Molar Volumes in Molten KCl, RbCl, TlCl, KCl–TlCl, and RbCl–TlCl

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Densities in molten KCl, RbCl, TlCl, KCl–TlCl and RbCl–TlCl at various temperatures (t °C) were measured to within ±0.1% by iridium pyknometry. For the pure melts the results fit empirical equations of the form $\varrho = a - b\,t$. The molar volumes at the melting points were derived and tested against other melting-point data for thermodynamic consistency. In the mixtures the volumes deviate from additivity in both directions, and it is again evident that the sign and magnitude of the deviation at a given composition are sensitive to temperature. In the present systems the negative deviations are much less persistent at high temperatures than in KBr–TlBr.

The pyknometric method[1] has been successfully used to measure densities in molten metallic halides and their mixtures with considerable precision. Its advantage over the commoner method of Archimedean displacement lies in the reduction in the evaporation losses that is achieved, and it has proved especially useful for halide mixtures containing thallium-I. We now report densities of the pure melts of KCl, RbCl and TlCl and molar volumes of the binary mixtures KCl – TlCl and RbCl – TlCl obtained by the pyknometric method. These results extend our previous data on the volumetric and conductimetric properties of the molten systems MX – TlX, where M is an alkali metal and X a halogen. The solid systems are unremarkable in forming eutectics or solid solutions, and, except for the pairing tendency of Tl^+, there are close similarities in the aqueous solution chemistry of alkali and thallium-I cations. It is therefore of considerable interest that the melts have volumetric anomalies that vary considerably in strength with the choice of M and X and which provide indirect but fairly clear evidence of composition-dependent co-ordination in these media.

Experimental

The KCl was of analytical quality. The TlCl and RbCl were prepared by Johnson-Matthey from metal of 99.9% and 99.95% purity, respectively. The TlCl was vacuum-dried at ordinary temperatures for several days prior to use. The other compounds were oven-dried at 200 °C and then stored *in vacuo*. Melts were prepared by mixing weighed amounts of the dried powders and melting in silica test-tubes[1] under dry, oxygen-free argon. The pyknometric apparatus, manipulations and chemical analysis were as previously described[1]. The TlCl was a white powder which melted to a straw-yellow liquid. The mixtures also were yellow. This was in contrast to TlBr and TlI and their mixtures, which were deep red[1, 2].

Results and Discussion

1. *Pure Salts*

KCl

The density (ϱ, g cm^{-3}) was measured at 15 temperatures (t, °C) in the range 773 – 948 °C. It is linear in this range and fits the equation:

$$\varrho = 1.942_8 - 0.519_4 \times 10^{-3}\, t$$

with standard deviation 0.000_9. Of the many previous determinations[3], all of which gave lower densities, the dilatometric data of Klemm[4] and the Archimedean data of Bloom et al.[5] are closest to ours (within 0.5%). The differences are apparently the result of systematic errors as the coefficients of t show reasonable agreement among authors. The molar volume of the liquid, v_L, derived from the extrapolated density (1.584_4) at the melting point, T_f, (670 °C, Ref. [6]), is 47.08 cm³.

Expansion measurements by Bockris et al.[7] gave $v_S = 40.65$ cm³ for the molar volume of the solid at the melting point, from which we obtain $\Delta v_f = 6.43$ cm³ for the molar expansion on fusion at 1 atm. and

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$\Delta v_f/v_S = 0.158$. By direct measurement, SCHINKE and SAUERWALD [8] found $\Delta v_f = 7{,}20$ cm^3 but LANDON and UBBELOHDE [9] gave 8.35 cm^3. Agreement with these measured Δv_f is not improved by taking the value of $v_S = 41.86 \pm 0.01$ derived from the results of two earlier investigations [10, 11] to calculate $v_L - v_S$.

The several values of Δv_f may be tested by combining them with the entropy of fusion in Clapeyron's equation. Taking $\Delta s_f = 6.08$ cal K^{-1} (Ref. [6]) we obtain $(\mathrm{d}T_f/\mathrm{d}p)_{p=1} = 2.56 \times 10^{-2}$ K atm^{-1} for the pressure coefficient of the melting point at 1 atm when Δv_f is taken as 6.43 cm^3. This result for the pressure coefficient is in best agreement with the value of 2.65×10^{-2} obtained by extrapolation of the direct measurements of CLARK [12].

RbCl

Density measurements at 6 temperatures in the range 757 – 850 °C gave

$$\varrho = 2.909_1 - 0.896_2 \times 10^{-3}\, t\,,$$

standard deviation 0.000_2. This line lies about 0.5% higher than the lines of KLEMM [4] and YAFFE and VAN ARTSDALEN [13]. The present result gives $v_L = 53.47$ cm^3 at the melting point (722 °C, Ref. [6]).

SCHINKE and SAUERWALD [9] gave $\Delta v_f = 6.72$ cm^3, from which we derive $v_S = 46.75$ cm^3 and $\Delta v_f/v_S = 0.144$. DWORKIN and BREDIG [6] gave $\Delta s_f = 5.70$ cal K^{-1}, from which we obtain $(\mathrm{d}T_f/\mathrm{d}p)_{p=1} = 2.85 \times 10^{-2}$ K atm^{-1}. This may be compared with the value 2.49×10^{-2} obtained from CLARK's data [12].

TlCl

KLEMM [4] gave $\varrho = 5.628 - 1.8 \times 10^{-3}\ (t - 430)$ in the range 435 – 642 °C. We have extended the range by making measurements at 646.7, 690.1 and 761.6 °C, for which we obtain:

$$\varrho = 6.449_6 - 1.878_7 \times 10^{-3}\, t\,,$$

standard deviation 0.001. The agreement with Klemm's line is excellent.

From the density and expansivity of the solid at room temperature [14] we estimate $v_S = 36.47$ cm^3 at the melting point (430.8 °C, Ref. [15]). Our equation for ϱ_L gives $v_L = 42.51$ cm^3. Therefore $\Delta v_f = 6.04$ cm^3 and $\Delta v_f/v_S = 0.166$. This value for the relative expansion on melting is comparable to the value for KCl, whereas the value estimated for TlBr was much larger and closer to the values for the caesium halides of simple cubic structure [1].

2. *Mixtures*

Each system was investigated at 3 temperatures. The results are presented in Tables 1 and 2 in the form of the mean molar volume, $v = \varrho^{-1} \sum x_i M_i$ at various compositions, x_{TlCl}. The composition of the melt in the main bath varied slightly during each density determination as the result of volatilization of TlCl. The mean compositions and the limits of variation are given in the tables and were determined by analysis of bath samples taken immediately before and after the pyknometer was filled [1]. Losses of TlCl by evaporation from inside the pyknometer may be neglected because of the small bore of the stopper and the short time that the orifice was exposed to the atmosphere at high temperatures. The extent of loss of TlCl by diffusion into the main bath while the pyknometer attained temperature equilibrium after filling is not known with certainty but must also have been very small. It is therefore reasonable to assume that the contents of the pyknometer had compositions very close to that of the bath when the stopper was lowered into place. The values given for v were calculated from the density and the mean bath composition. The limits of error on v depend on x as well as on ϱ so that if the error limits for x in the bath were used for the calculation the precision on v would be grossly underestimated. The v's in the tables are consequently given to the 4-th significant figure because the relative error of density measurement was below ± 0.001 and we have ignored the uncertainty in x.

Isotherms of the relative excess volume, $V^E/V^0 = (V - V_1 - V_2)/(V_1 + V_2)$, are drawn in Figures 1 and 2. Both systems show negative and positive excess volumes, the negative giving way completely to positive with increase in temperature. They therefore show an essential difference from KBr – TlBr, for which a region of negative v^E with a sharp minimum has been observed. The minimum in this system continues to penetrate the broad positive deviation that develops at the highest temperatures investigated [1]. Apart from its sharpness, the depth of the v^E minimum in KBr – TlBr exceeds 6% of v^0, while in the present systems the deviations nowhere exceed 2% in either direction. Furthermore, the negative v^E in Figs. 1 and 2 are not obviously concentrated about the composition 2 MCl · TlCl although they are stronger on the MCl side.

The persistence of the sharp minimum in KBr – TlBr led us to suspect the existence of separate nega-

Table 1. Mean molar volumes (cm^3) in molten KCl—TlCl mixtures.

650 °C		700 °C		750 °C	
x_{TlCl} * (± 0.001)	v (± 0.05) **	x_{TlCl} * (± 0.002)	v (± 0.05) **	x_{TlCl} * (± 0.002)	v (± 0.05) **
0.000	46.4_5	0.000	47.2_1	0.000	48.0_0
0.488	45.6_7	0.316	46.9_2	0.257	48.3_6
0.540	45.7_1	0.349	46.9_2	0.274	48.3_7
0.643	45.7_7	0.367	46.9_1	0.290	48.3_9
0.671	45.7_6	0.397	47.0_1	0.303	48.5_0
0.793	45.8_8	0.408	47.0_0	0.354	48.5_7
0.800	45.8_8	0.474	47.2_0	0.358	48.5_8
0.904	45.8_8	0.483	47.2_3	0.405	48.6_3
1.000	45.8_7	0.502	47.3_2	0.449	48.6_4
		0.594	47.4_5	0.478	48.7_0
		0.695	47.4_6	0.555	48.6_5
		0.847	46.9_5	0.575	48.6_8
		1.000	47.2_1	0.656	48.3_9
				0.671	48.5_0
				0.773	48.2_8
				0.855	48.0_5
				1.000	47.5_8

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

Table 2. Mean molar volumes (cm^3) in molten RbCl—TlCl mixtures.

650 °C		690 °C		750 °C	
x_{TlCl} * (± 0.001)	v (± 0.05) **	x_{TlCl} * (± 0.001)	v (± 0.05) **	x_{TlCl} * (± 0.001)	v (± 0.05) **
0.000	51.9_8	0.000	52.8_0	0.000	54.0_7
0.337	49.6_7	0.187	51.7_0	0.206	53.0_0
0.357	49.5_0	0.277	51.4_2	0.272	52.4_8
0.443	49.3_0	0.385	50.7_3	0.327	52.5_5
0.502	48.9_5	0.444	50.3_7	0.368	52.3_5
0.582	48.6_5	0.557	49.8_0	0.358	52.3_2
0.645	48.1_5	0.594	49.5_5	0.400	52.2_5
0.732	47.6_0	0.657	49.2_0	0.505	51.7_4
0.809	47.0_5	0.682	49.0_0	0.520	51.7_7
0.912	46.3_5	0.733	48.6_7	0.558	51.4_4
1.000	45.8_7	0.800	48.1_7	0.605	51.0_4
		1.000	46.5_4	0.664	50.7_5
				0.761	49.8_2
				1.000	47.5_8

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

tive and positive volumetric effects and to suggest that the contraction, centred on the composition 2 KBr $\cdot$TlBr, was indicative of a complex anion, $TlBr_3^{2-}$. A minimum was also found in the electrical conductance of this system[2, 16]. The suggestion was made on the basis of observations at various compositions and temperatures[1]. It is now even more clearly apparent that it is important to vary the temperature because the sign as well as the magnitude of v^E may alter at any composition. This must be borne in mind in any attempt to interpret the volume and heat effects in mixtures by means of the quasi-chemical and conformal solution theories, which do not give the temperature dependance explicitly.

The hypothesis of separate positive and negative volume effects was also used by GRJÖTHEIM et al.[17] to interpret deviations in binary mixtures of $MgCl_2$ and $CaCl_2$ with alkali-metal and alkaline-earth-metal chlorides at 800 °C. They attributed the expansion effect to changes in Coulombic interactions or anionic polarizations and the contraction, which was absent in $CaCl_2$ mixtures, to breakdown of the bridge

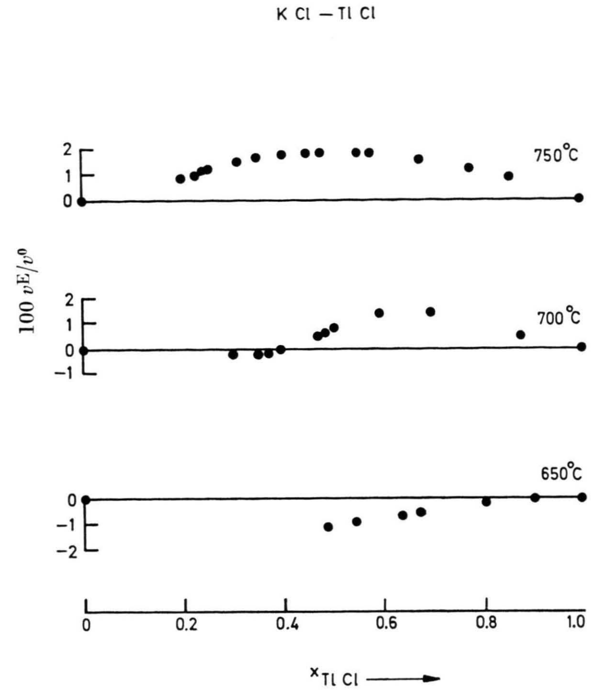

Fig. 1. Relative excess volumes in KCl–TlCl at 650°, 700° and 750 °C.

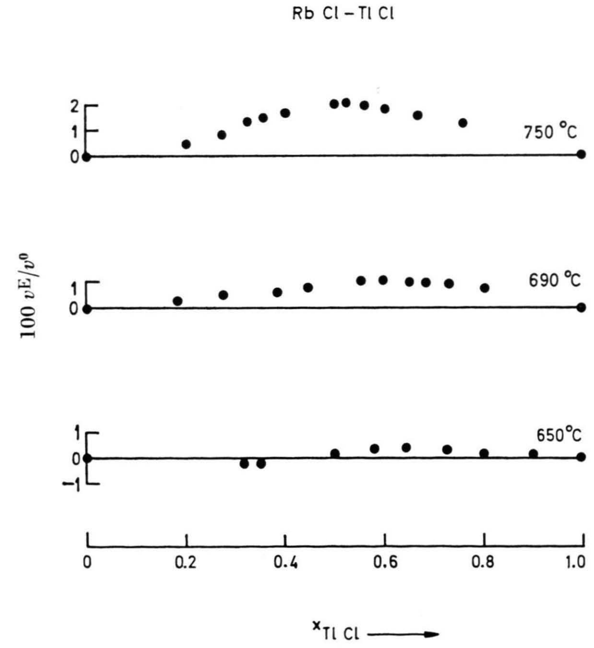

Fig. 2. Relative excess volumes in RbCl–TlCl at 650°, 690° and 750 °C.

structure of $MgCl_2$. The same authors tested their v^E data for the ternary systems (Na – Ca – Mg) Cl and (K – Ca – Mg) Cl against the expression given by the simple regular solution, or zeroth-order quasi-chemical, theory. The fit was poor, however, and could only be improved by introducing a ternary concentration term [17].

While our sigmoid curves can be fitted by the polynomial expressions for v^E which result from the extension of the conformal theory to the fourth order of approximation [18, 19] the procedure is entirely empirical and gives only values for the coefficients which are not susceptible of interpretation. Of more recent theoretical developments in which the form of the interionic potential was modified to include terms for van der Waals and polarization interactions [20–22] the Davis and Rice version was recently compared with experimental v^E for various binary nitrates by CLEAVER and NEIL [23]. It was concluded from the results of measurements on equimolar mixtures at a single temperature that the discrepancies found for systems containing either Ag(I) or Tl(I) were to be attributed to shortcomings of the theoretical potential model, in particular the absence of any term for covalent interaction between Ag^+ or Tl^+ and the ligand, NO_3^-.

With the fewer halide systems at our disposal we are of the opinion that the conformal theory is not likely to prove fruitful in interpreting v^E in MX – TlX, in which there are good reasons to suspect the occurrence of even stronger electron donation. Among other experimental studies on these systems, heats of mixing in MCl – TlCl were determined in a very narrow composition range at the TlCl end and showed that h^E is positive [24]. The volumetric excess is also positive or zero here (Figs. 1 and 2) but the systems do not obey the requirement of first-order conformal solution theory that the h and v deviations be symmetrical and of the same sign at all compositions, excepting possibly KCl – TlCl at 750 °C.

A considerable amount of evidence on ionic interaction in melts of the thallium halides and their mixtures with other univalent metal halides has resulted from nmr studies [25–28]. The chemical shift in the frequency of the Tl^{205} resonance is attributed to alterations in the screening of the nucleus by the 6s electrons which are excited into mixed sp orbitals and become paramagnetic [26, 29]. Screening is diminished by an increase in overlap of the thallium sp orbitals with orbitals of the ligands, X^-, and the effect of the foreign cations is in turn due to their power to polarize the ligands [28]. The chemical shifts relative to the resonance frequency in the pure TlX (X = Cl, Br, I) indicate that the Tl – X overlap is increased by Cs, Rb and K but decreased by Na and Li. In the pure TlX and in all the binary mixtures studied, an increase of temperature results in descreening of the nucleus and is therefore attributed to increase in Tl – X overlap, or *covalence*. Of the TlX, the covalence, judged by comparison of the resonance frequencies with that in equimolar $TlClO_4 - AgNO_3$, increases in the order X = Cl, Br, I, and increases substantially faster with temperature in the iodide than in the chloride and bromide.

In reviewing our volumetric data in the light of the nmr results it is most noticeable that the effect of temperature rise indicates that expansion is accompanied by increasing interaction between Tl and X. This is interpreted by Nachtrieb and Hafner as an increase in covalence although they were not insistent that their viewpoint of covalence rather than polarization between Tl and X was necessarily the correct one[28]. A rule connecting large molar volumes with high covalency was enunciated for pure salts by Drossbach on the basis of general experimental observations[30]. The deep contraction in KBr – TlBr is, however, relatively little affected by the temperature[1] and occurs in a region not investigated by nmr. According to Fig. 2 of Ref. [28] the nmr work was done on mixtures mostly up to 20 mol % in MX and certainly not above 50 mol %.

Another complication is revealed when it is recalled that the electrical conductance in KBr – TlBr has a positive temperature coefficient at all compositions[2, 16]. For, if the expansion on temperature rise is accompanied by an increase of covalence between Tl and the ligands the conductance rise is presumably the result of an increased freedom of the M^+ to migrate under the external field. It is not then clear how these same cations can also be responsible for an increase in the overlap over that already existing in the pure TlX, as is deduced by Hafner and Nachtrieb for M = Cs, Rb, K.

It was also observed[28] that at fixed composition the chemical shift in MX – TlX relative to equimolar $TlClO_4 - AgNO_3$ increases linearly with the difference in the cation radii: $r_{M^+} - r_{Tl^+}$, where M is an alkali metal. Although the Pauling radii for Tl and Rb are the same, the points for TlX lie below the plots for the alkali metals and the conclusion was that the Tl – X covalence is promoted in the order K < Rb < Cs and suppressed in the order Na < Li.

As we see it, the position regarding the systems for which we have obtained v^E data is therefore as follows (Figs. 1 and 2, this paper; Fig. 2, Ref. [28]). According to the results and interpretation of HAFNER and NACHTRIEB, KBr – TlBr has the highest chemical shift and therefore the most covalence in Tl – X. The chemical shifts in RbCl – TlCl and KCl – TlCl are considerably lower and close together, the former system showing increasingly more Tl – X covalence than the latter as MX is added. Over the same narrow ranges of composition the KBr – TlBr system also shows the largest expansion on heating but the order in the chloride systems is apparently reversed; KCl – TlCl shows a larger overall increase in v^E even though the maximum value is the same in the two systems. This behaviour, together with the formation of minima and the stability of the deep minimum in the bromide system is not explicable in terms of the nmr work. We therefore conclude that our postulate of a separate contraction effect is still tenable although we are no nearer an explanation of it in structural terms.

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Infrarot-Intensitäten von Acetylenen des Typs (XYZ)Si−C≡C−H

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IR-intensities of acetylenes of the type (XYZ)Si—C≡C—H

The infrared absorption intensities of the ≡C—H and C≡C streching vibrations of 13 ethinylsilanes of the type $(XYZ)\mathrm{Si{-}C{\equiv}C{-}H}$ have been measured in CCl_4-solution. The results were compared to those for 1-alkines $(XYZ)\mathrm{C{-}C{\equiv}C{-}H}$ of BAYER[3]. A linear relationship between the square root of the ≡C—H infrared intensity and the sum of Taft's parameters $\sum \sigma^*$ of the substituents X, Y and Z was found. The relations are:

$$|I(\equiv \mathrm{C{-}H})^{1/2}| = 0.021_7 \sum \sigma^* + 0.65_4$$

for the ethinylsilanes and

$$|I(\equiv \mathrm{C{-}H})^{1/2}| = 0.019_9 \sum \sigma^* + 0.76_6$$

for the 1-alkines. Assuming an additional parameter for Si ($\sigma^*_{\mathrm{Si}} = -5.50$; $\sigma^*_{\mathrm{C}} = 0$ is defined), one can find a common relation for both series of acetylenes:

$$|I(\equiv \mathrm{C{-}H})^{1/2}| = 0.020_1 (\sum \sigma^* + \sigma^*_{\mathrm{M}}) + 0.74_2 .$$

By this procedure the correlation coefficient increases from 0.93 for Si and 0.98 for C to 0.99_5 for both. Assuming "characteristic intensities", i.e. mechanical and electronical decoupling, this behaviour demonstrates that the ≡C—H bond moment of polarity $\mathrm{C^-{-}H^+}$ is altered by the substituent with the same inductiv mechanism for both clases of acetylenes. This means that the electron withdrawing effect in the ethinyl groups of the ethinylsilanes is not reduced in respect to other substituents by the $(d\text{-}p)_\pi$ back bonding.

In both cases the square root of the C≡C intensity is also linearly correlated to the sum of Taft's parameters. The relations are:

$$|I(\mathrm{C{\equiv}C})^{1/2}| = 0.091_4 \sum \sigma^* + 0.79_3$$

with a correlation coefficient of 0.94 for ethinylsilanes and

$$|I(\mathrm{C{\equiv}C})^{1/2}| = -0.043_1 \sum \sigma^* + 0.41_5$$

with a correlation coefficient of 0.95 for 1-alkines. The opposite dependence on the substituent can be explained in terms of the strong restriction on "characteristic intensities" in a very simple model. The bond moments $\mu(\equiv\mathrm{C{-}H})$ and $\mu(\mathrm{C{\equiv}C})$ have the same polarity in the case of ethinylsilanes, namely $(XYZ)\mathrm{Si{-}C{\equiv}}\overset{-}{\mathrm{C}}{-}\overset{+}{\mathrm{H}}$ and $(XYZ)\mathrm{Si{-}}\overset{-}{\mathrm{C}}{\equiv}\overset{+}{\mathrm{C}}\mathrm{{-}H}$. In 1-alkines, however, they have the opposite polarity: $(XYZ)\mathrm{C{-}C{\equiv}}\overset{-}{\mathrm{C}}{-}\overset{+}{\mathrm{H}}$ and $(XYZ)\mathrm{C{-}}\overset{+}{\mathrm{C}}{\equiv}\overset{-}{\mathrm{C}}\mathrm{{-}H}$ due to the changed electronegativities of neighbour atoms ($\chi_{\mathrm{C}} > \chi_{\mathrm{H}}$ in 1-alkines, $\chi_{\mathrm{Si}} < \chi_{\mathrm{H}}$ in ethinylsilanes).

Total charge calculations using the CNDO/2-approximation confirm the expected charge distribution in the C≡C—H group and also the observed dependence of the total charges on the polar electron withdrawing effect of the substituents.

Einleitung

Unsere molekülphysikalischen Untersuchungen an Acetylenen[1] wurden an 13 verschieden substituierten Äthinylsilanen, $(XYZ)\mathrm{Si{-}C{\equiv}C{-}H}$, fortgesetzt. Die IR-Intensitäten der ≡C—H- und der C≡C-Valenzschwingungen, $I(\equiv\mathrm{C{-}H})$ und $I(\mathrm{C{\equiv}C})$, wurden bestimmt.

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