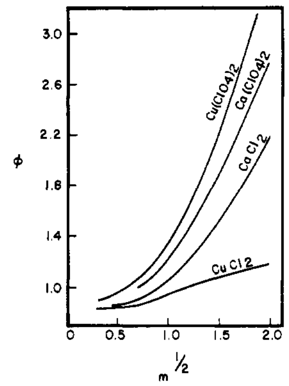

Figure 1. Dependence on concentration of the osmotic coefficients of cupric perchlorate (*3*), calcium perchlorate (*6*), calcium chloride (*12*), and cupric chloride (*5*)

perchlorate (*3*), and cupric chloride (*5*). The curves for the first three salts are typical of fully dissociated, highly solvated electrolytes; that for cupric chloride is such as to suggest incomplete dissociation. Spectrophotometric measurements of cupric chloride in lithium chloride solution (*1*) suggest that formation of $CuCl^+$ is likely. Any such reduction in the number of Cu^{2+} ions in a $CuCl_2$ solution suffices to explain, at least qualitatively, why b_{01} is different in the $CaCl_2$–$Ca(ClO_4)_2$ and $CuCl_2$–$Cu(ClO_4)_2$ systems.

NOMENCLATURE

ϕ = osmotic coefficient of a mixed salt solution
ϕ_A^0, ϕ_B^0 = osmotic coefficients of solutions of salts A and B, respectively, at ionic strength equal to the total ionic strength of the mixed salt solution, I
y_A = m_A/m, $y_B = m_B/m$
m_A and m_B = molalities (mole kg^{-1}) of A and B, respectively, in the mixed salt solution
m = $m_A + m_B$
$\Delta \equiv \nu(\phi - y_A\phi_A^0 - y_B\phi_B^0)$

In this paper, $A = CaCl_2$, $B = Ca(ClO_4)_2$, $\nu = 3$

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Densities of Some Nitrate and Sulfate Melts

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The densities of $NaNO_3$–KNO_3 (45:55 mol %), $LiNO_3$–KNO_3 (41:59), KNO_3–$LiNO_3$ (41:59), and $NaNO_3$–$LiNO_3$ (46:54) melts are reported for a temperature range of some 200° together with that of Li_2SO_4–Na_2SO_4–K_2SO_4 eutectic at 550° C. Molar volumes of the nitrate mixtures are additive to within 1.3%.

Although the densities of several molten nitrate mixtures are recorded in the literature, the data for four mixtures, employed in a series of electrochemical investigations, are not known. It was therefore necessary to make density measurements of these, and the values have been compared with those calculated upon the assumption of additivity of molar volumes. The density of a ternary sulfate eutectic, also a common solvent, was also measured and is recorded here.

EXPERIMENTAL

Densities were measured by the buoyancy method favored for its simplicity coupled with accuracy (*3*). A silver bob (about 2 cm length), suspended on a 1-mm diameter silver wire below an analytical balance, was immersed to 10 ± 1 mm below the surface of the melt in a glass container. The ±1-mm error represents a volume error of $\pm 8 \times 10^{-4}$ cc or ±0.02%. Temperatures were measured by a chromel-alumel thermocouple immersed in the melt and were controlled by a Proportio Null, 1300 Series, controller (Cole-Parmer Instrument and Equipment Co.) connected to the power circuit of a simple box furnace.

In making temperature measurements, the zero point was ice water, and recordings were taken from a Cropico Type P3 potentiometer. The thermocouples were calibrated against the fixed points (mp of ice, Sn, Cd, Pb, and Zn, bp of water) used to define the International Temperature Scale of 1948 (*4*), a pressure correction being included. In taking measurements, a constancy of ±0.0005 gram and ±0.25° C for 15 min was required, and both heating and cooling cycles were used for each system. The volume of the silver bob as a function of temperature from 325° to 475° C was obtained by measuring the density of sodium nitrate which is given by ref. *6*:

$$\rho = 2.125 - 7.15 \times 10^{-4}\ T\ (°C)$$

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Table I. Densities (ρ, Grams Cm^{-3}) as a Function of Temperature (T, °C)

0.54 $LiNO_3$, 0.46 $NaNO_3$		0.41 $LiNO_3$, 0.59 KNO_3		0.59 $LiNO_3$, 0.41 KNO_3		0.45 $NaNO_3$, 0.55 KNO_3		0.78 $LiSO_4$, 0.085 Na_2SO_4, 0.135 K_2SO_4	
T	ρ	T	ρ	T	ρ	T	ρ	T	ρ
207.6	1.8887	158.8	1.9639	209.7	1.8957	252.2	1.9328	549.8	2.1267
228.1	1.8727	182.0	1.9406	232.1	1.8754	260.0	1.9266	549.9	2.1222
263.9	1.8467	208.9	1.9260	265.0	1.8585	268.5	1.9187	550.0	2.1235
284.9	1.8317	244.0	1.8975	286.6	1.8251	287.0	1.9019	550.1	2.1248
313.1	1.8130	257.8	1.8870	314.4	1.8064	318.2	1.8769	550.2	2.1280
315.0	1.8076	293.7	1.8466	344.3	1.7866	357.2	1.8481	550.2	2.1280
334.4	1.7984	317.4	1.8258	350.2	1.7771	374.6	1.8334	Av 550.0	2.125[a]
361.6	1.7751	344.2	1.8017	391.8	1.7531	375.6	1.8352		
391.0	1.7506	365.1	1.7916	418.0	1.7346	401.9	1.8131		
		399.7	1.7666			428.3	1.7958		
						449.8	1.7752		
						476.5	1.7606		
						501.7	1.7437		

[a] Literature value 2.2 by a crude method (*2*).

Table II. Density Parameters for $\rho = \alpha - \beta \times 10^{-4} T$

Melt	α	β	Std dev	Range, °C
0.45 $NaNO_3$, 0.55 KNO_3	2.122	7.648	0.002	250–550
0.46 $NaNO_3$, 0.54 $LiNO_3$	2.042	7.399	0.002	200–400
0.41 $LiNO_3$, 0.59 KNO_3	2.099	8.436	0.005	150–400
0.59 $LiNO_3$, 0.41 KNO_3	2.058	7.842	0.005	200–400

and was checked by measuring the density of lithium potassium sulfate at 550° C. The volume of the bob in cm^3 with T in °C was

$$\gamma = 3.6916 + 3.2 \times 10^{-4}\ T$$

with a standard deviation of 0.0018 cm^3. For 0.80 Li_2SO_4–0.20 K_2SO_4, our value was 2.117 grams cm^{-3} compared to the previousvalue of 2.120 grams cm^{-3} (*5*).

The nitrates were recrystallized from water and dried at a pressure of <2 mm Hg at 100° to 120° C. Mixtures were made up, melted, and purged with dry nitrogen for 2 hr prior to cooling and storing over P_2O_5.

The sulfates were vacuum dried at 120° C for 24 hr, the mixtures melted and purged with dry nitrogen, and then any cloudiness was removed by the addition of $Na_2S_2O_7$.

The mixtures were analyzed for alkali metals by atomic absorption spectrophotometry with a Techtron AA 100 instrument and all values fell well within the 1% error limits of the analyses.

RESULTS AND DISCUSSION

The measured densities are presented in Table I. The values for the nitrate melts were fitted by a least-squares method to the linear equation

$$\rho = \alpha - \beta \times 10^{-4}\ T$$

where ρ is the density in grams cm^{-3} at T° C. The coefficients α and β for each system appear in Table II.

The molar volumes of simple mixtures are often the sums of those of the constituents to within 1% (*1, 5, 10, 11*). This has been used to estimate densities of several mixtures, even including extrapolations of data for single salts to the low temperatures of melting of mixtures. We have tested this assumption for the mixtures studied here and find the calculated values higher by amounts up to 1.3%. A similar result was obtained by Powers et al. (*9*) for other alkali nitrate mixtures.

The previous literature includes densities for four nitrate mixtures close in composition to those studied here, and the appropriate pairs are compared in Table III. For the first three, the differences are small but one would anticipate a lower density for a mixture containing more of the lighter component. For the fourth pair, the temperature coefficient given by Papaioannou and Harrington (13×10^{-4}) seems inordinately large so that their results for this system are suspect.

Table III. Densities in Grams Cm^{-3} of Some Nitrate Melts at Selected Temperatures

Temp, °C	This work		Literature		
	Mixture	Density	Density	Mixture	Ref.
300	0.54 $LiNO_3$	1.820	1.854	0.60 $LiNO_3$	*7*
350	0.46 $NaNO_3$	1.783	1.822	0.40 $NaNO_3$	
400		1.746	1.790		
300	0.41 $LiNO_3$	1.846	1.877	0.43 $LiNO_3$	*8*
350	0.59 KNO_3	1.804	1.838	0.57 KNO_3	
400		1.762	1.799		
300	0.59 $LiNO_3$	1.823	1.836	0.60 $LiNO_3$	*7*
350	0.41 KNO_3	1.784	1.802	0.40 KNO_3	
400		1.744	1.765		
300	0.45 $NaNO_3$	1.893	1.891	0.43 $NaNO_3$	*8*
350	0.55 KNO_3	1.854	1.825	0.57 KNO_3	
400		1.816	1.758		

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