

Surface Tension Around Eutectic Compositions of Molten Alkali Carbonate Mixtures

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The surface tension around the eutectic composition of molten binary and ternary mixtures composed of Li_2CO_3 with Na_2CO_3 and/or K_2CO_3 has been measured by the maximum bubble pressure method. The surface tensions of all the three systems were represented as functions of temperature.

In recent years, much attention has been paid to the molten carbonate fuel cell as a promising power-generating device based on gasified fossil fuel. In this fuel cell, molten binary or ternary eutectic mixtures [1] composed of lithium, sodium, and potassium carbonates, maintained in a lithium aluminate, LiAlO_2 , matrix, are used as electrolyte because of low melting point, high electrical conductivity, and little fluctuation of composition during thermal cycles. In connection with this, numerous investigations on the thermodynamic and electrochemical properties of molten alkali carbonate mixtures [2] have been performed. The surface tension is involved in the dissolution of gas into the electrolyte and in the wettability of the electrode material by the electrolyte. Data on the surface tension at eutectic compositions of molten alkali carbonate mixtures are available [3, 4], but there are considerably differences in the results.

In the present study we report on the surface tension of the molten binaries $(\text{Li, Na})_2\text{CO}_3$ and $(\text{Li, K})_2\text{CO}_3$ in a small range including the eutectic composition and ternary $(\text{Li, Na, K})_2\text{CO}_3$ at the eutectic composition.

Experimental

Chemicals. The Li_2CO_3 , Na_2CO_3 , and K_2CO_3 of analytical reagent grade were dried to constant weight

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in a platinum crucible at 620 K. Known amounts of these chemicals were weighed in a glove box filled with dry argon and then melted in a Pt-10% Rh crucible under argon atmosphere at near their liquidus temperatures [5]. After 30 min the melts were quenched to prevent segregation. The solidified mixtures were stored in ampules until used.

Measurement. The maximum bubble pressure method as mentioned in [6] was applied. In deriving the surface tension by use of Schrödinger's equation [7], the molar volume of the melt is required. The molar volumes of these molten binary carbonate mixtures are given by Spedding [8]. In order to acquire the surface tension at the desired temperature and composition, these molar volumes were represented as functions of composition and temperature by a least squares fitting. The empirical equations obtained are for molten $(\text{Li, Na})_2\text{CO}_3$

$$V_m = 0.3997E + 2 - 0.5380E + 1X - 0.8106E + 1X^2 + 0.4454E + 1X^3 + (0.1206E - 1 - 0.4238E - 2X + 0.3449E - 2X^2 - 0.2186E - 2X^3)T \quad (1)$$

and for molten $(\text{Li, K})_2\text{CO}_3$

$$V_m = 0.5217E + 2 - 0.1689E + 2X - 0.9344E + 1X^2 + 0.4968E + 1X^3 + (0.1751E - 1 - 0.1025E - 1X + 0.5773E - 2X^2 - 0.4015E - 2X^3)T, \quad (2)$$

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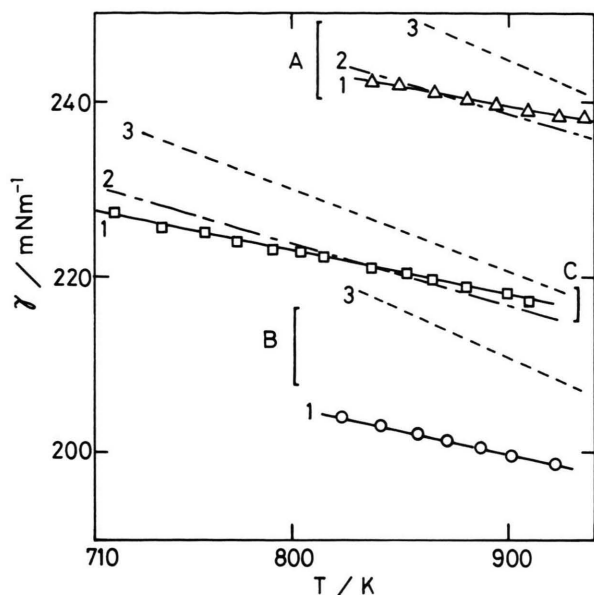


Fig. 1. Surface tension of molten $(\text{Li, Na})_2\text{CO}_3$ (A) and $(\text{Li, K})_2\text{CO}_3$ (B) and $\text{Li}_2\text{CO}_3\text{--Na}_2\text{CO}_3\text{--K}_2\text{CO}_3$ (C) mixtures of eutectic composition. 1: present study, 2: [4], 3: [3].

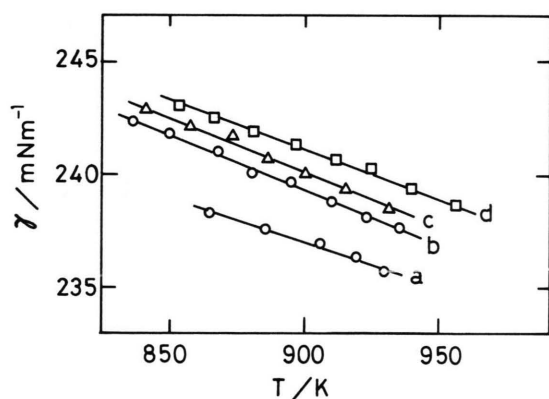


Fig. 2. Surface tensions of molten $(\text{Li, Na})_2\text{CO}_3$ mixtures. a: 43.6, b: 53.3, c: 58.3, d: 63.3 mol% Li_2CO_3 .

where T is the temperature in K and X the mole fraction of Li_2CO_3 . The density of the molten ternary system was taken from the values of Ward and Janz [3].

Prior to the measurements of the samples, the surface tension of molten KNO_3 was measured to obtain the precision of the apparatus. The surface tension of molten KNO_3 represented as a function of temperature is as follows:

$$\gamma = (157.2 - 74.21 \times 10^{-3} T/\text{K}) \text{ mNm}^{-1}. \quad (3)$$

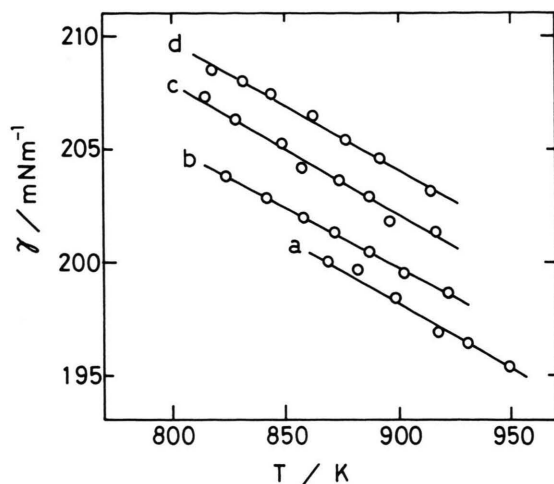


Fig. 3. Surface tension of molten $(\text{Li, K})_2\text{CO}_3$ mixtures. a: 37.7, b: 42.7, c: 47.7, d: 52.7 mol% Li_2CO_3 .

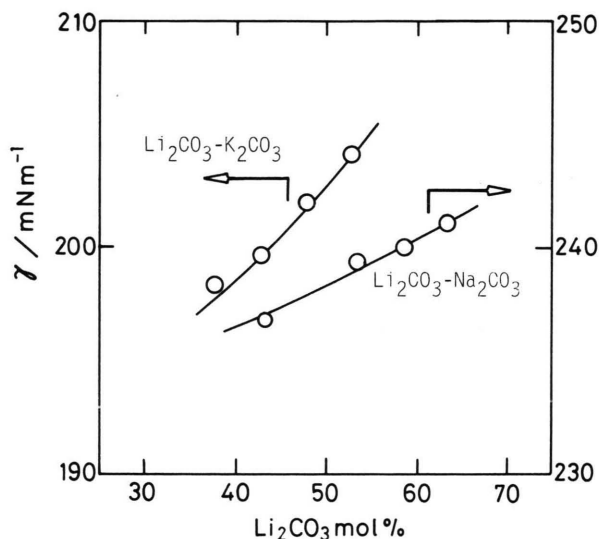


Fig. 4. Surface tension isotherms of molten $(\text{Li, Na})_2\text{CO}_3$ and $(\text{Li, K})_2\text{CO}_3$ mixtures at 900 K.

A comparison was made among the recommended values [9] and observed ones. Our results yield smaller values than the recommended ones, but the departures are within 1%.

Results and Discussion

As mentioned above, the surface tensions of the molten alkali carbonate mixtures $(\text{Li, Na})_2\text{CO}_3$ [3, 4], $(\text{Li, K})_2\text{CO}_3$ [3], and $(\text{Li, Na, K})_2\text{CO}_3$ [3, 4] at the eutectic compositions, 53.3:46.7 mol%, 42.7:57.3, and 43.5:31.5:25.0, respectively, have been reported.

Our present results for the eutectic compositions are compared with those of [3, 4] in Figure 1. Our data for $(\text{Li, Na})_2\text{CO}_3$ and the ternary system agree satisfactorily with those reported by Moiseev and Stepanov [4] while for all the three systems the surface tensions reported by Ward and Janz [3] are higher than those reported by us.

The surface tensions at four composition of the binary melts are shown in Figs. 2 and 3. From these values, linear functions of temperature were obtained by least squares fitting. The corresponding parameters are given in Table 1.

The surface tension isotherms for the binary melts at 900 K are shown in Figure 4. As seen in Fig. 4, the surface tension of the molten $(\text{Li, K})_2\text{CO}_3$ mixture varies much with composition because of the large difference of the surface tension of the constituting single melts. If the $(\text{Li, K})_2\text{CO}_3$ is used as electrolyte of the fuel cell, for the reason mentioned in the introduction a careful composition control would be required to maintain a constant performance.

Table 1. Surface tensions of molten binary $(\text{Li, Na})_2\text{CO}_3$, $(\text{Li, K})_2\text{CO}_3$, and $(\text{Li, Na, K})_2\text{CO}_3$ mixtures. SE indicates the estimated standard error. $\gamma = (a - b \cdot T/\text{K}) \text{ mNm}^{-1}$.

Li_2CO_3 mol%	a	$b \times 10^2$	SE	Temp. range
$(\text{Li, Na})_2\text{CO}_3$				
43.6	269.0	3.55	0.071	(865–925)/K
53.3	282.6	4.80	0.099	(838–936)/K
58.3	286.2	5.13	0.205	(827–931)/K
63.3	279.3	4.24	0.122	(883–957)/K
$(\text{Li, K})_2\text{CO}_3$				
37.7	249.5	5.70	0.271	(869–950)/K
42.7	247.5	5.31	0.057	(823–922)/K
47.7	256.4	6.05	0.247	(815–916)/K
52.7	255.3	5.69	0.170	(818–914)/K
$\text{Li}_2\text{CO}_3 - \text{Na}_2\text{CO}_3 - \text{K}_2\text{CO}_3$ (43.5–31.5–25.0 mol%)				
	263.5	5.08	0.206	(719–910)/K

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