versity of Leeds, for allowing this work to be done in his department.

Glossary

A, B, C	constants
ΔG^E	Gibbs excess free energy of mixing, J/mol
M	molecular weight
$\underline{V}$	molal volume, L/mol
$\bar{V}$	partial molal volume, L/mol
x_i	mole fraction of (i) in the liquid
μ	viscosity coefficient, (N s)/m^2
ν	kinematic viscosity, m^2/s
μ_{ij}	constant
ν_{ij}, ν_{ji}	constants
ϕ	volume fraction

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Additivity of Volumes in Hydrated Melts: Mixtures of Magnesium Nitrate Hexahydrate with Sodium and Potassium Nitrate

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Densities of molten mixtures of $Mg(NO_3)_2{\cdot}6H_2O$ with $NaNO_3$ and KNO_3 were measured as a function of temperature and univalent nitrate content. The equivalent volume–composition isotherms were linear with respect to equivalent fraction of $NaNO_3$ or KNO_3, over the composition range investigated. Partial equivalent volumes ($\bar{V}_i$s) of the constituents were computed by extrapolating these linear isotherms.

The volumes in many binary molten nitrate mixtures (*5, 6*) and hydrated melts (*1, 3*) are reported to be additive. The principle of additivity provides a useful basis for estimating the equivalent volumes of mixtures from limited density data. In continuation of the studies (*3, 4*) regarding physicochemical behavior of hydrated salts, the results of the density measurements for the system $Mg(NO_3)_2{\cdot}6H_2O$–(Na, K)NO_3 are presented in this paper.

Experimental Section

Material. Salts used in this study were AnalaR (BDH) grade. Alkali metal nitrates were dried by heating at about 200–250 °C for several days. Volumetric analysis of $Mg(NO_3)_2{\cdot}6H_2O$ using EDTA established its water content within ±0.02 of the stoichiometric value of 6.

Apparatus. A manometric densitometer originally designed by Husband (*2*) was modified so as to permit a direct measurement of volume of a known amount of the melt. The densitometer, its calibration, and the measuring technique have been described earlier (*3*). The temperatures of the oil bath (ca. 15 L) were controlled and measured with a precision of ±0.1 °C. The estimated precision of the reported densities is ±0.1%.

Results and Discussion

The density data for the mixtures investigated have been presented in Tables I and II. The coefficients of linear density/equivalent volume–temperature equations, for various compositions, along with the standard deviation of the fit and the maximum departure of any experimental observation from the "best" straight line drawn through the points, are recorded in Table III. Isotherms of equivalent volume (V_e) vs. equivalent fraction (x') of the univalent nitrate in the mixture were linear (Figure 1) within the limits of experimental accuracy, over the composition range studied, and could be described by equations of the type

$$V_e(\text{cm}^3\ \text{equiv}^{-1}) = A - Bx'$$

Table I. Density Data for $Mg(NO_3)_2{\cdot}6H_2O$–$NaNO_3$ Mixtures

Temp, °C	Density, g cm^{-3}	Temp, °C	Density, g cm^{-3}
9.63[a]		14.9[a]	
94.7	1.5520	93.0	1.5610
100.2	1.5470	95.4	1.5590
107.0	1.5420	100.0	1.5550
117.0	1.5330	105.1	1.5520
120.0	1.5320	109.0	1.5490
128.0	1.5260	115.0	1.5450
		121.0	1.5360
		126.0	1.5320
		132.0	1.5270
20.5[a]		25.0[a]	
89.0	1.5860	96.3	1.5940
91.0	1.5830	97.6	1.5930
95.1	1.5800	100.2	1.5900
99.7	1.5770	108.0	1.5790
105.5	1.5720	112.0	1.5760
110.0	1.5670	116.0	1.5720
116.5	1.5640	121.0	1.5690
123.0	1.5590	128.0	1.5630
129.0	1.5520		

[a] Mole percent $NaNO_3$.

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Table II. Density Data for $Mg(NO_3)_2 \cdot 6H_2O-KNO_3$ Mixtures

Temp, °C	Density, $g\ cm^{-3}$	Temp, °C	Density, $g\ cm^{-3}$	Temp, °C	Density, $g\ cm^{-3}$
4.0[a]		14.46[a]		19.0[a]	
85.6	1.5482	82.7	1.5623	89.6	1.5693
90.9	1.5447	85.7	1.5597	90.5	1.5684
95.6	1.5407	87.5	1.5588	92.4	1.5665
98.7	1.5377	90.7	1.5562	95.5	1.5646
102.6	1.5258	95.7	1.5518	101.6	1.5595
107.4	1.5225	100.0	1.5483	106.7	1.5568
112.5	1.5183	103.0	1.5457	109.0	1.5545
117.0	1.5149	107.0	1.5423	116.5	1.5480
122.0	1.5120	112.0	1.5388	122.0	1.5417
128.0	1.5083	116.0	1.5354	130.0	1.5358
		121.0	1.5320		
		125.2	1.5278		
		132.0	1.5252		
22.36		26.56		40.0	
86.8	1.5952	87.6	1.6090	82.2	1.6384
90.8	1.5888	91.5	1.6061	93.2	1.6356
95.8	1.5874	96.1	1.6022	96.3	1.6338
101.5	1.5827	100.8	1.5985	99.3	1.6310
105.6	1.5813	107.0	1.5928	103.1	1.6274
114.0	1.5727	115.0	1.5890	115.0	1.6167
120.0	1.5686	118.7	1.5834	123.5	1.6111
125.0	1.5625	122.0	1.5806	131.0	1.6031
131.0	1.5589	127.0	1.5784		
		131.5	1.5724		

[a] Mole percent KNO_3

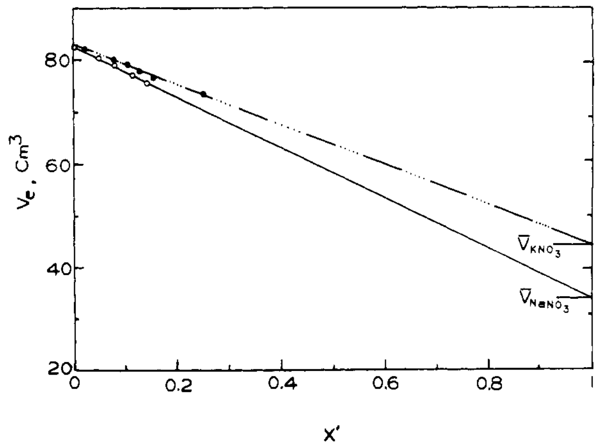

Figure 1. Equivalent volume vs. equivalent fraction of a univalent nitrate plot (at 100 °C) for $Mg(NO_3)_2 \cdot 6H_2O-(Na, K)NO_3$ systems.

with the values 41.46 and 49.64 cm^3 $equiv^{-1}$, obtained by extrapolating the equivalent volumes of molten $NaNO_3$ and KNO_3, computed from the data of McAuley et al (*5*), from the temperature of measurements to 100 °C. This discrepancy could be considered as a reflection of some systematic changes in the hydration of Mg^{2+} with the composition, in such a way that the volume–composition plots still remain linear.

Table III. Density–Temperature and Equivalent Volume–Temperature Equations for $Mg(NO_3)_2 \cdot 6H_2O-MNO_3$ Mixtures

Mol % MNO_3	Temp range, °C	$\rho = a - bt$ ($g\ cm^{-3}$)				$V_e = A + Bt$ ($cm^3\ equiv^{-1}$)				$10^4\ \alpha$, deg^{-1}
		a	$10^3 b$	SE	Max dev	A	$10^2 B$	SE	Max dev	
				$Mg(NO_3)_2 \cdot 6H_2O-NaNO_3$						
9.63	94–128	1.6258	0.784	0.0007	−0.0011	77.29	4.17	0.03	+0.04	5.12
14.9	93–132	1.6435	0.879	0.0013	+0.0026	75.58	4.58	0.07	−0.13	5.71
20.5	89–129	1.6571	0.807	0.0009	−0.0013	74.09	4.09	0.05	+0.07	5.23
25.0	96–128	1.6902	1.007	0.0016	−0.0024	71.85	4.93	0.07	+0.12	6.42
				$Mg(NO_3)_2 \cdot 6H_2O-KNO_3$						
4.0	85–128	1.6360	1.024	0.0031	−0.0050	77.73	5.56	0.16	+0.27	6.67
14.46	82–132	1.6267	0.783	0.0007	+0.0018	77.30	4.14	0.03	−0.07	5.08
19.0	89–130	1.6433	0.823	0.0008	+0.0013	76.02	4.28	0.04	−0.07	5.33
22.36	86–131	1.6638	0.799	0.0012	−0.0024	74.57	4.05	0.07	−0.11	5.15
26.56	87–131	1.6804	0.813	0.0010	+0.0020	73.66	3.93	0.05	−0.12	5.06
40.0	82–131	1.7058	0.771	0.0023	−0.0041	70.92	3.60	0.10	+0.19	4.83

Table IV. Equivalent Volume–Composition Isotherms (at 100 °C) for $Mg(NO_3)_2 \cdot 6H_2O-MNO_3$ Systems

System	Comp range (equiv fraction of MNO_3)	V_e ($cm^3\ equiv^{-1}$) $= A - Bx'$				$\bar{V}_{Mg}$	$\bar{V}_M$
		A	B	SE	Max dev		
$Mg(NO_3)_2 \cdot 6H_2O-NaNO_3$[a]	0.0–0.143	83.99	50.23	0.10	+0.18	83.99	33.76
$Mg(NO_3)_2 \cdot 6H_2O-KNO_3$	0.0–0.25	84.05	39.10	0.42	+0.5	84.05	44.95

[a] Equiv volume for $Mg(NO_3)_2 \cdot 6H_2O$ adopted from ref 4.

in which A and B are characteristic of the temperature. Values of these coefficients (at 100 °C) for the $Mg(NO_3)_2 \cdot 6H_2O-MNO_3$ system are presented in Table IV. The partial equivalent volumes ($\bar{V}_i$s) of the constituents were obtained by extrapolating these isotherms. A computed value of 84.02 cm^3 $equiv^{-1}$ for the partial equivalent volume of magnesium nitrate hexahydrate at 100 °C agrees favorably with the value 83.94 cm^3 $equiv^{-1}$ obtained from direct measurement (*4*). The values of 33.76 and 44.95 cm^3 $equiv^{-1}$, for the partial equivalent volume of $NaNO_3$ and KNO_3, respectively, at 100 °C, are considerably lower as compared

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