Apparent Molal Volumes of Alkali Metal Nitrates at 30°C

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The apparent molal volumes of the alkali metal nitrates were determined by the pycnometric and dilatometric methods. Extrapolated values were analyzed by the method of Glueckauf.

The molal volumes of ions in aqueous solution were studied by Glueckauf (*3, 4*) according to the equation:

$$\varphi_v{}^\circ = V^\circ - V^e$$

where $\varphi_v{}^\circ$ is the apparent molal volume at infinite dilution, V° the intrinsic volume of the ion, and V^e the volume change produced by electrostriction; the latter is given by either of two equations with $\sqrt{z}/\bar{r} \gtrless 0.5$ (Z = charge of the ion; $\bar{r}$ = distance between the center of the ion and the center of the dipole of the first water layer) for the spherical, tetrahedral, and octaedral ions:

$$V_e = A \frac{z^2}{\bar{r}} \quad \text{(when } \sqrt{z}/\bar{r} < 0.5\text{)}$$

$$V_e = A \frac{z^2}{r^*} - 0.083\,[2.5 \cdot r^{*3} - V^\circ] \quad \text{(when } \sqrt{z}/\bar{r} > 0.5\text{)}$$

The latter takes in consideration that a certain layer around the ion has a density similar to ice, while beyond a certain critical distance r^*, the electrostriction effect persists; 0.083 is $\Delta V/V$ for the crystallization of the water, and A is a constant. We plan to begin a study of less symmetric ions with the nitrate.

Experimental

The experimental methods employed for alkali metal nitrates are pycnometric for concentrations above $0.05M$ and dilatometric for lower concentrations. Figure 1 shows the pycnometer and dilatometer employed.

Pycnometer. The pycnometer was filled with H_2O sucked in by a capillary. After the pycnometer was thermostated, some of the liquid was removed with a very fine plastic tube, and the height of the remaining liquid in the two capillaries was read and weighed. This procedure was repeated for various heights of the liquid in the capillaries and a graph was made: weight vs. height.

By oscillating the pycnometer, the difference in level of the liquid in the two capillaries was never allowed to go beyond the millimeter. When the pycnometer was filled with solution and thermostated, the height of the *menisci* in the two capillaries was read and weighed. The weight of an equivalent amount of H_2O was obtained by interpolation in the calibration graph.

Dilatometer. The container-plug *a* was filled with solution and closed with the *d* lens tied to the *b* magnet. The *d* lens was held back by means of an external *c* magnet, and container-plug *a* was inserted into the *e* balloon, filled with solvent and·kept in motion by an agitator (*f, g*). After the solvent and the solution were thermostated, the external magnet was moved away, thus causing the *d* lens to open and the solution and the solvent to mix. The con-

traction in the capillary was then read, by a cathetometer. The capillary was calibrated by Hg, and the bottle and the container-plug were calibrated by conductivity water. The solutions were deaerated.

The thermostat was a 100-liter water-bath stirred by a $\frac{1}{2}$-HP motor and controlled by a mercury–toluene regulator. The variation shown on a Beckmann thermometer was 0.005°C. The chemicals were $LiNO_3$, $RbNO_3$, and $CsNO_3$, Schuchardt; $NaNO_3$ and KNO_3, C. Erba RP-ACS. Purity was not less than 99.8%.

All salts were carefully dried by prolonged heating under vacuum at progressively increasing temperatures up to 200°C.

Results and Discussion

The apparent molal volumes were calculated from density by the following equation:

$$\varphi_v \frac{1000\,(d_0 - d)}{m d d_0} - \frac{M_2}{d}$$

where m is the solution molality, M_2 the molecular weight of the salt, and d and d_0 were the densities of solution and water, respectively.

The apparent molal volumes were also calculated from dilatometric measurements by:

$$\varphi_v = \varphi_v{}' - \frac{\Delta V}{n_2}$$

where $\varphi_v{}'$ is the apparent molal volume of the salt (n_2 moles) dissolved in the container plug, and ΔV the contraction occurring when the solution and the solvent are mixed.

The curves of the apparent molal volumes of the alkali nitrates vs. $\sqrt{c}$ are shown in Figure 2. They are linear, following the equation of Masson (*5*):

$$\varphi_v = \varphi_v{}^\circ + S_v \sqrt{c}$$

Values $\varphi_v{}^\circ$ and S_v are given in Table I.

These values are hard to compare with data from the literature (*1, 2, 6*), owing to the different temperatures. Srinivasan gives $\varphi_v{}^\circ$ KNO_3:40.8; $\varphi_v{}^\circ$ $NaNO_3$:30.3 and the slopes 0.96 and 1.27, respectively.

Chakravarti gives $\varphi_v{}^\circ$ $NaNO_3$:30.3 and the slope 1.27, but these measurements were carried out only above $0.03M$. Gibson gives $\varphi_v{}^\circ$ KNO_3:38.2 and the slope 2.30. In all these cases, the experimental temperature is a little different. Experimental values are given in Table II. As shown in Figure 2, the experimental slopes are larger than the theoretical slope, except for the lithium nitrate probably because of the large hydration. To separate the value $\varphi_v{}^\circ$ into the anionic and cationic contributions, we used the method of Glueckauf, viz., $V_1{}^\circ - \varphi_v{}^\circ$ is plotted vs. $\sqrt{z}/\bar{r}$ for the larger alkali nitrates; where $\bar{r} = r + 1.38$, r = crystallographic radius of the cation; 1.38 = molecular radius of water; $V_1{}^\circ$ = crystallographic volume of the cation + dead space.

In fact,

$$\frac{V_1{}^\circ - \varphi_v{}^\circ}{Z^{3/2}} = \frac{V_1{}^\circ - \varphi_{M^+}{}^\circ - \varphi_{NO_3^-}{}^\circ}{Z^{3/2}} = V_e - \varphi_{NO_3^-}{}^\circ$$

(because $Z = 1$); i.e., $V_1° - \varphi_v°$ represents the electrostriction volume except for $\varphi(NO_3^-)°$ and the equation

$$V_1° - \varphi_v° = A \frac{\sqrt{z}}{r} - \varphi_{NO_3^-}°$$

can be written.

The linear equation obtained is:

$$V_1° - \varphi_v° = -33.8 + 31.9 \sqrt{z}/r$$

which is followed by all alkali nitrates except the lithium nitrate. 33.8 represents the molal volume of the ion NO_3^- and 31.9 the constant of the electrostriction law, in agreement with the value proposed by Glueckauf (33.0). The sizes of NO_3^- proposed by Ubbelohde (7) are used to calculate the molal volume of the discoid NO_3^- as a cylinder whose base radius is 2.31 Å and height 2.2 Å.

This calculation gives the value 22.2 ml·mol^{-1}, much lower than 33.8. If the method of Hepler is used to calculate the $\varphi_v°$ (NO_3^-), the average value 30.2 is obtained. The method of Mukerjee gives 33.8.

The calculated value 22.2 is quite different from both 33.8 and 30.2. It is noteworthy that the molal volume of NO_3^-, calculated as a sphere whose radius is 2.31 Å (7), is 31.1 ml·mol^{-1}.

The ions (Na^+, K^+, Rb^+, and Cs^+), for which $\sqrt{z}/r < 0.5$, follow the electrostriction law of Glueckauf:

$$V^e = A \frac{z^2}{r}$$

as shown in Table III.

Lithium ion, for which $\sqrt{z}/r > 0.5$, is an exception since it has a structure-making effect on the solvent. Applying the rule:

$$V^e = \frac{Az^2}{r^*} - 0.083 \left[2.5 (r^*)^3 - V°\right]$$

that takes in consideration the formation of icebergs around the ions ($\sqrt{z}/r > 0.5$), the value -4.7 ml·mol^{-1} is obtained, in good agreement with the experimental value:

$$\varphi_v° (LiNO_3) - 33.8 = -4.9 \text{ ml·mol}^{-1}$$

and a value of $r^* = 2.65$ Å, the distance from the center of the ion beyond which the electrostriction effect prevails over the effect of structure making.

Therefore, in the solution of alkali nitrates, the molal volumes of the alkali ions follow the rule:

$$\varphi_v° = V° - V^e$$

On the contrary, the volume of the asymetrical nitrate ion almost coincides with the volume of the rotating ion.
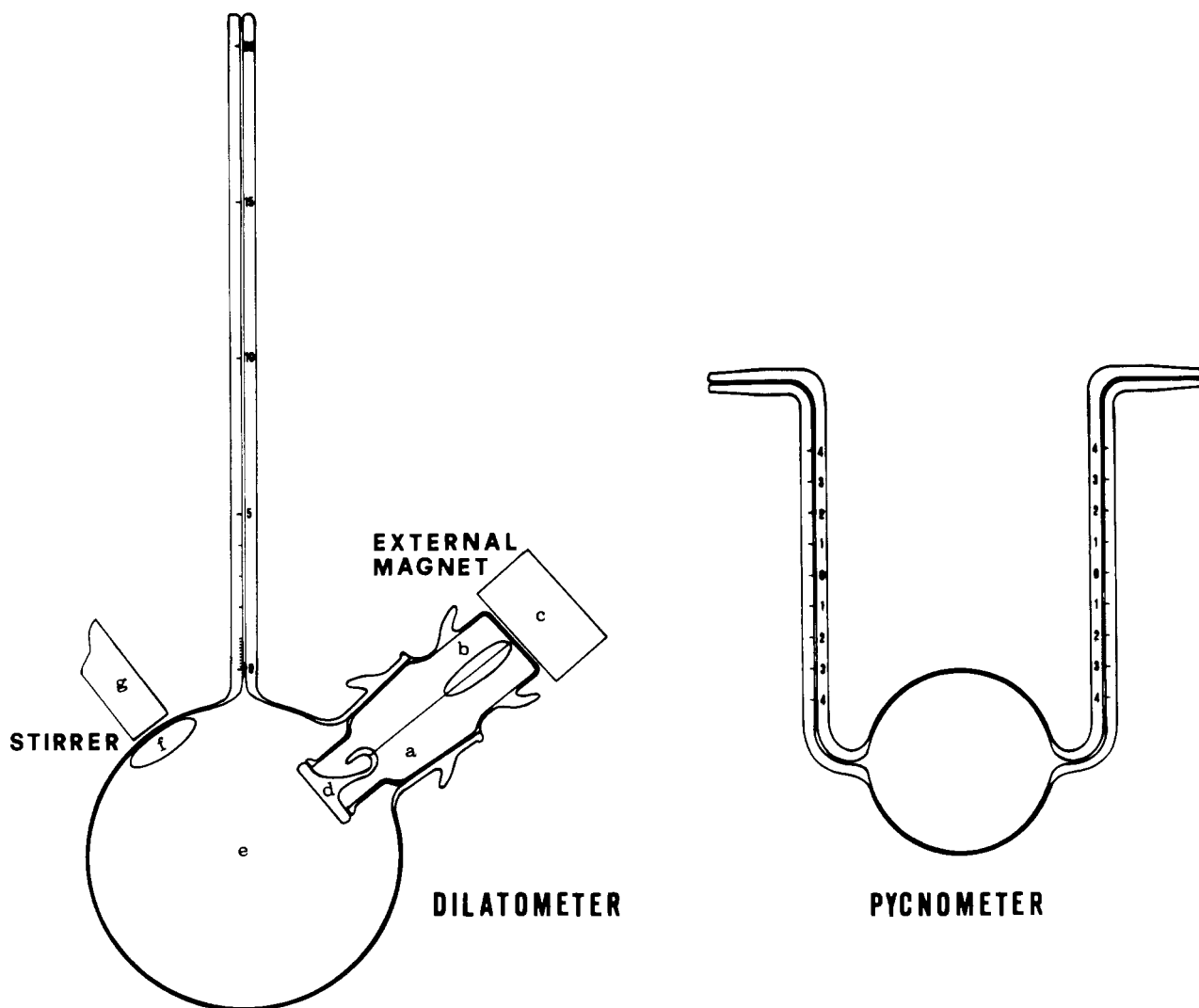

EXTERNAL
MAGNET

STIRRER

DILATOMETER

PYCNOMETER

Figure 1. Dilatometer and pycnometer

Table I. Extrapolated $\varphi_v°$ and Experimental Slope of Alkali Metal Nitrates

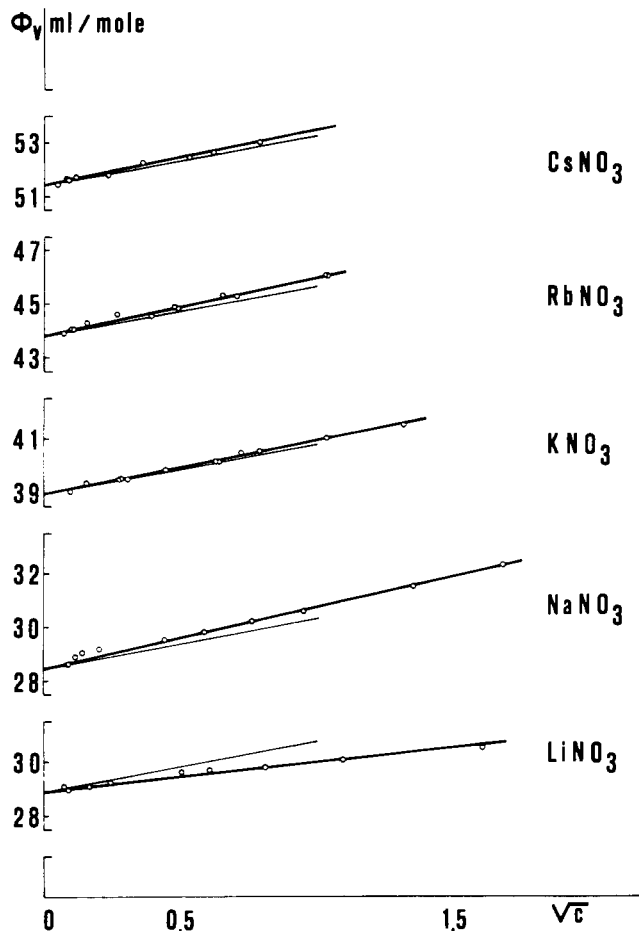| Salt	$\varphi_v°$	S_v
LiNO$_3$	28.9	1.122
NaNO$_3$	28.5	2.293
KNO$_3$	39.0	2.025
RbNO$_3$	43.8	2.204
CsNO$_3$	51.4	2.050

Table III. Experimental and Calculated $\varphi_v°$ of Alkali Metal Ions

	$\varphi_v°$	$V° - 31.9\,z^2/r$
Na$^+$	−5.4	−5.2
K$^+$	5.2	5.0
Rb$^+$	10.0	9.9
Cs$^+$	17.6	17.9

Table II. φ_v and Density of Solutions of Alkali Metal Nitrates

$\sqrt{C}$, mol$^{\frac{1}{2}}\cdot$l.$^{-\frac{1}{2}}$	d, g·ml^{-1}	φ_v, ml·mol^{-1}
	LiNO$_3$	
1.6112	1.09562	30.6
1.0975	1.04264	30.1
0.8103	1.02141	29.8
0.6079	1.01019	29.7
0.5049	1.00558	29.7
0.2410	..	29.3
0.1642	..	29.1
0.0908	..	29.0
0.0754	..	29.1
	NaNO$_3$	
1.6861	1.14570	32.4
1.3528	1.09368	31.6
0.9508	1.04495	30.6
0.7610	1.02744	30.2
0.5857	1.01461	29.9
0.4439	1.00657	29.5
0.2020	..	29.2
0.1420	..	29.1
0.1136	..	28.9
0.0875	..	28.6
	KNO$_3$	
1.3183	1.09959	41.5
1.0360	1.06037	41.0
0.7894	1.03352	40.6
0.7210	1.02758	40.5
0.6425	1.02090	40.2
0.6301	1.01990	40.2
0.4447	1.00781	39.9
0.3065	1.00149	39.5
0.2817	1.00055	39.6
0.2779	..	39.5
0.1550	..	39.4
0.0961	..	39.0
0.0942	..	39.0
	CsNO$_3$	
0.7895	1.08423	53.1
0.6197	1.05034	52.7
0.5328	1.03614	52.5
0.3600	1.01413	52.3
0.2322	1.00340	51.9
0.1181	..	51.7
0.0927	..	51.6
0.0797	..	51.7
0.0539	..	51.4
	RbNO$_3$	
1.0454	1.10670	46.1
1.0365	1.10478	46.1
0.7084	1.04703	45.3
0.6547	1.03951	45.3
0.4925	1.02059	44.9
0.4753	1.01886	44.9
0.3910	1.01141	44.6
0.2679	1.00304	44.6
0.1550	..	44.3
0.1060	..	44.1
0.0979	..	44.1
0.0711	..	43.9

Figure 2. Plot of φ vs. $\sqrt{c}$ at 30°C. Experimental points, O; theoretical curve, —

In the crystalline and fused state, the ion NO$_3^-$ is not in free rotation, owing to the high strength of interaction of the ions and to steric reasons that hinder a complete rotation. That the ionic volume of NO$_3^-$ in aqueous solutions is very near to 31.1 and that the hydration lessens the ionic interaction encourage the assertion that probably in the solution state, the discoid NO$_3^-$ reaches a state of complete rotation at this temperature.

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