Volumetric Anomalies in the Molten Salt Systems KI-TlI and TlCl-TlBr

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The densities of molten KI and TlI measured pyknometrically at various temperatures are slightly higher (0.1–0.2%) than the Archimedian values previously found by other workers. Molar volumes in the molten systems KI-TlI and TlCl-TlBr have also been measured pyknometrically. In the first system the relative excess volume is negative and in the second positive but as usual the melts expand on heating. The maximum deviations are about 2.5% and 1.5% respectively. In KI-TlI the excess volume-composition isotherm shows a double minimum at low temperatures, resembling the shape of the electrical conductance isotherms. The attribution of volumetric contractions to the relaxation of the thallium-ligand binding is supported by these results and by nmr evidence.

The electrical conductance of molten KI, TlI and their mixtures was reported previously[1], the mixture isotherms at 640 °C and 697 °C showing negative deviations from additivity with slight double minima. In the present paper we give volumetric data for these melts and also for the system TlCl-TlBr.

Experimental

As before[2–4] the pyknometric method was used to measure liquid densities. The sources and methods of purification of the materials were also as before[1].

Results and Discussion

1. *Pure Salts*

KI

The density (ϱ, g cm^{-3}) data determined at 6 temperatures (t, °C) between 740 °C and 920 °C conform to the equation

$$\varrho = 3.124_3 - 0.976_1 \cdot 10^{-3}\, t$$

with a standard deviation of 0.001_2. Our values were within 0.2% of those of Bloom et al.[5] and Yaffe and Van Artsdalen[6], being once again[2–4] higher. Jaeger[7] gave an appreciably more negative value for the temperature coefficient and his data diverge more extensively than ours from the other Archimedean results[5, 6].

From the molar volume of fusion[8], $\Delta v_{\mathrm{f}} = 9.30$ cm^3, and the molar entropy of fusion[9], $\Delta s_{\mathrm{f}} = 6.02$ cal/K, we derive for the slope of the melting curve $(\mathrm{d}T_{\mathrm{f}}/\mathrm{d}p)_{p=1} = 3.62 \cdot 10^{-2}$ K/bar, while our density equation gives with Δv_{f} the value $v_{\mathrm{s}} = 58.20$ cm^3 for the molar volume of the solid at the melting point (681 °C at 1 bar, Reference[9]). This compares with $v_{\mathrm{s}} = 59.41$ cm^3 estimated from linear expansion measurements on the solid made by Eucken and Dannoehl[10].

TlI

Data obtained at 7 temperatures between 535 °C and 740 °C gave

$$\varrho = 6.994_0 - 1.981_3 \cdot 10^{-3}\, t$$

with standard deviation 0.001_5. It is of interest that the density of molten TlBr follows a closely similar equation[2]. The two melts have equal densities at about 600 °C, the bromide being slightly the denser above this point and the iodide below it. Other sources of data on ϱ_{TlI} appear to be lacking, as are the values of the solid expansivity and the fusion volume.

2. *Mixtures*

The system KI-TlI was studied at 2 temperatures and TlCl-TlBr at 3 temperatures. Molar volumes are given in Tables 1 and 2 and relative excess volumes in Figs. 1 and 2. The nature of the errors was discussed previously[3].

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Table 1. Mean molar volumes (cm³) in molten TlCl-TlBr mixtures.

513 °C		576 °C		650 °C	
x_{TlBr} * (±0.002)	v (±0.10)**	x_{TlBr} * (±0.002)	v (±0.10)**	x_{TlBr} * (±0.002)	v (±0.10)**
0.000	43.7_2	0.000	44.6_8	0.000	45.8_7
0.210	44.8_1	0.207	45.7_3	0.340	47.9_2
0.257	45.1_1	0.250	46.0_3	0.398	48.1_4
0.340	45.4_1	0.337	46.4_6	0.471	48.5_0
0.391	45.6_2	0.345	46.5_0	0.520	48.7_4
0.438	45.7_0	0.355	46.5_4	0.588	49.0_7
0.477	45.8_9	0.454	46.9_6	0.707	49.4_7
0.566	46.2_7	0.466	47.0_6	0.796	49.5_6
0.642	46.6_1	0.556	47.4_3	0.813	49.7_4
0.695	46.8_3	0.574	47.4_6	1.000	50.2_4
0.790	47.2_2	0.600	47.5_7		
0.775	47.1_6	0.616	47.5_8		
0.824	47.3_3	0.693	47.9_2		
1.000	48.0_0	0.732	48.0_8		
		0.832	48.4_1		
		1.000	49.0_1		

* Mean value of mol fraction with limits of variation during experiment.

** Limits of error ignoring the uncertainty in x.

Table 2. Mean molar volumes (cm³) in molten KI-TlI mixtures.

640 °C

x_{TlI} * (±0.001)	v (±0.10)**	x_{TlI} * (±0.001)	v (±0.10)**
0.000	66.4_1	0.505	61.6_7
0.242	63.4_7	0.554	61.2_8
0.278	63.1_2	0.563	61.1_5
0.293	62.8_7	0.581	60.9_1
0.324	62.7_5	0.617	60.3_8
0.330	62.7_3	0.632	60.2_2
0.338	62.7_6	0.666	59.6_2
0.345	62.7_1	0.680	59.4_9
0.392	62.4_6	0.697	59.4_2
0.397	62.4_2	0.728	59.1_3
0.435	62.2_6	0.768	58.7_6
0.451	62.2_1	0.820	58.5_4
0.450	62.1_5	0.837	58.5_2
0.491	61.8_9	1.000	58.3_7
0.490	61.7_8		

697 °C

x_{TlI} * (±0.001)	v (±0.10)**	x_{TlI} * (±0.001)	v (±0.10)**
0.000	67.9_2	0.515	63.1_9
0.077	67.2_1	0.564	62.5_1
0.159	66.4_6	0.617	62.2_0
0.198	66.2_6	0.666	61.7_2
0.185	66.2_0	0.667	61.6_7
0.242	65.6_4	0.768	60.8_1
0.291	65.1_1	0.865	60.1_7
0.339	64.6_6	1.000	59.5_5
0.367	64.4_0		
0.406	64.0_5		
0.413	64.0_1		
0.429	63.8_9		
0.445	63.7_0		
0.500	63.2_6		

* Mean value of mol fraction with limits of variation during experiment.

** Limits of error ignoring the uncertainty in x.

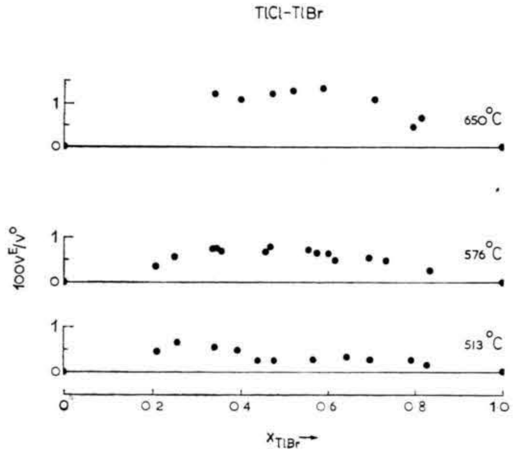

Fig. 1. Relative excess volumes in TlCl-TlBr at 513°, 576° and 650 °C.

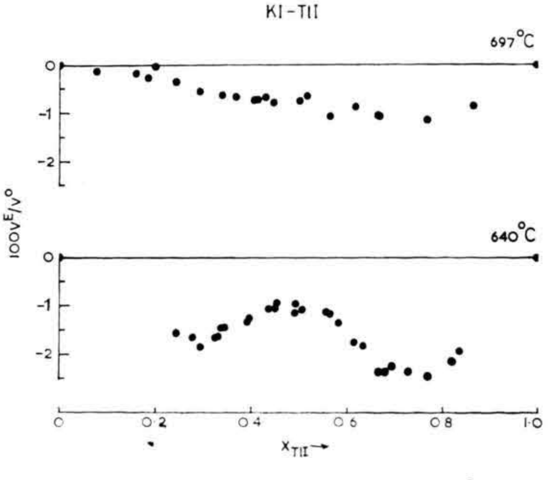

Fig. 2. Relative excess volumes in KI-TlI at 640° and 697 °C.

The tendency of negative v^E to decrease and positive v^E to increase with rise in temperature is once more evident. The results are different from those for the other MX-TlX systems reported on in showing wholly positive excess volumes in TlCl-TlBr and negative excess volumes in KI-TlI. An additional new feature is the double minimum in the latter case, recalling the shapes of the conductance isotherms in this system [1].

If it may be assumed as an approximation that in the common-cation system TlCl-TlBr isothermal dilution of one molten salt by the other has a negligible effect on the nearest cation-anion coordination, the anomalous volume would only be attributable to variation with composition of the average distances between more remote neighbours. What we have put forward as the contraction mechanism[4], viz., an increase in the Tl-X separation, is then absent in this system. The separation of the anion X from Tl affects the chemical shift in the nmr frequency of Tl^{205}, and it was observed by Hafner and Nachtrieb[11] that the system TlCl-TlBr has a single resonance line and a linear variation of chemical shift with composition. It was concluded that local configurations in which either Cl or Br were the only nearest neighbours of Tl were unlikely to be present.

The hypothesis that atomic configurations special to the molten mixtures are indicated by anomalous contractions is strengthened by this evidence. Among the systems we have studied the anionic polarizability is highest in KI-TlI. The tendency for the cation $M = K^+$ to induce the separation of Tl and X and achieve an economy in the total volume is also most notable in this system even though the degree of contraction around $x_{\mathrm{TlX}} = 1/3$ is not as great as in KBr-TlBr. It seems logical to connect the power of MX to separate Tl and X with the strength of the attraction of M for X. However it is not necessarily polarization or incipient covalence behind the effects observed. Recent calculations by the method of molecular dynamics[12, 13] have shown that for a melt composed of K^+, Mg^{2+} and Cl^- a preponderance of local configurations such as $MgCl_3^-$ or $MgCl_4^{2-}$ may be predicted on the basis of a pair-interaction model depending on the values taken for the repulsion radii in the expressions for the interionic potentials. An important point about the calculations is that the potentials are representative of central forces, and so do not involve directed valencies. It is possible that similar calculations on the present systems could provide a test of our contraction hypothesis.

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