higher extinction coefficients. An identical shift had been found (*3*, *9*) in very dilute cobalt chloride where the chloride-cobalt ratio reached high values—e.g., 38 to 1—and interpreted by Gruen (*2*) as the gradual replacement of bidentate nitrate ligands by chloride ions. It would seem that the higher cobalt chloride concentrations used here counterbalanced the lower chloride-cobalt ratios. The unusually low nickel chloride solubility was almost certainly due to the relatively insoluble nature of the complex formed. X-ray powder data and thermogravimetric analysis showed this to be a new compound and not merely nickel chloride with adhering melt. Quantitative analysis indicating chloride-nickel and nitrate-nickel ratios of between 2 and 2.5 suggested that it might be a complex ion of the type $(LiK)_2NiCl_2(NO_3)_2$.

Measurements on the dehydrated solutions of initially hydrated transition metal salts showed that complete dehydration occurred without appreciable hydrolysis. The small amount of acid formed from the dehydration of $Co(NO_3)_2 \cdot 6H_2O$ could be accounted for by the slow reaction $Co(II) + NO_3^- \rightarrow Co_3O_4 + NO_2$ (*8*). The kinetic data, determined at 350° to 400° C. in sodium-potassium nitrate, extrapolated and applied to lithium-potassium nitrate, indicated the correct order of magnitude.

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LITERATURE CITED

(1) Freeman, J.H., Smith, M.L., *J. Inorg. Nucl. Chem.* **7**, 224 (1958).
(2) Gruen, D.M., "Fused, Salts," B.R. Sundheim, ed., pp. 324-5, McGraw-Hill, New York, 1964.
(3) Gruen, D.M., *J. Inorg. Nucl. Chem.* **4**, 74 (1957).
(4) Horsley, G.W., At. Energy Res. Estab. (Gt. Brit.), Rept. **M/R 1441** (1954).
(5) Jänecke, E., *Z. Anorg. Chem.* **188**, 72 (1930).
(6) Kohlmuller, R., *Ann. Chim.* **4**, 1183 (1959).
(7) Seward, R.P., Field, P.E., *J. Phys. Chem.* **68**, 210 (1964).
(8) Sláma, I., *Collection Czech. Chem. Commun.* **28**, 1069 (1963).
(9) Tananaev, I.V., Dzhurinskiĭ, B.F., *Dokl. Akad. Nauk. SSSR* **134**, 1374 (1960).
(10) Tien, H.T, Harrington, G.W., *Inorg. Chem.* **2**, 369 (1963).

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Densities of Molten $AlCl_3$ and NaCl-$AlCl_3$ Mixtures

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The "float" method was used to measure liquid densities of $AlCl_3$ and NaCl-$AlCl_3$ mixtures containing 52.0, 61.8, and 73.0 mole % $AlCl_3$. All melts were studied over a range of temperatures and the data fitted to equations of the form $\rho = \alpha - \beta t$ by a least-squares analysis. Molar volumes showed negative deviations from additivity as large as 22%.

SALT mixtures containing $AlCl_3$ are useful solvents for various molten salt studies largely because of their highly acidic character. This feature has been used to advantage by Corbett (*4*) in the stabilization of lower oxidation states such as Bi(I), Cd(I), and Ga(I). These solvents are also optically transparent over a very wide wavelength region. This combination of high acidity and transparency makes them particularly attractive for spectrophotometric studies of lower oxidation state systems. An example of such systems, which is under study in this laboratory (*1*), is the lower oxidation state(s) of bismuth dissolved in NaCl-$AlCl_3$ mixtures. The purpose of the present work was to determine densities of these mixtures which are required for the calculation of optical extenction coefficients.

Previous density measurements on the NaCl-$AlCl_3$ system were done by pycnometric methods. Kryagova (*6*) measured the densities of several compositions between 50.2 and 67.4 mole % $AlCl_3$ and at temperatures from 190° to 280° C. Yamaguti (*11*) measured the densities of a 50 mole % $AlCl_3$ mixture at several temperatures between 182° and 350° C. Both of these authors reported density values larger than those reported here—e.g., for a 50 mole % $AlCl_3$ mixture at 250° C. values of 1.690, 1.674, and 1.639 grams per cc. were obtained by Yamaguti, Kryagova, and this work, respectively. Loss of $AlCl_3$ either by vaporization to a cold zone or by reaction with ambient moisture is one of the most serious sources of error in working with these systems and may explain the higher density values obtained in previous work.

EXPERIMENTAL

Density Determination. The float method for measuring density consists of measuring the temperature at which quartz floats of known density neither fall nor rise in the liquid under study. This method is capable of high accuracy and is particularly well suited to measurements on the volatile $AlCl_3$-containing melts.

The floats were made by blowing a small bubble of quartz and leaving a solid quartz "tail" which could be ground off until the desired density was obtained. The float densities were determined by weighing first in air and then submerging in water using the buoyancy apparatus described by Smith and Petersen (*9*). The floats had a "teardrop" shape and were approximately 8 mm. in diameter and 20 mm. long.

Melts were held in 12-mm. i.d. × 15-mm. o.d. quartz tubes which were loaded in a dry box with weighed amounts (15 to 20 grams, total) of the purified salts. Three or four floats of known density were placed in the tubes in order of decreasing density. Since the floats could not pass each other, they remained in this order and each float dropped in succession as the temperature was raised. This eliminated the problem of float identification during a run. The loaded tubes were removed from the dry box and sealed off under vacuum to a length of about 15 cm. This sealed tube was then attached to a 20-cm. length of 6-mm. quartz rod which served as a handle during the density measurements.

Table I. Density Equations for NaCl-$AlCl_3$ Mixtures

Composition, Mole % $AlCl_3$	$\rho = \alpha - \beta t$ α, grams/cc.	 $\beta \times 10^4$, grams/cc./° C.	Std. Dev. $\times 10^3$, Grams/Cc.	Molar Volume at 220° C., Cc./Mole	Exptl. Temp. Range, ° C.
52.0	1.839	8.38	0.8	58.91	124-294
61.8	1.797	8.66	0.7	65.21	162-275
73.0	1.760	9.20	1.1	72.61	183-337
100.0	1.734	23.3	1.7	109.2	202-221

The density tubes were heated in either a silicone oil bath or an aluminum block. The silicone oil (Dow Corning 710) bath was satisfactory for temperatures up to the decomposition point (300° C.) of the oil. The aluminum block heater was the preferred method, since it was simple to operate, could be used at higher temperatures, and gave results which were in good agreement with the oil bath heater.

The block heater consisted of an aluminum tube, $\frac{5}{8}$-inch i.d. × 2-$\frac{1}{2}$ inch o.d. × 12 inches long. The density tubes were placed in the $\frac{5}{8}$-inch hole and centered in the block. Heating was by means of four 400-watt Firewood heaters (Watlow Electric Manufacturing Co., St. Louis, Mo.). The $\frac{3}{8}$ × 11 inch cylindrical heaters were inserted in close-fitting, symmetrically placed holes drilled axially in the aluminum block. A $\frac{1}{16}$ × 4 inch slot centered vertically in the block permitted visual observation of the floats. A borosilicate glass jacket surrounded the aluminum block to reduce convection cooling in the viewing slot and also to protect the block from uneven cooling by variable room air currents.

Temperature measurement was by means of a Pt, Pt–10% Rh thermocouple located in a $\frac{1}{8}$-inch hole drilled parallel and as close to the sample hole as possible. The thermocouple e.m.f. was read on a Leeds & Northrup Model K-3 potentiometer.

Since pressures in these sealed tubes may be as high as 5 or 6 atm., the following precautions were taken in handling them at elevated temperatures: Fairly heavy-walled (1.5-mm.) quartz tubing was used in the construction of density tubes. Care was taken when sealing off these tubes to avoid thinning the quartz. In case of explosion, the aluminum block furnace itself provided some shielding and, finally, the entire apparatus was set up in a fume hood behind safety glass shields.

Materials. The NaCl was purified by the method described by Boston and Smith (*3*) for the LiCl-KCl eutectic, except that the apparatus was constructed of quartz instead of borosilicate glass. The $AlCl_3$ was prepared from high-purity aluminum metal and HCl by the method described by Bjerrum, Boston, and Smith (*1*). All purified compounds were handled in an evacuatable dry box under a dry nitrogen atmosphere.

RESULTS AND DISCUSSION

At each composition the temperature dependence of the density ρ is given by the usual expression, $\rho = \alpha - \beta t$, where α and β are constants and t is the temperature in ° C. The results are listed in Table I. Each composition was measured at four temperatures, except the 52.0 mole % $AlCl_3$ melt which was measured at three temperatures. The standard deviations for the least squares fit and the experimental temperature range are listed in Table I.

Molar volumes for this system show unusually large deviations from additivity. For example, at 220° C. and 63 mole % $AlCl_3$ a negative deviation of over 20% was observed, based on the molar volumes of $AlCl_3$ and NaCl extrapolated to this temperature. For NaCl this involves an extrapolation into the supercooled region, a procedure which Smith and Petersen (*9*) have discussed in detail. Deviations from additivity are to be expected for these strongly interacting compounds which form the stable $NaAlCl_4$ and possibly $NaAl_2Cl_7$ (*7*). However, the magnitude in this case is still striking when compared with other molten salt systems. For noninteracting systems (*5*, *8*, *9*, *10*) deviations of 0 to 1% are common and for interacting systems, values of 1 to 10% may be observed. An example of the latter is the KCl-$BiCl_3$ system measured by Boston, Ewing, and Smith (*2*), where negative deviations as great as 7% were observed.

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LITERATURE CITED

(1) Bjerrum, N.J., Boston, C.R., Smith, G.P., *Inorg. Chem.* (to be published).
(2) Boston, C.R., Ewing, W.M., Smith, G.P., unpublished results.
(3) Boston, C.R., Smith, G.P., *J. Phys. Chem.* **62**, 409 (1958).
(4) Corbett, J.D., *J. Am. Chem. Soc.* **78**, 2906 (1956).
(5) James, D.W., Liu, C.H., J. Chem. Eng. Data **8**, 469 (1963).
(6) Kryagova, A., *J. Gen. Chem. USSR* **9**, 1755 (1939).
(7) Oye, H.A., Gruen, D.M., *Inorg. Chem.* **3**, 836 (1964).
(8) Petersen, G.F., Ewing, W.M., Smith, G.P., J. Chem. Eng. Data **6**, 540 (1961).
(9) Smith, G.P., Petersen, G.F., *Ibid.*, **6**, 493 (1961).
(10) VanArtsdalen, E.R., Yaffee, I.S., *J. Phys. Chem.* **59**, 118 (1955).
(11) Yamaguti, Y., Sisido, S., *J. Chem. Soc. Japan* **62**, 304 (1941).

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