Densities of Liquid Aluminum Chloride–Sodium Chloride Mixtures
I. Single Liquid-Phase Region

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Densities of liquid aluminum chloride–sodium chloride
mixtures containing 50–75 mol % aluminum chloride
were measured from their melting points to 346°C (293°
for 70 and 75 mol % mixtures). Melt densities were
calculated from the expansion of the liquids contained in
dilatometric tubes. An empirical equation was obtained
which expresses density as a function of composition and
temperature with an overall standard deviation of ±0.003
g cm^{-3}.

As part of an investigation of certain low-melting molten salt electrolytes for high-energy density batteries, we needed to know the densities of liquid mixtures of aluminum chloride and sodium chloride. References to many of the physical properties of $AlCl_3$–NaCl mixtures are cited in the review by Boston (2). We required densities at more composition values and over larger temperature ranges than were available from the chemical literature (1, 7, 8, 12).

Experimental

Densities were calculated by measuring the volumes of known masses of liquid mixtures contained in sealed, borosilicate dilatometric tubes, each having a volume calibrated region at the liquid-vapor phase boundary. Except as otherwise described below, the procedures for tube calibration were the same as we followed earlier (6). Ten tubes were used, each consisting of two bulbs connected by a length of small bore tubing. Four of the tubes (tubes I–IV) were connected by the stems of measuring pipets. These capillaries were factory marked at 0.1 cm^3 per division, with divisions approximately 1.0 cm apart. Neither of these values was exactly correct, and the measured values are shown in Table I (deposited with the ACS Microfilm Depository Service). These tubes are analogs of our previously described tubes S, T, U, and V (6). Their total enclosed volumes ranged from 9 to 12 cm^3.

The remaining six tubes correspond to tubes A, B, C, and D of ref. 6 and utilized connecting capillaries (radius = 0.28 cm) having a single index mark on them. These six tubes had total enclosed volumes ranging from 26 to 43 cm^3. Calibration data for these tubes are given in Table II (deposited with the ACS Microfilm Depository Service). The calibration data in Tables I and II have been corrected for air buoyancy and meniscus effects as indicated in ref. 6.

Crystals of $AlCl_3$ were grown from saturated vapor by a procedure we have described previously (10). NaCl was dried by maintaining it molten for several hours (9). The $AlCl_3$–NaCl mixtures were prepared by thoroughly grinding and mixing in a glove box weighed amounts of $AlCl_3$ crystals with weighed amounts of dry NaCl crystals. The glove box atmosphere was nitrogen recirculated through a Linde (trademark of Linde Division, Union Carbide Corp.) Molecular Sieve. The dew point was below −60°C

(less than 15 ppm H_2O). An aliquot of each solid mixture was added to a density tube, and the density tubes were evacuated and sealed. After the mixtures were melted, the upper bulbs were pulled off, thus minimizing the vapor space in each tube. (The upper bulbs were necessary to load the tubes with enough of the rather bulky solid powder to permit the liquid-gas interface to occur in the small bore region.) The amount of each mixture and its composition and the total enclosed volume for each tube are given in Table III (deposited with the ACS Microfilm Depository Service).

The density tubes were immersed in a thermostated bath, and at each different temperature the distance from the bottom of the meniscus to the nearest graduation mark (tubes I–IV) or to the index mark (tubes V–X) was measured with the aid of a cathetometer. From this measurement and the tube calibration data, the liquid volume was calculated. There were 485 experimental points, and these are given in Table IV (deposited with the ACS Microfilm Depository Service) as calculated volumes. These volumes have been corrected for the thermal expansion of the density tubes. The data in Table IV were not all taken in the order listed; measurements were made with both ascending and descending temperatures.

Most of the measurements were made with the tubes immersed in a well-stirred bath of the ternary eutectic $NaNO_3$–$NaNO_2$–KNO_3 (mp ca. 145°C); however, a cottonseed oil bath was used at the lowest temperatures. Bath temperatures were maintained and controlled with the aid of a platinum resistance element and Leeds and Northrup controller described elsewhere (3). Bath temperatures were measured to ±0.05°C by determining the resistance of a nominal 100 Ω, four-wire platinum resistance element similar to the element used for control. The platinum resistors were calibrated against a platinum Air Force Reference Standard Thermometer, which was calibrated at the freezing point of zinc, freezing point of tin, boiling point of water, triple point of water, and the boiling point of oxygen by the U.S. Air Force Measurement Standards Laboratory, Aerospace Guidance and Metrology Center, Newark Air Force Station, Ohio.

Results

Measurements were made at values of mole fraction and temperature that lay within a polygon on the X, t plane described by the coordinates (X, t) = (0.50, 346), (0.65, 346), (0.70, 293), (0.75, 293), (0.75, 182), (0.70, 163), (0.65, 122), (0.60, 85), (0.55, 104), (0.50, 134). The lower temperatures are approximately the freezing points of each composition (supercooled in some instances), and the upper temperatures represented either the highest temperature we cared to take our bath, or, at higher X, temperatures at which we became concerned about internal pressure.

$AlCl_3$–NaCl mixtures become saturated with NaCl very slightly below X = 0.50 [$X_{saturation}$ = 0.498 at 175°C (11)], and separate into two phases at $X > 0.82$ (5). We did not find it practical to work with a density tube having $X > 0.75$; when $AlCl_3$ froze out and floated in the capil-

Table V. Empirical Polynomial for Densities of AlCl₃–NaCl Melts
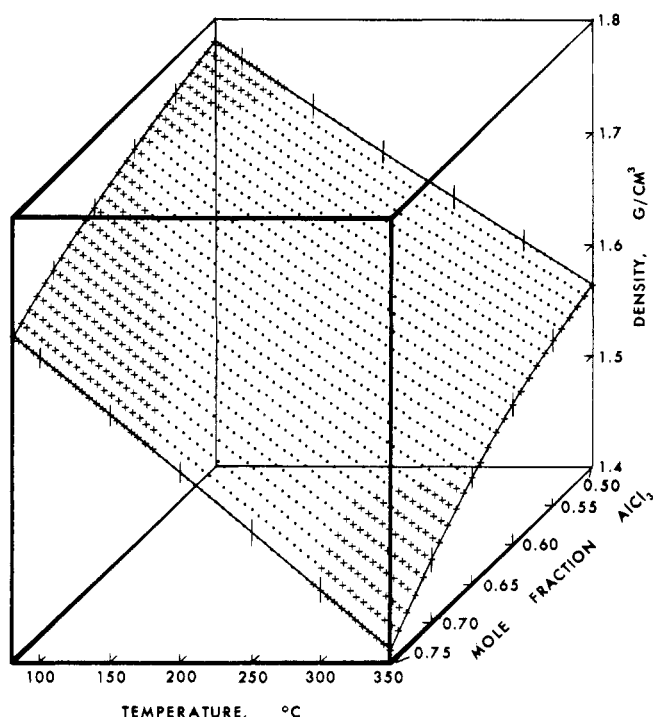
$$D = a_{00} + a_{01}t + a_{02}t^2 + a_{10}X + a_{11}Xt + a_{12}Xt^2 + a_{20}X^2 + a_{21}X^2t + a_{22}X^2t^2 \qquad (2)$$

where

$$
\begin{aligned}
a_{00} &= 1.6736 \\
a_{01} &= 1.601 \times 10^{-3} \\
a_{02} &= -8.08 \times 10^{-6} \\
a_{10} &= 7.45 \times 10^{-1} \\
a_{11} &= -7.497 \times 10^{-3} \\
a_{12} &= 2.733 \times 10^{-5} \\
a_{20} &= -7.99 \times 10^{-1} \\
a_{21} &= 5.233 \times 10^{-3} \\
a_{22} &= -2.2029 \times 10^{-5}
\end{aligned}
$$

and

$$\sigma = 0.003 \text{ g/cm}^3$$

Figure 1. Densities of AlCl₃–NaCl melts

Points calculated from Equation 2. ·, density within X. t range experimentally covered; +, extrapolated density. For clarity, surface is extrapolated to intersect edges of cube

$$\sigma = \left[\frac{1}{N - (m + 1)(n + 1)} \sum_{k=1}^{N} (z_k)^2 \right]^{1/2}$$

Fits of the data to Equation 1 were made both with and without composition corrections owing to volatilization, for the following values of m and n: $(m, n) = (2, 2)$, $(3, 3)$, and $(4, 2)$. Virtually the same σ resulted in each case; therefore, we report here the smallest values of m and n. The volatilization corrections were small but, of course, were always in the same direction and are included in the present results. At each X and t the vapor volume was the total enclosed volume minus the liquid volume. From the vapor volume, the vapor pressure given by Davey et al. (4), and the ideal gas law, the mass of Al_2Cl_6 in the vapor was calculated at each point. This information, together with the original mass and X in each tube, led to a corrected X. A corrected X yielded a revised vapor pressure, and so on. The D_k in Equation 1 was obtained by dividing the mass of the mixture by the liquid volume at each point. Corrected masses also were required at each point. The calculation was iterated for each data point until $\Delta X / X_{\text{corrected}} < 5 \times 10^{-6}$. In no case did this require more than three iterations; the maximum change in X was 0.0008.

The polynomial resulting from fitting the data to Equation 1 is given as Equation 2 in Table V. The D, X, t surface calculated by Equation 2 is shown in Figure 1. The diameter of the dots in Figure 1 is nearly σ.

Throughout the relatively narrow temperature and composition limits within which other workers measured mixture densities, their values matched ours quite closely. Boston's densities (1) were generally greater (-0.5 to 1.0%), and Midorikawa's (8) were somewhat less (-0.2 to -1.0%). Neither author gave his experimental data, but they apparently made 11 and 23 individual measurements, respectively.

Safety

The same precautions should be taken as reported previously (6) for the containment of liquids above their normal boiling points in glass vessels.

Nomenclature

a_{ij} = empirical coefficients
D = liquid density, g/cm³
i = exponent on mole fraction
j = exponent on temperature
k = an index for individual experimental points
m = the maximum exponent on mole fraction
n = the maximum exponent on temperature
N = the total number of individual experimental points
t = temperature, °C
X = mole fraction AlCl₃
z = residual; function to be treated by least-squares fitting
σ = standard deviation in D

lary region of the tube, it was difficult to reestablish a single phase upon reheating, since our tubes were not equipped with a means of internal stirring.

In the absence of any widely recognized model for the relationship of the density of two component systems of the present type to both temperature and composition, we chose to least-squares fit our data to the function

$$\sum_{i=0}^{m} X_k^i \sum_{j=0}^{n} a_{ij}t_k^j - D_k = z_k \qquad (1)$$

and solve for the values of a_{ij} which minimized the sum

$$\sum_{k=1}^{N} (z_k)^2$$

Standard deviations were calculated from

Literature Cited

(1) Boston, C. R., *J. Chem. Eng. Data.* **11**, 262 (1966).
(2) Boston, C. R., in "Advances in Molten Salt Chemistry," J. Braunstein, G. Mamantov, and G. P. Smith, Eds., Chap. 3, Plenum, New York, N.Y., 1971.
(3) Brabson, G. D., Fannin, Jr., A. A., *Rev. Sci. Instrum.*, **44**, 338 (1973).
(4) Davey, T. R. A., Floyd, J. M., Marcantonio, P. J., paper presented before the Meeting of American Institute of Metallurgical Engineers, New York, N.Y., March 1971.
(5) Kendall, J., Crittenden, E. D., Miller, H. K., *J. Amer. Chem. Soc.*, **45**, 963 (1923).
(6) King, L. A., Seegmiller, D. W., *J. Chem. Eng. Data.* **16**, 23 (1971).
(7) Kryagova, A. I., *J. Gen. Chem. USSR.* **9**, 1755 (1939).
(8) Midorikawa, R., *J. Electrochem. Soc. Jap.*, **23**, 310 (1955).

(9) Pinching, G. D., Bates, R. G., *J. Res. Nat. Bur. Stand.*, **37**, 311 (1946).
(10) Seegmiller, D. W., Rhodes, G. W., King, L. A., *Inorg. Nucl. Chem. Lett.*, **6**, 885 (1970).
(11) Torsi, G., Mamantov, G., *Inorg. Chem.*, **10**, 1900 (1971).
(12) Yamaguti, Y., Sisido, S., *J. Chem. Soc. Jap.*, **62**, 304 (1941).

Relative Apparent Molar Enthalpies of Aqueous Lanthanum Perchlorate

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Relative apparent molar enthalpies (ϕ_L) were measured at 25°C for lanthanum perchlorate solutions over the molality range 0.004–4.74m. The results were fitted to a Debye-Hückel equation for smoothing and extrapolation to $m = 0$.

Previous measurements (*3, 8, 9*) of relative apparent molar enthalpies (ϕ_L) for $HClO_4$, $NaClO_4$, $Mg(ClO_4)_2$, $Sr(ClO_4)_2$, and $Ba(ClO_4)_2$ yielded ϕ_L values which could be fitted to 0.4m or higher with an equation based on the Debye-Hückel theory, and thereby could be extrapolated reliably to the standard reference state $m = 0$. For a 3-1 perchlorate free from hydrolysis effects, $La(ClO_4)_3$ was chosen as a suitable convenient substance for this study. Since the ion is isoelectronic with that of barium, the effect of increased cationic charge would be revealed for the multiply charged ions.

Experimental

Materials. Freshly distilled water, collected at about 75°C, was used for all solutions and in all of the dilution measurements.

Preparation of the $La(ClO_4)_3$ solutions followed the method of Roberts and Silcox (*6*). An excess of lanthanum oxide (Matheson Coleman & Bell; purity 99.99%) was slurried with distilled water, and AR perchloric acid (Baker and Adamson, 60% $HClO_4$) was added slowly with stirring until most of the La_2O_3 was dissolved. The mixture was heated to about 90°C, with constant stirring, for 24 hr, after which the mixture was cooled and filtered through a Buchner funnel with a 1-cm thick asbestos mat. A second filtering, either through a similar mat or through filter paper, was done to ensure removal of colloidal solid. No Tyndall effect was observed on the resulting solutions. The pH of the solutions was adjusted to between 5 and 6 with small amounts of $HClO_4$, and the concentrations of the solutions were then increased as needed by evaporation at 90–100°C.

The stock solutions were analyzed by precipitating the lanthanum as the oxalate, which was then converted to La_2O_3 by ignition for 5 hr at 850°C in a muffle furnace (*4*). Analytical precision for triplicate analyses was generally better than 0.05% for the ratio (mass of $La(ClO_4)_3$/

mass of solution). All weighings of solutions and solids were appropriately reduced to masses, with densities from literature sources (*2, 6*). Nine different solutions were analyzed. Other solutions of intermediate concentrations were prepared by mass dilutions from analyzed stock solutions and freshly distilled water.

Calorimetric equipment and procedures. The configuration of the solution calorimeter used in this work was that described previously (*8*), and these measurements on $La(ClO_4)_3$ occurred in the same time period as those on $HClO_4$ and $NaClO_4$. The first 18 dilution runs were made with the Maier transposed bridge (*8*), with a temperature sensitivity of $\pm 5 \times 10^{-5}$ K, except for a few dilution runs at a sensitivity of $\pm 2 \times 10^{-5}$ K. The remaining dilution runs with thermistor bridge circuits (*8*) were made with a sensitivity of $\pm 1.5 \times 10^{-5}$ K. The electrical energy equivalents are considered accurate to $\pm 0.02\%$. The isothermal jacket (bath) was controlled to ± 0.003K during this work.

Corrected temperature increments were evaluated by Dickinson's method (*1*). Temperature-time data for 10-minute fore and after periods were fitted by least squares, and "midtimes" were determined by detailed examination of typical temperature-time curves for dilution and electrical calibration measurements. Main periods were sufficiently long (4–6 min plus duration of the mixing or calibration period) to allow attainment of equilibrium drift rates in the after period. Dilutions were initiated at 25.00 $\pm$ 0.02°C, and electrical calibrations were made on the final state of the system.

The pattern for dilution measurements was that used in the previous studies (*8, 9*), with about 1.05 liters of water or dilute $La(ClO_4)_3$ of measured mass in the calorimeter vessel, and with the 39-ml dilution capsule filled with a measured mass of concentrated solution, molality m. The general process is:

$$La(ClO_4)_3(m_0) + rLa(ClO_4)_3(m_1) = (1 + r) La(ClO_4)_3(m_2) \quad (1)$$
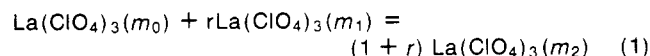
where r (and m_1) are zero for the first step in a series (dilution into water). Several such series were run, with up to six steps in a series, plus a substantial number of single-step runs. For each step, the enthalpy change is

$$\Delta H = (1 + r) (\phi_2 - \phi_0) - r(\phi_1 - \phi_0) \quad (2)$$

where ϕ is the apparent molar enthalpy referred to an arbitrary zero point, and the subscripts identify the particu-

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