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Densities of Molten NaBr–AlBr₃ Mixtures

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Liquid densities of NaBr–AlBr₃ mixtures were measured using the float method. Compositions of 33.3, 50.0, 66.7, and 80.0 mole % AlBr₃ were measured over a range of temperatures and the data fitted to linear equations by a least-squares analysis. Molar volumes showed negative deviations from additivity of about 10% at 220° C and 50% at 600° C.

The haloaluminates continue to be of interest as molten salt solvents. Recent measurements of electrical conductivities of AlCl₃–KCl (5) and AlBr₃–NaBr (4) mixtures showed interesting compositional effects. The purpose of the present work was to determine densities of the latter mixture, to permit the calculation of equivalent conductivities. In addition, the densities are of interest in themselves and will be needed for the calculation of optical extinction coefficients when this mixture is used as a solvent for spectrophotometric studies.

EXPERIMENTAL

Density Determination. Densities were measured by the float method, which consisted of measuring the temperature at which quartz floats of known density neither fell nor rose in the liquid under study. Floats of different densities were made by sealing off various lengths of platinum wire in approximately 3-cm lengths of 0.4-cm-o.d. quartz tubing. Details of the apparatus and techniques have been described (2, 3). The aluminum block heater used in earlier work was replaced by a silver block which increased the upper temperature limit from about 550° to 850° C.

The new heater block consisted of a silver tube, ⅝ inch in i.d., 2½ inches in o.d., and 16 inches long. The density tubes were placed in the ⅝-inch hole and centered in the block. The heating units consisted of four 600-w Firerod heaters (Watlow Electric Manufacturing Co., St. Louis, Mo.). The ¾ × 16-inch (15-inch heated length) cylindrical heaters were inserted in close-fitting, symmetrically placed holes drilled axially in the silver block. A ¹⁄₁₆ × 4-inch slot centered vertically in the block permitted visual observation of the floats. To reduce heat losses, the block was surrounded by two concentrically placed quartz tubes, each silvered on the inside except for viewing slots which were aligned with the viewing slot in the block.

Temperature measurement was by means of a Pt, Pt-10% Rh thermocouple calibrated against a National Bureau of Standards traceable transfer standard and located in a hole ⅛ × 8 inches deep drilled parallel and as close to the

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sample hole as possible (about 0.45 inch from block center). The thermocouple electromotive force was determined by means of a Leeds & Northrup Model K-3 potentiometer.

Vapor pressures of several atmospheres were reached at higher temperatures and AlBr₃ compositions. The precautions taken in earlier work (2) were adhered to in this study.

Materials. AlBr₃ was prepared by the method described (1) for AlCl₃, except that high purity HBr (99.99%, Precision Gas Products, Inc., Rahway, N. J.) instead of HCl was made to react with aluminum metal.

Anhydrous NaBr was prepared from reagent grade material by a method similar to that used by Boston and Smith (6) for the purification of LiCl-KCl eutectic. The apparatus was constructed of quartz instead of borosilicate glass. The method consisted essentially of passing dry HBr through molten NaBr, followed by filtration through a sintered quartz disk.

RESULTS AND DISCUSSION

The density results are shown in Table I. The density, ρ, at each composition is given by the expression, $\rho = \alpha - \beta t$, where α and β are constants and t is the temperature in °C. Constant β is the expansivity of the melt. The standard deviations for the least-squares fit are somewhat higher than in our previous measurements using this same technique. This may be due to the wider temperature range covered here.

Densities of the pure components were not measured in this study. The density of pure aluminum bromide was measured by Johnson, Silva, and Cubicciotti (7), using the quartz float method. Pure sodium bromide was measured by Yaffe and Van Artsdalen (10), using the Archimedean method.

Molar volumes were calculated at 220° C and are listed in Table I. Enough data now exist to make a comparison of compositional effects on molar volumes for several kinds of haloaluminate melts. The results for four systems at 220° C are shown in Figure 1. The AlCl₃-KCl system was measured by Morrey and Carter (9), using the quartz float method.

Table I. Density Equations for NaBr–AlBr₃ Mixtures

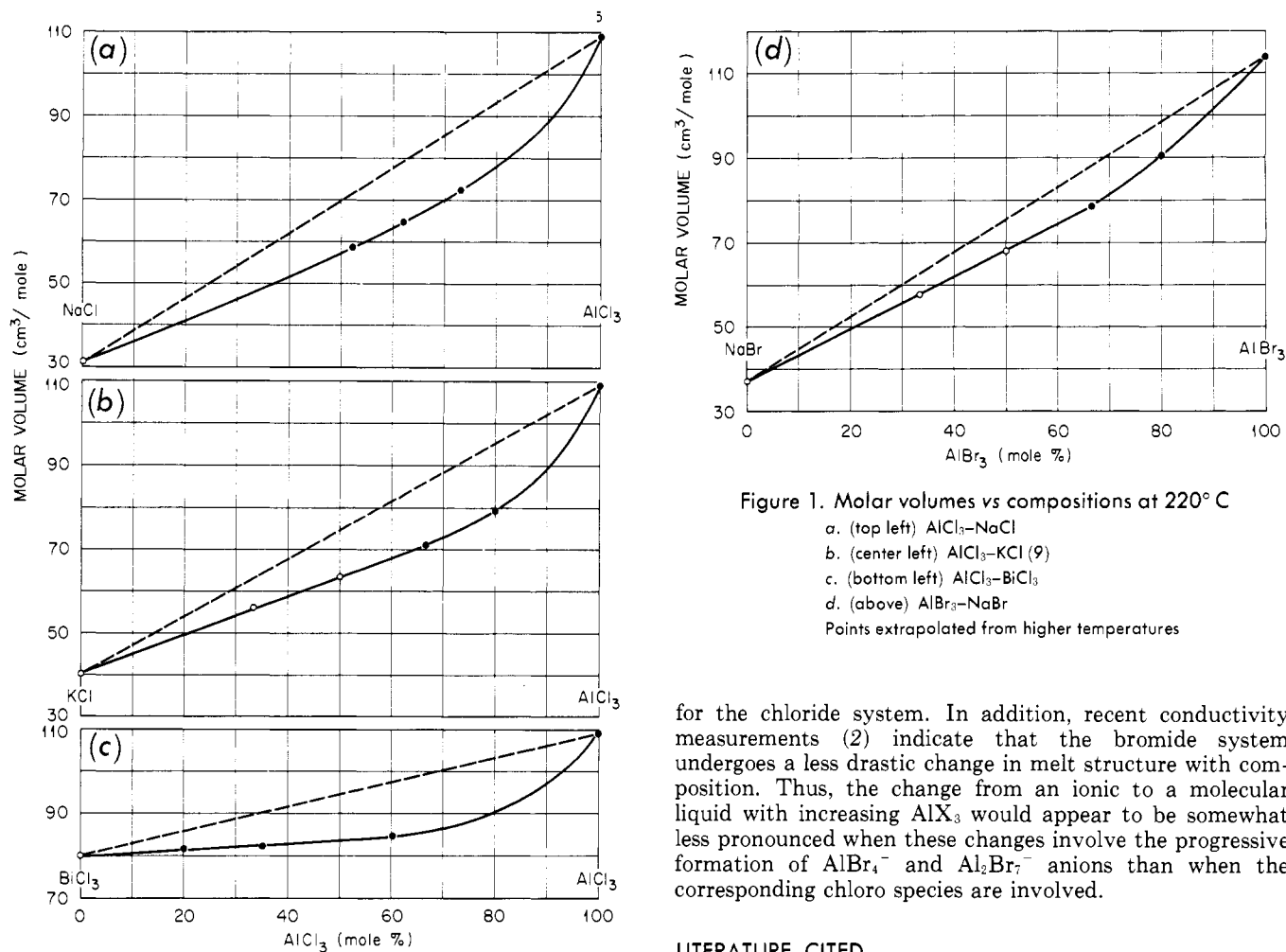| Composition, mole % AlBr₃ | $\rho = \alpha - \beta t$ | | Std dev $\times 10^3$, grams/cc | Molar volume at 220° C, cc/mole | Exptl temp range, °C | No. of exptl points | Ref |
	α, grams/cc	$\beta \times 10^4$, grams/cc/°C					
0.0	2.9518	8.169	0.3	37.2ᵃ	733–945	9	(10)
33.3	2.804	8.12	6	58.0ᵃ	678–873	4	
50.0	2.958	11.3	7	68.2ᵃ	315–884	4	
66.7	2.960	13.2	6	78.8	171–534	5	
80.0	2.957	17.0	5	90.8	125–388	7	
100.0	2.905	25.7	10	113.8	101–334	8	(7)

ᵃ Extrapolated values.

Figure 1. Molar volumes vs compositions at 220° C

a. (top left) AlCl₃–NaCl
b. (center left) AlCl₃–KCl (9)
c. (bottom left) AlCl₃–BiCl₃
d. (above) AlBr₃–NaBr
Points extrapolated from higher temperatures

Negative deviations from linearity occur in all four systems, reflecting the change from a highly ionic to a highly molecular liquid. Although not apparent from Figure 1, these deviations increase rapidly with increasing temperature, since the expansivities of the pure aluminum halides are relatively high. Another feature common to all four systems is the linear behavior to fairly high (60 to 70 mole %) AlX₃ compositions, indicating that the change from an ionic to a molecular liquid occurs rapidly in the 80 to 100 mole % AlX₃ composition range. In the chloride systems, the maximum deviation from linearity is influenced very little by changing the metal ion from sodium to potassium or even to bismuth. In contrast, a change of anion from chloride to bromide in the NaX–AlX₃ systems substantially reduces the deviation from linearity. Qualitatively, one might expect this, since the phase diagram (8) has a narrower two-liquid region for the bromide than

for the chloride system. In addition, recent conductivity measurements (2) indicate that the bromide system undergoes a less drastic change in melt structure with composition. Thus, the change from an ionic to a molecular liquid with increasing AlX₃ would appear to be somewhat less pronounced when these changes involve the progressive formation of AlBr₄⁻ and Al₂Br₇⁻ anions than when the corresponding chloro species are involved.

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