Densities of Neodymium Nitrate–Molten Alkali Nitrates and Lithium Perchlorate Mixtures

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The densities of mixtures of lithium perchlorate and $NaNO_3$–KNO_3 eutectic mixtures with or without neodymium nitrate have been studied as a function of temperature, and the data fitted to the expression d = a—bt by a least squares analysis. As a part of a general study of lanthanide–nitrate interaction in molten media, the densities needed to calculate molar absorbance from spectrophotometric measurements were determined. The media used were the sodium–potassium nitrate eutectic with or without lithium perchlorate admixture. The densities were measured as a function of the concentration of neodymium nitrate and the temperature over the range 230–400° C.

EXPERIMENTAL

Apparatus. The method used was similar to that employed by Janz (*1*). The apparatus consisted of a platinum bicone suspended from a balance by means of a fine platinum wire and immersed to an exactly known depth in the melt kept in a platinum crucible. The whole assembly was inside a furnace at a temperature controlled within 0.3° C.

Materials. Reagent grade chemicals were used. The $NaNO_3$–KNO_3 eutectic contained 50 mole % of each salt. The proper proportions of the two salts, dried to constant weight, were mixed, ground, and melted. The melt was broken and ground again and stored in a dessicator until needed. The neodymium oxide used had a stated purity of 99.99%. The dried oxide was weighed, placed in a vessel, dissolved in a minimum amount of HNO_3, and evaporated to dryness at 150° C. The desired weight of eutectic was then added, together with some NH_4NO_3 and heated to approximately 210° C. During dissolution, the neodymium nitrate was stirred by bubbling dry argon through the solution.

The NH_4NO_3 acts as an acid in the nitrate melt and prevents the formation of small amounts of oxynitrates. The excess of NH_4NO_3 was removed by bubbling the argon through the system at 250° C. for several hours. The mixture was then placed in the platinum crucible and the densities determined. When mixtures of $LiClO_4$ and eutectic were used, the dry salt was added together with the eutectic under the same conditions.

RESULTS AND DISCUSSION

The density results were fitted to the expression:

$$d = a - bt$$

by the least squares method, d being the measured density, a and b constants dependent on the composition, but not on the temperature, and t is expressed in ° C. The results are listed in Table I and the experimental results are reproduced to the third decimal, the highest deviation being 0.0018 for all the solutions.

In molten salt systems, which form simple solutions, only small deviations from additivity have generally been found. On the other hand, a considerable deviation indicates that specific interactions occur. The molar volume of neodymium nitrate at 300° C. has been found to be constant (119 ml./mole) down to 0.8 molar, but to increase at dilution approximately 160 ml./mole at 0.04 molar. It should also be noted that the temperature coefficient of the density b, suffers an abrupt change at about 1 molar. These facts indicate a change in the species present in the solution and point to a structural change happening at lower concentrations, confirming spectrophotometric evidence (*2*). The results obtained for pure $LiClO_4$ are in good agreement with those in the literature (*3*).

Table I. Density of $Nd(NO_3)$–$NaNO_3$–KNO_3 Mixtures at 230–400° C.

$d = a - bt$

$Nd(NO_3)_2$ Molality	a Grams/Ml.	$b \times 10^4$ Grams/Ml./t°
0	2.1147	7.035
0.0254	2.1167	7.050
0.0508	2.1285	7.317
0.1524	2.1404	7.407
0.2545	2.1587	7.254
0.3811	2.1863	7.380
0.5082	2.2186	7.571
0.7623	2.2376	6.785
1.0163	2.2741	6.867
1.2704	2.3081	6.977
1.5245	2.3371	7.087
1.7786	2.3716	7.267
2.0327	2.4183	7.533

Table II. Density of $LiClO_4$–KNO_3–$NaNO_3$ Eutectic at 230–400° C.

% $LiClO_4$ in Mixtures	a	$b \times 10^4$
100	2.1712	6.223
15	2.1394	7.441
10	2.1275	7.232
5	2.1201	7.110

Table III. $Nd(NO_3)_3$ 2.0327 Mole/Kg. Solvent in 10% $LiClO_4$, 45% KNO_3, 45% $NaNO_3$ at 230°–400° C.

$d = 2.4128 - 7.071 \times 10^{-4} t$

LITERATURE CITED

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