Molar Volumes in Molten NaBr, RbBr, NaBr-TlBr and RbBr-TlBr

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Densities in molten NaBr and RbBr and molar volumes in their binary mixtures with TlBr are reported. The pyknometric method again gave slightly higher densities (0.1—0.2%) than previous Archimedean methods. In the mixtures the excess volume is no greater than ±1% but its variation with composition and temperature broadly resembles that in the MX-TlX systems reported previously. A relationship is apparent between the overall trend in the molar volume with composition and temperature and the variation in the Tl-X overlap by nmr. Together with the stoichiometry, this suggests that in the region of strong negative deviation coordination is high and localized orbital overlap low between cations and anions.

In continuation of our studies on the constitution of salt melts by the measurements of physical properties, we have applied the techniques of iridium pyknometry [1, 2] to the following: NaBr, RbBr, NaBr-TlBr, RbBr-TlBr.

Experimental

The NaBr was of analytical grade (B.D.H.) and the RbBr was of 99.95% purity (Johnson-Matthey). The TlBr was of the same quality as before and all techniques were as previously described.

Results and Discussion

1. Pure Salts

NaBr

The density (ϱ, g cm^{-3}) was measured at 7 temperatures (t, °C) in the range 780.3 – 958.1 °C and gave:

$$\varrho = 2.948_7 - 0.807_3 \times 10^{-3}\, t$$

with a standard deviation of 0.000_8. The Archimedean data of Yaffe and Van Artsdalen [3] lie consistently 0.2% lower although their temperature coefficient (-0.8169×10^{-3}) was slightly higher. Earlier determinations [4–7] are characterized by lower values of ϱ but the temperature coefficients were not greatly different.

From our equation for ϱ we obtain 43.87 cm^3 for the molar volume $v_{\rm L}$ of the melt at the melting point (747 °C, Ref. 8). Extrapolation of the room-temperature density using 42.52×10^{-6} for the linear expansivity [9] gives $v_{\rm s} = 35.21$ cm^3 for the molar volume of the solid at the melting point and hence $\Delta v_{\rm f} = 8.66$ cm^3 for the molar expansion on fusion and $\Delta v_{\rm f}/v_{\rm s} = 0.246$ for the relative expansion. The dilatometric measurements of Schinke and Sauerwald [10] gave $\Delta v_{\rm f} = 8.07$, from which one obtains from our $v_{\rm L}$ the values $v_{\rm s} = 35.80$ and $\Delta v_{\rm f}/v_{\rm s} = 0.225$. The molar entropy of fusion is [8] $\Delta s_{\rm f} = 6.1$ cal K^{-1}, and gives $({\rm d}T_{\rm f}/dp)_{p=1} = 3.19 \times 10^{-2}$ atm^{-1} K when we use Clapeyron's equation and the dilatometric $\Delta v_{\rm f}$. From Clark's data [11], $({\rm d}T_{\rm f}/{\rm d}p)_{p=1} = 2.87 \times 10^{-2}$. The discrepancy between these values is made worse by employing $\Delta v_{\rm f} = 8.66$.

RbBr

The following equation was obtained from 5 density measurements between 750.0 and 873.0 °C:

$$\varrho = 3.448_6 - 1.070_9 \times 10^{-3}\, t\,,$$

standard deviation 0.000_9. Yaffe and Van Artsdalen [3] found by Archimedean displacement:

$$\varrho = 3.446_4 - 1.071_8 \times 10^{-3}\, t$$

over the range 700 – 910 °C. Our results are again higher but only by 0.1%. We estimate that this is of the order of magnitude of the surface tension correction in Yaffe and Van Artsdalen's measurements. Jaeger's results [6] were 0.5% lower than ours but his value for the melting point was 683 °C (cf. 692 °C, Ref. 8), suggesting substantial amounts of impurities.

From our results, $v_{\rm L} = 61.09$ cm^3 so that $v_{\rm s} = 53.83$ cm^3 if we take the figure of $\Delta v_{\rm f} = 7.26$ cm^3 reported by Schinke and Sauerwald [10]. Dworkin and Bredig [8] gave $\Delta s_{\rm f} = 5.77$ cal K^{-1} so that we estimate $({\rm d}T_{\rm f}/{\rm d}p)_{p=1} = 3.04 \times 10^{-2}$ atm^{-1} K for the slope of the melting line at atmosphere pressure.

2. Mixtures

NaBr-TlBr was studied at 750 and 790 °C, and RbBr-TlBr at 700 and 760 °C. Tables 1 and 2 give

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the data for the mean molar volume, v, and Figures 1 and 2 show the isotherms of the relative excess volume, v^E/v°. The tabulated values of x_{TlBr} are the means of the values obtained by analysis before and after filling the pyknometer. The uncertainty limits given for v and x were arrived at as before [2].

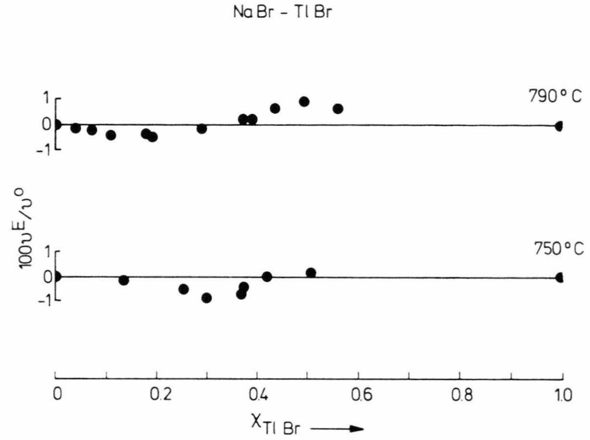

Fig. 1. Relative excess volumes in NaBr-TlBr at 750 °C and 790 °C.

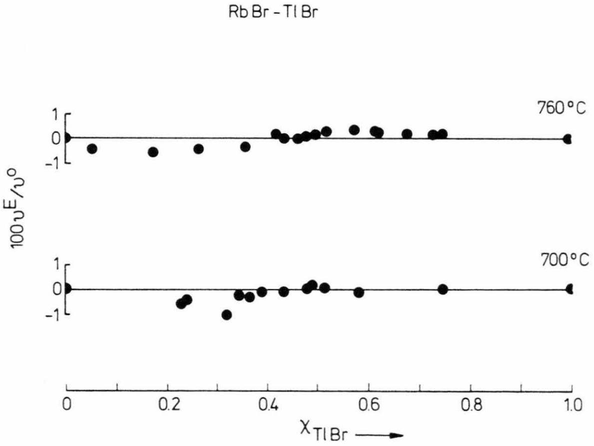

Fig. 2. Relative excess volumes in RbBr-TlBr at 700 °C and 760 °C.

The five MX-TlX systems we have examined show parallelism between the direction of the change in v and the direction of the chemical shift [12]. In RbCl-TlCl, RbBr-TlBr and KBr-TlBr the molar volume increases and the shift of the Tl^{205} resonance is "downfield" when MX is added to TlX. In NaBr-TlBr we have for the first time a system in which v decreases as x_{MX} increases, and in this mixture the chemical shift is upfield. The case of KCl-TCl is borderline. This system shows the weakest downfield shift and the smallest overall expansion on passing from pure TlX to pure MX.

From this correlation between the volumes and the chemical shifts it is possible to draw the following conclusions. When expansion occurs as the result of the dilution of TlX by MX, there is an increase in the average separation of the Tl cores which permits their tighter binding to the ligands X.

Table 1. Mean Molar Volumes (cm³) in Molten NaBr-TlBr Mixtures.

750 °C x_{TlBr} * (± 0.001)	v (± 0.05) **	790 °C x_{TlBr} * (± 0.002)	v (± 0.05) **
0.000	43.9_2	0.000	44.5_3
0.134	44.9_5	0.039	44.8_0
0.254	45.7_0	0.072	45.0_0
0.302	45.9_2	0.110	45.2_5
0.370	46.5_5	0.181	45.8_5
0.373	46.7_1	0.193	45.9_0
0.422	47.3_0	0.290	46.8_5
0.508	48.0_8	0.371	47.6_8
1.00	52.0_0	0.391	47.8_4
		0.437	48.4_3
		0.495	49.0_4
		0.559	49.4_3
		1.000	52.7_4

* Mean value of mol. fraction with limits of variation during experiment.
** Limits of error ignoring the uncertainty in $\varkappa$.

Table 2. Mean Molar Volumes (cm³) in Molten RbBr-TlBr Mixtures.

700 °C x_{TlBr} * (± 0.001)	v (± 0.05) **	760 °C x_{TlBr} * (± 0.001)	v (± 0.05) **
0.000	61.2_8	0.000	62.7_8
0.230	58.6_0	0.053	61.9_7
0.241	58.5_5	0.175	60.5_8
0.320	57.4_0	0.265	59.7_0
0.343	57.6_3	0.360	58.7_5
0.367	57.3_5	0.420	58.3_5
0.391	57.2_3	0.437	58.1_5
0.392	57.2_2	0.465	57.8_4
0.435	56.7_8	0.482	57.7_2
0.480	56.4_5	0.502	57.5_5
0.488	56.4_0	0.522	57.4_0
0.513	56.1_0	0.576	56.8_5
0.581	55.3_0	0.615	56.4_2
0.749	53.6_5	0.620	56.3_5
1.000	51.1_0	0.680	55.6_7
		0.732	55.1_0
		0.752	54.8_8
		1.000	52.1_9

* Mean value of mol. fraction with limits of variation during experiment.
** Limits of error ignoring the uncertainty in x.

In harmony with this is the general tendency of v to increase and the thallium resonance to shift downfield when a mixture is heated. The converse holds if v is decreased on passing from pure TlX to pure MX. The resonant frequency is then displaced upfield (that is, it decreases) because the electron density between Tl and X is falling off.

Although in its general direction the variation of v with composition is plainly linked to the chemical shift it is found on comparing systems that the relative strengths of the volumetric deviations do not follow the same order as the relative strengths of the chemical shifts. Two volumetric properties of mixed ionic melts may be distinguished, which relate to the change of v when either the composition or the temperature is fixed. The excess volume V^E conventionally refers to the anomalous expansion on mixing at constant temperature and pressure. For present purposes (isobaric experiments) this may be called the *anomalous isothermal expansion*. The other property is the *anomalous thermal expansion* and this becomes evident on comparing various V^E isotherms of a mixture at fixed composition. The problem is seen by noting first that NaBr-TlBr has a larger positive V^E than RbBr-TlBr but a smaller one than KBr-TlBr. The strength of the anomalous isothermal expansion therefore increases in the order Rb, Na, K but the downfield chemical shift increases in the order Na, K, Rb. Secondly, we have already noted[2] that the sizes of the anomalous thermal expansions in RbCl-TlCl and KCl-TlCl are in the order $K > Rb$, that is, the reverse of that shown by the downfield chemical shifts ($K < Rb$). It is now apparent that in the bromides also the strength of the anomalous thermal expansion increases as $Rb < Na < K$. There is the added complication here of the very strong negative V^E in KBr-TlBr which is resistant to temperature rise. It is clear that as applied to these three mixtures, the empirical rule[13] that thermal expansivity is greater in melts of high covalence is in conflict with Hafner and Nachtrieb's interpretation of the signs and magnitudes of the chemical shifts.

There appear to be structural effects not detected by nmr that influence v in these systems. Although thermal expansion is universal in melts, in the MX-TlX systems the anomalous thermal expansion shows a significant variation with the choice of M or X, being particularly small in RbBr-TlBr and high in KBr-TlBr. The tendency to contract at certain compositions (negative, anomalous isothermal expansion) is particularly sensitive to the choice of M but it is always stronger at low temperatures. Now at low temperatures the Tl-X binding is weak (Fig. 5, Ref. 12) so that the contraction mechanism probably involves an *increase* in the average separation of Tl and X. This conclusion is reached on the strength of the nmr results and contrasts with our earlier suspicion that the shrinkage was caused by complex-formation[1]. The increased Tl-X separation may come about as the result of greater prominence of the non-saturable attractive forces, such as the Coulomb and London attractions, at these compositions.

The conditions for a dense liquid structure are particularly favourable in KBr-TlBr, and achieve their optimum at the composition 2 KBr · TlBr. At this composition the volumetric contraction is comparable[1] to Δv_f in KBr but there is no solid compound. It suggests that as this point is approached during isothermal mixing there is a substantial rise in the average coordination between anions and cations without the onset of long-range order.

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