

Surface Tensions of LiF-ThF₄ Binary Melts and LiF-BeF₂-ThF₄ Ternary Melts

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The surface tensions of LiF-ThF₄ binary melts and LiF-BeF₂-ThF₄ ternary melts have been measured by the maximum bubble pressure method. The surface tension isotherm of LiF-ThF₄ binary melts shows a slight negative deviation from additivity with respect to the salt composition, while that of LiF-BeF₂-ThF₄ ternary melts has a significant negative deviation. These facts can be explained by considering the formation of complex ions such as ThF₆²⁻ and BeF₄²⁻.

Introduction

Molten salts are useful nuclear materials, for example, as the fuel solvent and the coolant in molten salt breeder reactors (MSBR). Although physical properties of molten salts have been investigated by many workers (1, 2), little is known of the interfacial properties such as surface tension in spite of their importance (3).

The purpose of this study following our previous work on LiF-BeF₂ binary melts (4) is to measure the surface tensions of LiF-ThF₄ binary melts and LiF-BeF₂-ThF₄ ternary melts. The latter melts are expected as the fuel solvents of MSBR. Their surface tension data are especially important in assessing the wetting behavior of the fuel solvents for the constituent materials of the reactor.

Experimental Section

The maximum bubble pressure method was applied for determining the surface tension because of the simplicity and the precision of the measurement at high temperatures in a moderately corrosive liquid.

The apparatus used is almost the same as that described in the previous paper (4).

All the reagents are of reagent grade obtained from Nakarai Chemicals, Ltd. Thorium tetrafluoride was prepared in the laboratory by precipitating from nitric acid solution with hydrofluoric acid. The complete fluorination and dehydration of the hydrated fluoride precipitates were achieved by heating with NH₄HF₂ (5) and were confirmed by X-ray diffraction analysis of the products.

Known amounts of each component salt were put into the crucible and dried by evacuating at 200 °C for 1 day in the furnace. The furnace was filled with argon gas purified by passing through molecular sieves and titanium sponges. Then the temperature was raised above the melting point of the sample and kept constant within 0.025 °C by a temperature-controlling device manufactured by Eikoh Electric Co., Ltd.

The bubble tube was lowered gradually by gear-type moving equipment while the argon gas was blown from a nickel capillary tip of 0.5-0.8-mm inner radius. When the tip came in touch with the free surface of the melt, a sudden increase of the pressure of the gas in the bubble tube was observed. By this observation the free surface was located within 0.05 mm of the moving-equipment reading. After a further immersion of the capillary, the maximum bubble pressure was measured by a manometer filled with dibutyl phthalate within a reading of 0.5 mm. The measurements were made with varying immersion depth of the capillary tip at a given temperature.

Table I. Surface Tension of LiF-ThF₄ Binary Melts

compn, mol %		temp, °C	surface tension, mN/m
LiF	ThF ₄		
80.0	20.0	686	268.4 ± 5.5
		722	266.3 ± 5.4
		769	259.5 ± 7.3
		772	254.9 ± 3.3
		792	255.5 ± 3.0
		800	254.3 ± 3.4
		829	250.1 ± 3.3
		755	254.0 ± 2.3
		802	248.6 ± 2.2
		828	246.5 ± 2.6
67.7	33.3	850	239.1 ± 5.0
		874	236.5 ± 2.6
		735	256.3 ± 2.5
		769	249.3 ± 1.9
		784	248.5 ± 3.7
		816	242.9 ± 7.5
		846	240.1 ± 5.1
60.0	40.0	874	234.4 ± 2.5
		806	242.0 ± 5.6
		825	238.8 ± 4.8
		851	235.2 ± 5.8
		873	229.0 ± 2.8
		899	227.5 ± 3.3
50.0	50.0	882	234.5 ± 5.0
		939	226.6 ± 3.0
		959	223.4 ± 3.5

The radius of the capillary tip was calibrated within 0.001 mm by the preliminary measurement of the surface tension of water.

According to Schrödinger (6), the surface tension γ of the sample melt is calculated with the equation

$$\gamma = \frac{1}{2}r\rho gh \left[1 - \frac{2}{3}(r/h) - \frac{1}{6}(r/h)^2 \right] \quad (1)$$

where r is the radius of the capillary tip, h is $(\rho_m l_m - \rho l)/\rho$, ρ and ρ_m are the densities of the sample melt and the manometer liquid, respectively, l is the immersion depth of the capillary tip, l_m is the measured manometer reading, and g is the acceleration due to gravity.

Typical density equations of LiF-ThF₄ binary melts have been provided by Hill et al. (7) and those of LiF-BeF₂ binary melts are also available (8, 9). As the molar volume of each binary system shows a linear dependence on its composition, the density at any composition of the LiF-BeF₂-ThF₄ ternary system was estimated by assuming a linear composition dependence of the molar volume. The density of dibutyl phthalate has also been given by Kemppinen and Gokcen (10). The thermal expansion of the capillary tip was taken into account.

Results and Discussion

The obtained values of surface tension for LiF-ThF₄ binary melts are shown in Table I. The measurements were not made for the melts containing more than 50 mol % of ThF₄ because of their high melting temperatures. The precision indices assigned to γ values are the combined standard deviation derived from the scatter of h values and the standard errors of r . Considering the other sources of errors such as those in the values of ρ , ρ_m , and l , the uncertainties in the γ

Table II. Surface Tension of LiF-BeF₂-ThF₄ Ternary Melts

compn, mol %			temp, °C	surface tension, mN/m
LiF	BeF ₂	ThF ₄		
70.6	11.8	17.6	790	202.3 ± 1.9
			826	199.5 ± 3.7
			830	203.7 ± 2.1
			851	196.2 ± 1.7
57.1	28.6	14.3	651	199.2 ± 4.4
			673	188.9 ± 4.9
			715	181.7 ± 4.3
			739	174.9 ± 3.9
			765	178.1 ± 4.1
54.5	18.2	27.3	795	184.0 ± 3.7
			798	182.8 ± 4.1
			826	182.4 ± 3.1
			837	181.5 ± 3.4
			735	186.1 ± 3.8
50.0	25.0	25.0	747	181.9 ± 3.4
			766	179.6 ± 3.0
			786	177.4 ± 3.5
			789	178.9 ± 3.2
			801	174.3 ± 3.1
			848	167.5 ± 3.9
			800	157.2 ± 3.7
			823	189.2 ± 4.1
44.4	44.4	11.1	843	188.8 ± 3.2
			853	186.2 ± 4.2
			868	189.6 ± 4.2
			823	189.2 ± 4.1
44.4	22.2	33.3	843	188.8 ± 3.2
			853	186.2 ± 4.2

Table III. Empirical Equation for the Temperature Dependence of the Surface Tension of LiF-ThF₄ Binary Melts

compn, mol %			surface tension (mN/m) = a - bt(°C)	
LiF	ThF ₄	temp range, °C	a	b
80.0	20.0	686-829	361.4 ± 7.4	0.134 ± 0.010
70.0	30.0	802-874	369.3 ± 11.3	0.151 ± 0.014
67.7	33.3	735-874	365.5 ± 4.6	0.150 ± 0.006
60.0	40.0	806-899	375.0 ± 9.8	0.165 ± 0.012
50.0	50.0	882-959	360.6 ± 2.8	0.143 ± 0.003

values become presumably a little greater than the precision indices shown in Table I.

In Table II we list the values of surface tension for LiF-BeF₂-ThF₄ ternary melts. The measurements were restricted in the composition range less than 44.4 mol % of BeF₂, because the addition of BeF₂ made the measurements difficult due to the increase in viscosity of the melts. The precision indices were obtained in the same manner as those for the LiF-ThF₄ binary melts.

As seen in Figure 1, the surface tension of a LiF-ThF₄ binary melt of a given composition decreases linearly with increasing temperature of the melt like most of the other salt systems. The empirical equations for the temperature dependence are summarized in Table III. Because of the narrow temperature range in the measurement for the LiF-BeF₂-ThF₄ ternary melts, the dependence of the surface tension on temperature was not expressed quantitatively.

Figure 2 shows the surface tension isotherm of the LiF-ThF₄ binary melts at 800 °C. The isotherm deviates slightly in the negative direction from the additive behavior and has a minimum value at about 40 mol % of ThF₄. Figure 2 also gives the measured surface tension isotherm for the LiF-BeF₂ binary melts having a large negative deviation, which was explained to be caused by the decrease of the number of constituent ions due to the formation of complex ion in the melts (4). The formation of the complex ion BeF₄²⁻ in these binary melts results in the minimum number of constituent ions and therefore in the minimum value of the surface tension at 33.3 mol % of BeF₂. By analogy with BeF₄²⁻, the existence of some complex ion such as ThF₆²⁻ may be expected in the LiF-ThF₄ binary

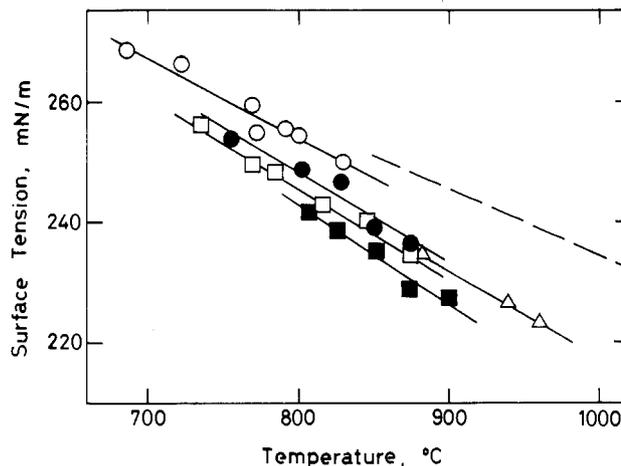


Figure 1. Variation of surface tension of LiF-ThF₄ binary melts with temperature. Open and closed circles, open and closed rectangles, and open triangles are the experimental values of the surface tension of 20, 30, 33.3, 40, and 50 mol % ThF₄ melts, respectively. The broken line represents those of pure LiF published in ref 12.

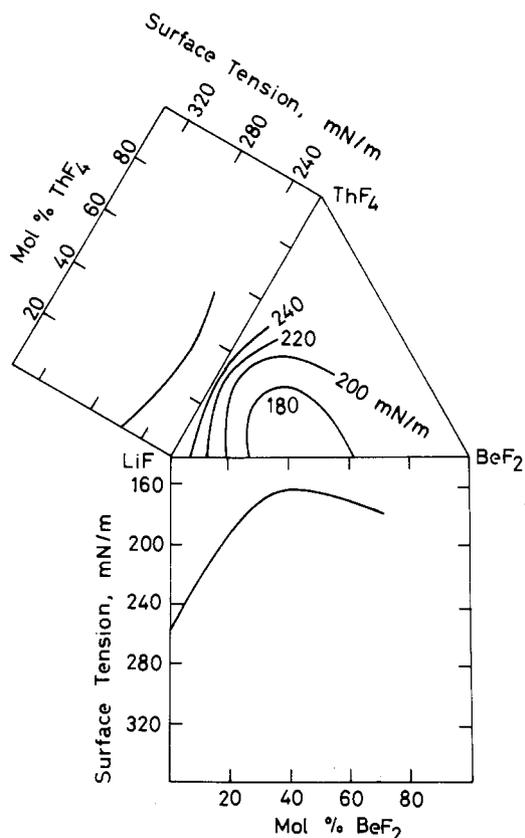


Figure 2. Surface tension isotherms for LiF-ThF₄ and LiF-BeF₂ binary melts at 800 °C and the surface tension contour of LiF-BeF₂-ThF₄ ternary melts at 800 °C.

melts from the minimum surface tension near 33.3 mol % ThF₄ (LiF:ThF₄ = 2:1). The complex ion ThF₆²⁻ has also been predicted in the study of reductive extraction between molten salt and liquid metal phases (11). The less negative deviation for the LiF-ThF₄ binary melts than for the LiF-BeF₂ melts indicates that the formation of ThF₆²⁻ occurs only partially in contrast with an almost complete formation of BeF₄²⁻.

The triangular diagram in Figure 2 shows the surface tension contours for the LiF-BeF₂-ThF₄ ternary melts at 800 °C drawn with the data given in Table II by assuming linear temperature dependence and linear composition dependence within a narrow range. Addition of a small amount of BeF₂ into the LiF-ThF₄ binary melts gives rise to an abrupt decrease in the sur-

face tension for the ternary melts. Judging from the shape of the contour, the lowest bottom of the surface tension isotherm seems to be near the point of $\text{LiF}:\text{BeF}_2 = 2:1$ on the $\text{LiF}-\text{BeF}_2$ axis, and the formation of BeF_4^{2-} is almost essentially complete in the ternary system as well as in the $\text{LiF}-\text{BeF}_2$ binary melts.

Conclusion

The surface tensions of $\text{LiF}-\text{ThF}_4$ binary melts and $\text{LiF}-\text{BeF}_2-\text{ThF}_4$ ternary melts were measured by the maximum bubble pressure method. The surface tension isotherm for the binary melts showed a slight negative deviation from additivity and a minimum near the composition of $\text{LiF}:\text{ThF}_4 = 2:1$. The addition of BeF_2 into the $\text{LiF}-\text{ThF}_4$ binary melts brought an abrupt decrease of the surface tension of the ternary melts. The former result may be attributed to a partial formation of a complex ion such as ThF_6^{2-} and the latter seems to be due to a complete formation of BeF_4^{2-} in the ternary melts.

These data are expected to be useful in handling the fuel solvent of MSBR.

Registry No. LiF , 7789-24-4; ThF_4 , 13709-59-6; BeF_2 , 7787-49-7.

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Diffusion of Propane in Helium

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The apparatus used by Yang and Hawkes had been modified to give greater mechanical reliability and its reliability has been demonstrated. The diffusion coefficients of a *n*-propane in helium at 1.0 atm from 21.3 to 60.3 °C were determined by using the new apparatus and follow the equation $\log D_{12} = -8.1277 + 3.0805 \log T$ with a correlation coefficient of 0.9976 where D_{12} is in cm^2/s and T is in Kelvin.

Yang, Hawkes, and Lindstrom have described (1) a method for the determination of diffusion coefficients of organic tracers in inorganic gases, using Knox and McLaren's "arrested-elution" variant (2) of the chromatographic method. Briefly, a narrow zone of tracer was injected into a stream of helium and carried to the center of a long, narrow tube. The flow was then stopped and the tracer was allowed to diffuse for a measured time. The flow was then restarted and the tracer was swept out of the column through a detector which recorded the concentration-time curve. This was approximately a Gaussian peak. The exact equation to the peak was derived and fitted to the data to give the value of D_{12} as the only fitted data point.

Supplying an initial input zone of negligible width required a specially designed valve. This failed repeatedly so that a new and more reliable inlet system seemed desirable.

Experimental Section

The apparatus and the methodology were similar to those of Yang and Hawkes (1) with the following modified injection system.

The diffusant (*n*-propane) was injected into a stream of helium by using a Loenco chromatographic injection valve. The mixture flowed through a Carle thermal conductivity detector whose output was observed on a strip-chart recorder. Near the top of the peak the flow was diverted into the main apparatus

Table I. Binary Molecular Diffusion Coefficient for $\text{C}_3\text{H}_8-\text{He}$

velocity of flow, cm/s	arrested time, s	temp, °C	D_{12}^* , cm^2/s	$10^3(\text{std error of } D_{12}^*)^a$
2.938	300	21.3	0.3005	1.0
3.060	300	30.3	0.3292	1.0
3.192	300	40.1	0.3601	1.0
3.461	300	51.0	0.4104	1.1
3.678	300	60.3	0.4365	1.5

^a From least-squares fit.

for a few carefully timed seconds. The input distribution of the tracer was therefore nearly rectangular and its width was precisely known. The input distribution was only 1% of the final distribution so that any errors in its measurement had negligible effect.

Calculations

The value of D_{12} was calculated from Lindstrom's equation (1) exactly as before. The result was corrected for the measured input distribution by assuming that the variance of the output distribution σ_{out}^2 was the sum of the variances of the input distribution and the distribution due to diffusion; i.e.

$$\sigma_{\text{out}}^2 = \sigma_{\text{in}}^2 + \sigma_{\text{diff}}^2 \quad (1)$$

Using the Einstein equation (3) $\sigma_{\text{diff}}^2 = 2Dt$ and the equation for a rectangular distribution $\sigma^2 = L^2/12$ where L is the length of the rectangular input in units of length gave

$$D_{12} = D_{\text{measured}} - L^2/(24t) \quad (2)$$

Comparison with Measurement by Yang and Hawkes

Two determinations of D_{12} at 18.8 °C for methane in helium gave an average value of $0.6431 \pm 0.0017 \text{ cm}^2/\text{s}$. Interpo-