of the solvent, the residue was distilled through a flash still: cut A, 5.0 grams, b.p. 48° to 63° C. (0.1 mm.); cut B, 3.0 grams, b.p. 66° to 72° C. (0.08 mm.); cut C, 8.3 grams, b.p. 76–80° C. (0.08 mm.); cut D, 4.3 grams, b.p. 78° to 102° C. (0.10 to 0.15 mm.); cut E, 13 grams, b.p. 111° to 137° C. (0.2 mm.). Cuts B and C and cuts D and E were combined and the cuts analyzed by gas-liquid chromatography. (An F & M Model 500 was employed with a 2-foot × ¼ inch SE 30 on Chromosorb W column and a helium flow of 80 cc. per minute.) The retention times for phenol (Ti = 100°; 15° per minute) was 1.66 minutes; the chloride, 6.3 minutes; *N*-vinyl-5-methyl-2-oxazolidinone, 4.0 minutes, and the phenyl ether, 10.0 minutes. The estimated total weight of phenol was 11.9 grams; the chloride, 14.2 grams; and the vinyl compound, 2.9 grams. The pot residue, which was the phenyl ether, weighed 29.3 grams. Infrared showed essentially no hydroxyl.

The same general procedure was used for the other phenols; however, the amount of dehydrochlorination was not determined in the other reactions.

General Procedure for 3-(Alkylthio-)-Derivatives. The general procedure was carried out as for the phenols. However, precipitation of NaCl began nearly immediately during addition of the chloro compound. The reaction was mildly exothermic during the addition. A reflux period of 4 hours was generally sufficient to give yields of product exceeding 80%. Physical properties and analytical data are included in Table I. The alkylthio compounds were generally colorless to light yellow liquids, while the benzthiozolyl compound was an orange, viscous liquid.

LITERATURE CITED

(1) Arend, W., Trieschmann, H.G., U. S. Patent **2,966,496** (Dec. 27, 1960).
(2) Close, W.J., *J. Am. Chem. Soc.* **73**, 95 (1951).
(3) Drechsel, E.K., *J. Org. Chem.* **22**, 849 (1957).
(4) Drechsel, E.K., U. S. Patents **2,818,362; 2,818,399** (Dec. 31, 1957).
(5) Hickner, R.A., *Ibid.*, **3,228,955** (1966).
(6) Homeyer, A.H., *Ibid.*, **2,437,390** (March 9, 1958).
(7) Kornblum, N., Berrigan, P.J., leNoble, W.J., *J. Am. Chem. Soc.* **85**, 1141 (1963).
(8) Kornblum, N., Seltzer, R., Haberfield, P., *Ibid.*, **85**, 1148 (1963).
(9) Lesher, G.Y., Surrey, A.R., *Ibid.*, **77**, 636 (1955).
(10) Steele, A.B., U. S. Patent **2,868,801** (Jan. 13, 1959).
(11) Viard, M.J., *Ibid.*, **2,773,067** (Dec. 4, 1956).

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Densities and Partial Molar Volumes in Some Aqueous Nitrate Melts

Lithium Nitrate–Potassium Nitrate–Water at 119° C. Potassium Nitrate–Calcium Nitrate Tetrahydrate at 100° C.

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The specific volume of mixtures of water with equimolar lithium nitrate–potassium nitrate at 119° C. and at water mole ratios (R_H) between 0.25 and 1.0 mole per mole nitrate is given by v(cc./gram) = $0.5093 + 0.0856\ R_H - 0.0087\ R_H^2$. The specific volume of mixtures of potassium nitrate with calcium nitrate tetrahydrate at 100° C. and with mole fraction (N_{Ca}) of the tetrahydrate between 1 and 0.4 is given by v(cc./gram) = $0.4976 + 0.1551\ N_{Ca} - 0.0603\ N_{Ca}^2$. Partial molal volumes in these systems are calculated and additivity relations are discussed.

PROPERTIES of very concentrated aqueous electrolyte solutions are of interest in relating the behavior of molten salts to that of aqueous electrolyte solutions (*1, 4*). During the course of an investigation of association constants, vapor pressures, and diffusion coefficients in some aqueous nitrate melts, density data were needed for solutions of water in equimolar lithium nitrate-potassium nitrate at 119° C. with water concentrations between 0.25 and 1.0 mole of water per mole of nitrate—i.e., at molalities between 55 and 220 moles of salt per kg. of water—and for mixtures of potassium nitrate with calcium nitrate tetrahydrate at 100° C. and containing between 40 and 100 mole % of calcium nitrate tetrahydrate. These densities, measured by an Archimedean method, are presented in this paper. Some partial molal volumes are calculated and additivity relations are discussed.

EXPERIMENTAL

Materials. Analytical reagent grade lithium nitrate, potassium nitrate, and calcium nitrate tetrahydrate from Mallinckrodt were used. No further purification was done

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other than oven-drying the lithium nitrate and potassium nitrate overnight at 120° C. The calcium nitrate tetrahydrate had been shown previously to have a composition within ±0.02% of stoichiometric by measuring the weight loss of molten mixtures of potassium nitrate with calcium nitrate tetrahydrate after slowly bringing the temperature to 260° to 300° C. and bubbling dry nitrogen or helium through the melt for 6 to 10 hours (*3*, *6*). Ordinary distilled water was used.

Apparatus and Procedure. A two-pan analytical balance with a hole drilled through the base was used with a plummet made of borosilicate glass tubing with lead shot sealed into it. A plummet, which weighed about 14 grams and displaced about 5 cc., was suspended in the melt (after weighing in air and in water at room temperature) by a platinum wire about 0.1 mm. in diameter. The borosilicate glass cell containing the melt was clamped in a constant temperature bath about 18 inches below the base of the balance and was sealed except for a 4-mm. borosilicate glass tube in the stopper through which the wire passed. In order to minimize evaporation of water, the tube was plugged for 30 to 60 minutes after filling to allow the contents to come to equilibrium with the bath. The weight of the plummet was then measured repeatedly over a period of several hours. A slow decrease of weight was observed after opening the tube through which the suspension wire passed. This drift, always less than 0.05% per hour, was corrected for by plotting the weights and extrapolating to zero time. This correction generally was no greater than the standard deviation of the mean of the successive weighings or of duplicate experiments.

About 100 cc. of melt were used in the cell. The salts were weighed into the cell and mixed, and the required quantity of water was added (to the lithium nitrate–potassium nitrate mixtures). A closely fitting borosilicate glass stirrer passed through the stopper in the top of the cell to permit manual mixing of the melt in the sealed cell during temperature equilibration. The plummet had been weighed previously in air and in distilled water. The volume of the plummet was corrected for the differences of temperature of the air, water, and melt. No correction was made for the effect of the surface tension of the melt or water, since the magnitude of the other errors probably exceeded this correction.

The temperature bath used for the measurements in $LiNO_3$-KNO_3-H_2O was a silicone oil bath controlled at 119° ± 0.02° C. The measurements of KNO_3-$Ca(NO_3)_2 \cdot 4H_2O$ were made at 100° C. using a boiling water jacket with the temperature controlled to ±0.1° C.

RESULTS

KNO_3-$Ca(NO_3)_2 \cdot 4H_2O$. The densities of mixtures of KNO_3 and $Ca(NO_3)_2 \cdot 4H_2O$ are given in Table I.

The specific volumes (cubic centimeters per gram) deviated little from a linear function of the concentration and were fitted to the equation

$$v(\text{cc./gram}) = 0.49764 + 0.15514\, N_{\text{Ca}} - 0.06030\, N^2_{\text{Ca}} \qquad (1)$$

where N_{Ca} is the mole fraction of calcium nitrate tetrahydrate. The standard deviations of the constants in the equation are 0.0035, 0.0109, and 0.0078, respectively. Ewing and Mikovsky (*5*) and Moynihan (*7*) have reported densities of calcium nitrate tetrahydrate at temperatures to 70° C. Moynihan reports a linear temperature dependence, $\rho = 1.768 - 0.00085\ t$ (° C.). Extrapolation of his equation beyond the range of measurement is not justified, but, for purposes of rough comparison, it would lead to a value of 1.683 grams per cc. at 100° C. compared with our measured value of 1.690, and the value calculated from our least squares equation (Equation 1) of 1.688.

The partial molal volumes of potassium nitrate and of calcium nitrate tetrahydrate are 50.0 and 139.8 cc. per mole in the range of compositions measured (0 to 60 mole % of KNO_3). A plot of the volume per mole of mixture *vs.* the mole fraction of potassium nitrate was a straight line. (The number of "moles of mixture" used to calculate the volume per mole of mixture is the sum of the number of formula weights of the two components, KNO_3 and $Ca(NO_3)_2 \cdot 4H_2O$. The partial molar volumes refer to these two components.) Three of the points deviated from the straight line by 0.7% and the other five points were within 0.2% of the straight line. Extrapolation of the density equation of Smith and Petersen (*8*) for molten potassium nitrate to hypothetical supercooled liquid at 100° C. gives a molar volume of 49.64 cc. per mole, which differs by 0.6% from the value 50.0 obtained by extrapolation of our results at 100° C. in mixtures of potassium nitrate with calcium nitrate tetrahydrate.

$LiNO_3$-KNO_3-H_2O. The densities of mixtures of water with equimolar lithium nitrate–potassium nitrate and of one mixture of water with 0.55 $LiNO_3$-0.45 KNO_3 are given in Table II.

The specific volumes were fitted by least squares to the equation

$$v(\text{cc./gram}) = 0.50928 + 0.08558\, R - 0.00869\, R^2 \qquad (2)$$

The standard deviations of the coefficients are 0.0012, 0.0042, and 0.0033, respectively. Smith and Petersen (*8*) have reported the density equation $\rho = 2.033 - 0.000683\ t$ (° C.) for anhydrous equimolar $LiNO_3$-KNO_3 in the temperature range 275° to 473° C. Again for purposes of rough comparison, the extrapolation of their equation to the supercooled liquid at 119° C. gives a density of 1.952 grams per cc., compared with the value 1.963 for the extrapolation of our data to the supercooled anhydrous $LiNO_3$-KNO_3, a difference of 0.6%.

The partial molar volume of water in the melts calculated from Equation 2 is $\bar{V}_H = (S + HR)\partial v/\partial R + Hv = 16.47 + 1.610\ R - 2.214\ R^2$, where H is the formula weight of water and S is the "formula weight" of equimolar $LiNO_3$-KNO_3 (85.02 grams per mole of nitrate ion). The extrapolated partial molal volume of water at infinite dilution of water in hypothetical supercooled $LiNO_3$-KNO_3 is 16.5

Table I. Density of Mixtures of KNO_3 and $Ca(NO_3)_2 \cdot 4H_2O$

Mole % $Ca(NO_3)_2 \cdot 4H_2O$	Density, G./Cc.	Standard Deviation × 10^4, 6 Measurements
100	1.690	7
95	1.691	8
85	1.705	10
75	1.726	12
60	1.757	13
50	1.787	13
45	1.800	15
40	1.818	14

Table II. Density and Mole Ratio of Water in $LiNO_3$-KNO_3 at 119° C.

R, Mole Ratio of Water, Moles H_2O/ Mole Nitrate	Density, G./Cc., $\sigma = 0.001$, 5 Measurements
0.25	1.886[a]
0.40	1.846[a]
0.50	1.819[a]
0.80	1.747[a]
1.00	1.707[a]
0.80	1.739[b]

[a] In 0.50 $LiNO_3$-0.50 KNO_3. [b] In 0.55 $LiNO_3$-0.45 KNO_3.

cc. per mole, compared with the molar volume of water at this temperature of 19.0 cc. per mole. The low partial molal volume of water at extremely high ionic concentrations is not unexpected, since most of the hydrogen-bonded clusters of water molecules will have been destroyed. Ewing and Mikovsky (*5*) reported a similar, but much smaller, decrease of the partial molal volume of water in aqueous calcium nitrate in the range between dilute aqueous solutions and calcium nitrate tetrahydrate.

A partial molal volume of potassium nitrate (and hence also of lithium nitrate) may be estimated at one composition using the specific volume measured in the mixture 0.45 KNO_3-0.55 $LiNO_3$-0.8 H_2O. We may write

$$\bar{V}_{KNO_3} = M_{KNO_3} v + W \left(\frac{\partial v}{\partial (n_{KNO_3}/n_{LiNO_3})} \right)_{n_H/n_{LiNO_3}}$$

where $W = M_{LiNO_3} + M_{KNO_3} (n_{KNO_3}/n_{LiNO_3}) + H(n_H/n_{LiNO_3})$, the M's are the formula weights of the salts, and the n's are numbers of moles of $LiNO_3$, KNO_3, and H_2O. [This follows by expressing the total volume of a mixture of the components $LiNO_3$, KNO_3, and H_2O as $V = n_{LiNO_3} \bar{V}_{LiNO_3} + n_{KNO_3} \bar{V}_{KNO_3} + n_H \bar{V}_H = (n_{LiNO_3} M_{LiNO_3} + n_{KNO_3} M_{KNO_3} + n_H M_H) v$, dividing by n_{LiNO_3}, and differentiating with respect to (n_{KNO_3}/n_{LiNO_3}), holding (n_H/n_{LiNO_3}) constant.] The partial derivative of the specific volume is estimated as

$$\left[\frac{\Delta v}{\Delta (n_{KNO_3}/n_{LiNO_3})} \right]_{n_H/n_{LiNO_3} = 1.452} = -0.0454$$

for (n_{KNO_3}/n_{LiNO_3}) between 0.819 (0.45 KNO_3-0.55 $LiNO_3$) and 1.00 (equimolar $LiNO_3$-KNO_3) at the constant mole ratio (n_H/n_{LiNO_3}) = 1.452. We obtain $\bar{V}_{KNO_3} = 49^{\pm 1}$ cc. per mole and $\bar{V}_{LiNO_3} = 38^{\pm 1}$ cc. per mole in the melt consisting of equimolar $LiNO_3$-KNO_3 containing 0.8 mole of water per mole of nitrate at 119° C. The hypothetical molar volumes of supercooled $LiNO_3$ and KNO_3 at 119° C., extrapolated with the density equations of Smith and Petersen (*8*), are 36.0 and 49.9 cc. per mole. The partial molar volume of water at this concentration is 16.3 cc. per mole.

Additivity of molar volumes in binary molten salt mixtures is well known (*8, 9*). The additivity of volumes in the system KNO_3-$Ca(NO_3)_2 \cdot 4H_2O$ suggests, as pointed out earlier (*1, 4*), that the cations in such a system behave as a mixture of "bare" potassium ions and hydrated calcium ions, with all the water bound to the calcium ions. [Such a model would not apply in systems containing ligands capable of displacing water from the coordination sphere of the central cation (*2*), or in systems in which both cations tend to be strongly hydrated.]

The molar volume of "supercooled" potassium nitrate, extrapolated from data on mixtures with either lithium nitrate and water or with calcium nitrate tetrahydrate, agrees within a few tenths of a per cent with the value extrapolated from high temperature data on anhydrous molten KNO_3. Although the agreement of the three extrapolations might be fortuitous, it suggests that the assumption of additivity in very concentrated aqueous solutions may be a useful approximation.

NOMENCLATURE

H = molecular weight of water, grams per mole
M_{LiNO_3}, M_{KNO_3} = formula weights of $LiNO_3$ and KNO_3, respectively
N_{Ca} = mole fraction of $Ca(NO_3)_2 \cdot 4H_2O$, number of formula weights of $Ca(NO_3)_2 \cdot 4H_2O$ per sum of number of formula weights of $Ca(NO_3)_2 \cdot 4H_2O$ and KNO_3 in KNO_3-$Ca(NO_3)_2 \cdot 4H_2O$ mixtures
n = number of formula weights
R, R_H = mole ratio of water, moles of water per mole of nitrate, in $LiNO_3$-KNO_3-H_2O mixtures
S = formula weight of equimolar $LiNO_3$-KNO_3, grams per mole of nitrate
t = temperature, ° C.
v = specific volume, cc. per gram
$\bar{V}$ = partial molar volume, cc. per mole
V = total volume, cc.
W = weight of $LiNO_3$-KNO_3-H_2O mixture per formula weight of $LiNO_3$, grams solution per gram formula weight of $LiNO_3$
ρ = density, grams per cc.
σ = standard deviation

LITERATURE CITED

(1) Angell, C.A., *J. Electrochem. Soc.* **112**, 1224 (1965).
(2) Braunstein, J., *J. Phys. Chem.*, to be published.
(3) Braunstein, J., Brill, J.D., *J. Phys. Chem.* **70**, 1261 (1966).
(4) Braunstein, J., Hess, J.M.C., Braunstein, H., *J. Inorg. Nucl. Chem.* **26**, 811 (1964).
(5) Ewing, W.W., Mikovsky, R.J., *J. Am. Chem. Soc.* **72**, 1390 (1950).
(6) Hagman, R.E., Braunstein, J., unpublished results.
(7) Moynihan, C.T., *J. Phys. Chem.* **70**, 3399 (1966).
(8) Smith G.P., Petersen, G.F., J. Chem. Eng. Data **6**, 493 (1961).
(9) Van Artsdalen, E.R., Yaffe, I.S., *J. Phys. Chem.* **59**, 118 (1955).

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