore, represented in the form of a linear equation in Table 1 by means of the least squares method.

4 Discussion

4.1 Molar volumes of binary molten salts

The isotherms of molar volume for the investigated fluoride mixtures are shown in Figs. 6 and 7. The molar volumes of the system (Li-K)F exhibit no significant deviations from additivity as shown in Fig. 6. Although our data of the system (Li-K)F are in good agreement with those obtained by Taniuchi *et al.*¹⁰⁾, an appreciable difference between ours and those of Meaker *et al.*¹¹⁾ is found. As shown in Fig.

Fig. 6 Isotherms of the molar volume of melts in the system (Li-K)F at 1123 K

Fig. 7 Isotherms of the molar volume of melts in the systems (Li-Rb)F and (Li-Cs)F at 1123 K

7, the value obtained by Cohen *et al.*¹²⁾ for the system (Li-Rb)F is slightly larger than ours. A small positive deviation from additivity can be observed for both (Li-Rb)F and (Li-Cs)F systems. Maximum deviations are 1.2% in (Li-Rb)F and 2.0% in (Li-Cs)F at equimolar

Table 2 Deviations of molar volume from additivity rule at equimolecular composition

	Nitrate mixture (): %					
	Li	Na	K	Rb	Cs	Ag
Tl	0.18(0.40)	0.23(0.45)	0.35(0.63)	0.17(0.29)	—	-0.3(-0.26)
Ag	0.12(0.28)	0.19(0.42)	0.41(0.82)	0.39(0.76)	0.26(0.45)	
Cs	0.23(0.41)	0.20(0.34)	-0.04(0.06)	0.12(0.18)		
Rb	0.34(0.69)	0.56(1.07)	0.67(1.17)			
K	0.30(0.65)	0.29(0.58)				
Na	0.37(0.87)					
	Chloride mixture					
	Li	Na	K	Rb	Cs	
Ag	—	—	0.85(2.05)	—	—	
Cs	0.66(1.4)	0.51(0.98)	0.32(0.56)	0.25(0.41)		
Rb	0.05(0.1)	0.28(0.61)	0.23(0.45)			
K	0.12(0.32)	0.27(0.62)				
Na	0.12(0.34)					
	Fluoride mixture					
	Li	Na	K	Rb		
Cs	0.61(2.0)	—	—	—		
Rb	0.35(1.2)	—	—			
K	0.05(0.23)	0.13(0.48)				
Na	-0.10(-0.5)					

..... our results

G.J. Janz, *et al.*, J. Phys. and Chem. Ref. Data, **3**, (1974)¹³⁾.

compositions. Even if the experimental errors of $\pm 1.0\%$ for pure fluorides and $\pm 0.6\%$ for mixtures are taken into account, we can still see a small positive deviation in the system (Li-Cs)F.

In Table 2 we have listed excess molar volumes at equimolar composition calculated by using our data and the references¹³⁾ on binary molten mixtures of nitrate, chloride and fluoride. The temperature at which density was calculated was chosen at the higher melting point of salts in each system. From the table small positive deviations can be seen almost in every system. We should acquaint ourselves with the relative precisions with which the density have been measured. We have estimated those approximately to be $\sim 0.3\%$ for nitrates, $\sim 0.6\%$ for chlorides and $\sim 1.0\%$ for fluorides. In consequence of the relation $\Delta V_m = (V_m)_{id.} - (V_m)_{obs.}$, ΔV_m is calculated by subtracting values relatively large in comparison with their difference. Although some results are included within these

errors, slightly positive deviations of molar volume from additivity could be seen in almost every system with the degree of reliability corresponding to above mentioned causes of inaccuracy. Considering the accuracy of density measurement, it appears difficult to conclude that a positive deviation increases with growing difference of the cation radii as suggested by Kleppa³⁾.

4.2 Ionic structure of molten alkali halides

In this section we discuss qualitatively how the interionic Coulomb forces of molten alkali halides affect the ionic structure in the melts when the volume expansion of liquid takes place during melting or thermal expansion with rise in temperature.

Alkali halides undergo a 10 to 30% volume increase on fusion. This volume increase introduces naturally empty spaces or free volume in melts. It is meaningful to investigate the amount of empty spaces by comparing the volume of

Fig. 8 Molar volume of molten halide salts at the melting point against $2n_ar^3$

the given molten alkali halide with that of the solid, NaCl-type structure being chosen hypothetically as a basic one. In Fig. 8 the molar volume of pure molten alkali halides at the melting points, V_m , is plotted against the third power of the nearest ionic distance multiplied by the double of Avogadro's number ($V_s = 2n_ar^3$) which represents the molar volume of unit lattice cells of NaCl-type. The data of densities are used from the reference¹⁴⁾ except our results of LiF, KF, RbF and CsF. The empirical crystal radii for alkali halides are taken from Pauling's values¹⁵⁾, while those for Ag^+ , Cu^+ and Tl^+ are 0.95, 0.96 and 1.40 Å, respectively. As shown in the figure molar volume of each alkali halide gives a very good fit to the straight lines, increasing in the order of Cs, Rb, K, Na and Li halide systems, which means that the rate of the empty volume in melts increases in the same order.

From the X-ray diffraction data¹⁶⁾ for molten alkali halides, it is known that the average nearest ionic distance in the liquid is about 5~10% smaller than that of the crystal, and second peak distance between like ions is somewhat larger than the corresponding distance in the solid. This fact suggests that the volume expansion on fusion would be attributed to the ionic positional disorder accompanying the decrease in the nearest cation-anion coordination

number, and that Coulomb forces tend to determine the equilibrium ionic distribution. This can be explained in the following way. At melting the fluidity of liquid is produced by a vigorously thermal motion of ions. Each ion might be forced to move along the equipotential surface of opposite charged ions since the strong repulsive or attractive force exert against the movement of cation-anion direction. This movement increases considerably the possibility of collision between the neighboring like ions, and makes like ions repulse each other owing to the Coulomb repulsion between like ions. This repulsive cation of like ions would induce the decrease in the nearest coordination number and the positional disorder of ions. As a result the volume of a salt would be expanded on fusion. As the repulsive Coulomb force is determined only by the interionic distance between like ions the value of the force should be large when the size of an ion is small. For example, an Li^+ ion is so small that it offers a possibility for contact and large repulsive action between anions. Since the Coulomb repulsive force is dependent only on the interionic distance, Fig. 8 shows that the repulsive action tends to increase with decreasing ionic radius between unlike ions, and the rate of empty space in melts increases regularly as the series from Cs, through Rb, K and Na, to Li with a given halide ion.

This figure also indicates that the empty spaces of cuprous, silver and thallos halides are appreciably smaller than those of alkali halides, although ionic radii of cuprous, silver and thallos ions are almost the same as those of sodium, potassium and rubidium ions, respectively. These metal halides seem to be different from alkali halides, *i. e.*, in the former case one might assume the presence of the non-Coulomb force of anion-cation pairs or next nearest neighbors which would weaken the Coulomb repulsion between like ions and cause the relatively smaller increase of empty space in melts.

In the next place, we discuss the thermal expansion with rise in temperature. In view of the existence of the strong Coulomb interactions exerted among ions of alkali halides, it is interesting to examine how molar volume of salts is related to an effective pair potential.

Fig. 9 Thermal expansion of molar volume and the reciprocal of an interionic force

Figure 9 shows the relationship between a thermal expansion of molar volume for alkali halides¹⁴⁾ and the reciprocal of an effective interionic force of unlike ions. The interionic force, $du(r)/dr$, was derived by differentiating the pair potential of Born-Mayer-Huggins form¹⁷⁾ with respect to r . For calculating $[du(r)/dr]_{r=r_1}$, Pauling's values¹⁵⁾ were taken as the sum of cation and anion radii, r_1 . Due to the lack of the pair potential data for CsCl, CsBr and CsI, the data points for those salts could not be plotted in the figure. The figure shows that all points lie on a smooth curve. The thermal expansion tends to be large in the order of Li, Na, K and Rb halides; the stronger interionic force between unlike ions, the smaller the thermal expansion. This would indicate that the interionic force between unlike ions play a dominant role in controlling the orientation of ions with change in temperature.

Among alkali ions Li^+ has the strongest interaction with adjacent anions, while Cs^+ has the weakest. According to the experimental results of fluoride mixtures as shown in Figs. 6 and 7, molar volumes of mixtures have not exhibited significant deviations from additivity. This result suggests that interionic forces be-

tween unlike ions in an alkali halide salt would not be affected by mixing, *i. e.*, in a lithium mixture Li^+ would hold the closeness of its cationic environment to anions, very similar to in a pure salt, while a larger cation like Cs^+ would be loosely surrounded by anions. The interionic force like a Born-Mayer-Huggins form might be effective even if in a mixture of an alkali halide salt.

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