

The Osmotic and Activity Coefficients of Some Salts Having Relatively Large Molar Volumes

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Osmotic and activity coefficients are reported for aqueous solutions of ammonium iodide, tetramethylammonium nitrate, and tetraethylammonium nitrate. One dilute solution value of the osmotic coefficient for each of several slightly soluble perchlorate salts is also included. Solvent structure enforced ion-pairing is evident in solutions of the tetraalkylammonium nitrates, a possibility of cation-anion hydrogen bonding is indicated by the data for the ammonium halides.

The osmotic and activity coefficients of most of the simple uni-univalent electrolytes have been available in the literature for many years. Plots of data of this type result in families of curves which are useful in estimating the relative solvation of

the ions, the magnitude of ion pairing, and other properties of the solutions. There are, however, still a few salts for which these data are not available and for this reason we are reporting measurements on three relatively soluble salts and data at one concentration each for several slightly soluble perchlorates.

Method

The isopiestic equilibration of solutions of the salts reported herewith and solutions of sodium chloride were performed in the usual manner. Special precautions were necessary, however, in the handling of ammonium iodide in solution due to its instability in the presence of air. The reagent grade solid ammonium iodide was found to be quite pure. The aqueous solution, when exposed to air, was observed to turn yellow in 10–15 min. In order to avoid decomposition, the solid salt was dissolved in

Table I. Molalities of Isoplestic Solutions

NaCl	Me ₄ NNO ₃	Et ₄ NNO ₃	NH ₄ I	KClO ₄	CsClO ₄	Me ₄ NClO ₄	Et ₄ NClO ₄
0.0527				0.0539	0.0541	0.0547	0.0551
0.0743					0.0769		0.0780
0.0801					0.0832		
0.0863							0.0913
0.1018							0.1080
0.1075				0.1103			
0.1326				0.1373			
0.3993	0.4387	0.4874					
0.4945			0.4995				
0.4965	0.5524	0.6245					
0.5910	0.6656	0.7627					
0.7145	0.8155	0.9494					
0.8752	1.104	1.203					
1.003			1.024				
1.050	1.223	1.489					
1.190			1.221				
1.227	1.456	1.778					
1.459	1.754	2.171					
1.589			1.650				
1.668	2.023	2.511					
1.768	2.154	2.681					
1.868	2.290	2.855					
2.002	2.463	3.064					
2.118			2.240				
2.275	2.823	3.519					
2.542	3.189	3.941					
2.623			2.832				
3.024	3.852	4.697					
3.044			3.345				
3.295	4.236	5.121					
3.652	4.739	5.687					
3.750			4.242				
3.948	5.179	6.233					
4.228	5.605	6.576					
4.275			4.956				
4.590	6.162	7.168					
4.860			5.799				
5.025	6.818	7.855					
5.124			6.177				
5.254		8.217					
5.474			6.700				
5.812			7.210				
6.138			7.748				

Table II. Osmotic and Activity Coefficients at 25 °C

<i>m</i>	Me ₄ NNO ₃		Et ₄ NNO ₃		NH ₄ I	
	ϕ	γ	ϕ	γ	ϕ	γ
0.1	0.903	0.731	0.870	0.679	0.930	0.775
0.2	0.876	0.658	0.824	0.584	0.921	0.729
0.3	0.857	0.612	0.794	0.524	0.916	0.701
0.4	0.843	0.578	0.770	0.480	0.913	0.683
0.5	0.832	0.552	0.751	0.447	0.912	0.669
0.6	0.823	0.531	0.736	0.420	0.911	0.659
0.7	0.817	0.514	0.722	0.398	0.911	0.650
0.8	0.812	0.498	0.711	0.379	0.912	0.642
0.9	0.807	0.485	0.701	0.363	0.913	0.637
1.0	0.804	0.473	0.692	0.348	0.915	0.631
1.2	0.800	0.454	0.678	0.325	0.918	0.624
1.4	0.797	0.439	0.666	0.304	0.921	0.617
1.6	0.794	0.426	0.658	0.289	0.924	0.614
1.8	0.793	0.416	0.651	0.275	0.928	0.611
2.0	0.795	0.407	0.645	0.263	0.932	0.609
2.2	0.797	0.400	0.641	0.254	0.936	0.607
2.4	0.799	0.394	0.640	0.246	0.939	0.605
2.6	0.801	0.389	0.639	0.239	0.942	0.605
2.8	0.803	0.384	0.639	0.232	0.945	0.604
3.0	0.807	0.380	0.640	0.227	0.950	0.605
3.5	0.815	0.373	0.645	0.216	0.959	0.606
4.0	0.823	0.367	0.657	0.208	0.969	0.609
4.5	0.833	0.363	0.668	0.203	0.977	0.612
5.0	0.844	0.360	0.681	0.198	0.984	0.615
5.5	0.853	0.358	0.695	0.195	0.989	0.618
6.0	0.862	0.357	0.709	0.193	0.995	0.621
6.5	0.871	0.356	0.724	0.191	1.001	0.624
7.0	0.880	0.357	0.738	0.190	1.008	0.628
7.5			0.753	0.190	1.015	0.633
8.0			0.767	0.189		

Table III. The Osmotic Coefficients of Some Representative Salts in Aqueous Solutions at 0.1 *m*^a

	F ⁻	Cl ⁻	Br ⁻	I ⁻	NO ₃ ⁻	ClO ₄ ⁻
Li ⁺		0.939	0.943	0.952	0.938	0.951
Na ⁺	0.924	0.932	0.934	0.938	0.921	0.930
NH ₄ ⁺		0.927	0.928 ^e	0.930 ^c	0.911	0.901 ^d
K ⁺	0.930	0.927	0.928	0.932	0.906	0.908 ^c
Rb ⁺	0.937 ^f	0.923	0.922	0.921	0.903	
Cs ⁺	0.938 ^f	0.917	0.917	0.916	0.902	0.896 ^c
Me ₄ N ⁺	0.945 ^g	0.914 ^b	0.910 ^b	0.885 ^b	0.903 ^c	0.889 ^{c,h}
Et ₄ N ⁺	0.976 ^g	0.913 ^b	0.892 ^b	0.855 ^b	0.870 ^c	0.880 ^c

^a All data are from ref 5 except where otherwise noted. ^b Reference 3. ^c This work. ^d Reference 2. ^e Reference 1. ^f Reference 6. ^g Reference 7. ^h Extrapolated from data obtained up to saturation.

degassed distilled water and immediately placed in the isopiestic apparatus which was then evacuated to the vapor pressure of water at 25 °C. It was found that the platinum clad silver dishes which are normally used in this work increased the rate of NH₄I decomposition, and glass dishes were substituted. An increase in the time necessary for equilibration using the glass dishes was noticeable but not excessive. The most dilute solutions required approximately 3 weeks for equilibration.

The tetramethyl- and tetraethylammonium nitrates were prepared by passing a solution of the reagent grade chloride salts through an anion exchange resin which had been converted to the nitrate form. The perchlorate salts were prepared by the addition of perchloric acid solution to solutions of the respective chlorides. The slightly soluble perchlorate salts were separated and recrystallized three times each from distilled water. All salts were vacuum dried prior to use.

Results and Discussion

The primary data are presented in Table I. The activity and osmotic coefficients at rounded concentrations are reported in

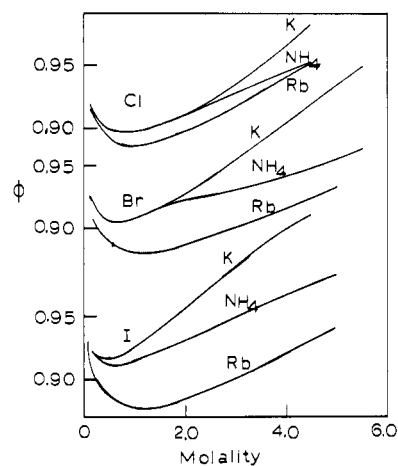

Figure 1. Osmotic coefficients of potassium, ammonium, and rubidium halides.

Table II, except that the osmotic coefficients of the perchlorates are included in Table III. Osmotic coefficients were calculated from the relationship

$$\phi = (m_{\text{ref}}/m) \times \phi_{\text{ref}}$$

Activity coefficients were calculated from the equation (4).

$$\ln \gamma = \ln \gamma_{\text{ref}} + \ln \frac{m_{\text{ref}}}{m} + 2 \int_0^{m_{\text{ref}}} \left(\frac{m_{\text{ref}}}{m} - 1 \right) d \ln (m\gamma)_{\text{ref}}^{1/2}$$

A comparison of the osmotic coefficients of some uni-univalent electrolytes in 0.1 *m* solutions is shown in Table III. The fluoride salts are unique among the cations in that the osmotic coefficients *increase* with increasing size of the cation. This is indicative of ion pairing of fluoride ion with the smaller cations. A similar trend is noted for lithium and sodium ion with increasing size of the halide ion. The nitrates and perchlorates do not continue the ion size pattern established by the halides but the osmotic coefficients of the perchlorates of the smaller cations, with the exception of ammonium ion, are larger than the coefficients of the corresponding nitrates. This is probably due to the larger size and smaller charge density of the perchlorate ion.

The ammonium salts in dilute solutions have almost the same osmotic coefficients as the corresponding potassium salts. In more concentrated solutions, however, the ammonium bromide and iodide osmotic coefficients (Figure 1) fall intermediate between the corresponding potassium and rubidium salts while the osmotic coefficients of ammonium chloride approach those of rubidium chloride. This indicates a special type of ammonium-anion association in concentrated solutions and is suggestive of hydrogen bonding.

The activity coefficients of the tetraalkylammonium nitrates in concentrated solutions are quite small, being comparable in size to those of the bromides but not so small as those of the iodides. Solvent structure enforced ion pairing has been cited (3) as an explanation for the small osmotic and activity coefficients of salts having both large cations and anions. The nitrates and perchlorates of the tetraalkylammonium series do not continue the pattern, however, as the osmotic coefficients of these salts are larger than those of the corresponding tetraalkylammonium iodides.

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