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EXCESS ENTHALPY AND ENTROPY OF AQUEOUS METHYL-SUBSTITUTED AMMONIUM NITRATE AND TETRAMETHYLGUANIDINIUM NITRATE

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ABSTRACT

Heats of dilution have been measured for aqueous solutions of methyl, dimethyl and trimethylammonium nitrate and for tetramethylguanidinium nitrate at 25°C. These data have been combined with similar data for ammonium and tetramethylammonium nitrate and with activity coefficient data for all of the salts to yield excess entropies. Apparent relative molal enthalpies increase in a regular manner from ammonium to dimethylammonium nitrate and then decrease to tetramethylammonium nitrate with tetramethylguanidinium nitrate having the largest values at any concentration. These results emphasize the inability to predict thermodynamic properties of tetramethylguanidinium salts from those of alkylammonium salts of comparable size.

INTRODUCTION

Colligative property data in the form of osmotic and activity coefficients are available in the literature for NH_4NO_3 [1], all methyl-substituted ammonium nitrates [2,3] and tetramethylguanidinium nitrate (Me_4GuNO_3) [4]. It was noted from these data that cation–anion hydrogen bonding appears to be favored over ion–solvent interactions for all methylammonium cations containing three or four protons, i.e. NH_4NO_3 and $MeNH_3NO_3$. It was speculated that since the nitrate anion contains three oxygen acceptor atoms, that perhaps three protons might be involved in the cation–anion association process. The osmotic coefficients of Me_4GuNO_3 in the more concentrated solutions are not too different from those of NH_4NO_3 solutions of the same concentration, but are smaller than those of the methyl-substituted salts, thus indicating that cation–anion association probably also occurs in aqueous solutions of this salt. Because of the interpretation given to these colligative property data, it seemed desirable to obtain confirming evidence in the form of calorimetric data.

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EXPERIMENTAL

The parent bases CH_3NH_2 and $(CH_3)_3N$ were obtained as aqueous solutions from Aldrich Chemical Company. $(CH_3)_2NH$ was obtained as an aqueous solution from Eastman Kodak. The tetramethylguanidine is available as a pure liquid from Pfaltz and Bauer. The method of preparation of the nitrate salts was identical in all cases. An aqueous solution of the free base was almost neutralized with aqueous HNO_3. A slight excess of the base was used since each base is volatile. The water and excess base from each of the solutions was removed by drying in a vacuum desiccator over concentrated sulfuric acid and then over P_4O_{10}. The dried salts were recrystallized at least three times from methanol–ether solutions and dried again in the same manner. They were then stored over P_4O_{10} under vacuum. Solutions of known weights of each salt were passed through ion-exchange columns in the hydrogen form. Titration of the eluent gave molecular weights which agreed with those calculated for the anhydrous salts within the accuracy of the titration (0.1–0.2%).

The heats of dilution of the salts were measured using the technique of the "broken ampoule". The experimental technique was the same as that used in earlier heat of dilution measurements [5]. The apparatus was that described [6] for previously reported heat capacity measurements. The heats of dilution data, given in Table 1, have a precision of about 1%. The average deviation of ϕ_L values for members of a series from the mean value is 0.5–3.4%.

RESULTS AND DISCUSSION

The apparent relative molal heat content of a solution is obtained by dilution to infinite dilution, thus

$$\phi_L = \frac{-\Delta H}{n_2} \qquad (1)$$

In practice a given solution is diluted to several finite concentrations and an extrapolation of the slope, $\Delta\phi_L/\Delta m^{1/2}$, is performed, knowing [7] that the limiting Debye–Hückel slope is 1975 J $mole^{-1}$ for 1,1 electrolytes. For all the nitrate salts, the initial slope of the ϕ_L vs. $m^{1/2}$ plot was positive, as expected from the Debye–Hückel limiting law, became zero in the vicinity of $m^{1/2} = 0.25$–0.35 and then became negative for higher concentrations. The approximate concentration at which this point occurred was determined by finding a solution of such a concentration that dilution produced neither heating nor cooling. The plot of ϕ_L values in Fig. 1 shows that the slope is nearly constant at concentrations greater than 1 m except for Me_4GuNO_3. Because of the inflections in the curves it was felt that more accurate values of $\bar{L}_2$ could be obtained from an expanded plot than from an attempt to

TABLE 1

Heats of dilution

ϕ_L values given in joules.

m_1	$10^2 m_2$	q/n_2	$-\phi_L$	$-\phi_L$(ave)
Me_4GuNO_3				
1.088	0.806	752	590	566
	1.322	727	527	
	1.402	760	554	
	1.521	753	542	
	1.749	798	565	
1.754	0.777	899	740	770
	1.087	928	745	
	1.156	948	762	
	1.372	1004	802	
	1.668	1018	799	
2.425	1.195	1079	889	909
	1.517	1125	913	
	1.867	1154	925	
3.902	1.459	1277	1069	1071
	2.100	1301	1061	
	2.727	1333	1070	
	3.505	1356	1072	
	3.585	1567	1082	
5.219	1.803	1242	1017	1019
	2.019	1284	1048	
	2.521	1261	1004	
	4.988	1293	1007	
7.182	1.917	1157	928	943
	2.220	1165	920	
	3.145	1256	981	
	4.397	1269	976	
$MeNH_3NO_3$				
1.014	1.013	775	600	633
	1.365	857	654	
	1.405	862	656	
	1.715	841	620	
1.732	1.814	1563	1337	1307
	2.201	1562	1323	
	2.442	1531	1285	
	2.515	1536	1287	
	2.969	1562	1304	
2.609	1.686	2134	1914	1927
	1.903	2131	1902	
	2.128	2154	1917	
	2.615	2186	1935	
	3.184	2228	1966	
	3.341	2185	1922	
	3.379	2196	1933	
3.503	2.424	2630	2383	2418
	3.001	2672	2413	
	3.481	2711	2447	
	3.796	2693	2429	
4.396	2.579	3096	2845	2884
	3.006	3115	2856	

TABLE 1 (continued)

m_1	$10^2 m_2$	q/n_2	$-\phi_L$	$-\phi_L$(ave)
	3.259	3165	2902	
	3.628	3164	2900	
	3.713	3179	2915	
$Me_2NH_2NO_3$				
1.021	1.167	707	517	506
	1.415	723	517	
	1.426	706	500	
	1.687	726	506	
	1.829	718	492	
1.827	2.102	1182	946	937
	2.191	1182	943	
	2.287	1166	924	
	2.428	1175	928	
	2.769	1193	939	
	2.795	1197	942	
2.693	3.155	1556	1294	1297
	3.346	1560	1297	
	3.463	1573	1309	
	3.992	1571	1307	
	4.148	1543	1280	
3.659	3.524	1857	1593	1618
	3.687	1860	1596	
	3.947	1883	1619	
	4.392	1900	1636	
	4.611	1913	1650	
4.543	4.456	2191	1926	1912
	5.212	2153	1904	
	5.469	2147	1907	
Me_3NHNO_3				
1.011	1.251	986	790	807
	1.376	997	795	
	1.600	1050	835	
1.802	2.026	1475	1246	1283
	2.197	1554	1319	
	2.408	1525	1288	
	2.562	1521	1280	
2.710	2.722	1908	1672	1688
	3.319	1923	1683	
	3.437	1947	1705	
	3.959	1903	1666	
	4.323	1945	1712	
3.549	2.732	2213	1972	1954
	3.163	2305	1964	
	3.413	2182	1940	
	4.563	2156	1933	
	4.563	2196	1970	
4.563	3.542	2535	2294	2304
	4.036	2533	2298	
	4.229	2524	2292	
	4.563	2544	2318	
	4.676	2541	2317	

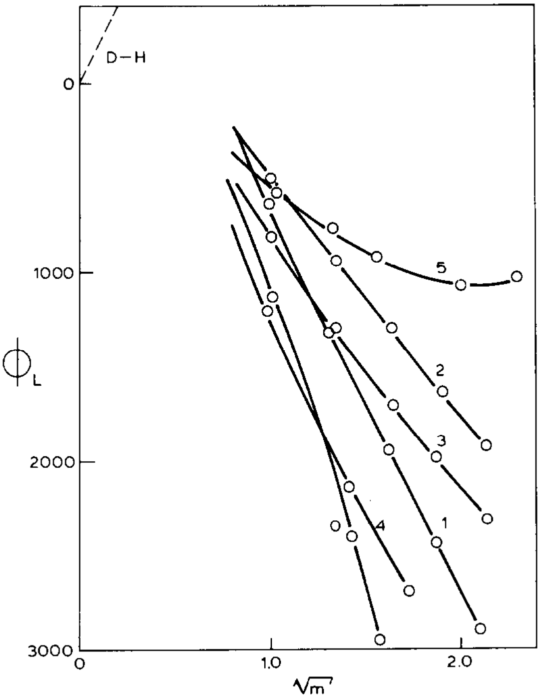

Fig. 1. Plots of ϕ_L vs. $m^{1/2}$. 0, NH_4NO_3; 1, $MeNH_3NO_3$; 2, $Me_2NH_2NO_3$; 3, Me_3NHNO_3; 4, Me_4NNO_3; 5, Me_4GuNO_3.

express the behavior analytically. The partial relative molal heat contents were calculated from

$$\bar{L}_2 = \phi_L + \tfrac{1}{2}m^{1/2}\left(\frac{d\phi_2}{dm^{1/2}}\right) \tag{2}$$

The partial molal excess entropies were calculated [8] from

$$\bar{S}_2^E = \frac{\bar{L}_2}{T} - \nu RT \ln\gamma_T = \frac{\bar{L}_2}{T} - \bar{G}_2^E$$

using known activity coefficient data [1–4].

The ϕ_L values for the ammonium nitrates follow a regular, if unexpected, pattern: $NH_4^+ < MeNH_3^+ < Me_2NH_2^+ > Me_3NH^+ > Me_4N^+$. This is reminiscent of the osmotic coefficient data for these compounds except that the larger ϕ_L values are for solutions of the $Me_2NH_2^+$ salt and the behavior continues for the more concentrated solutions. The ϕ_L curve for Me_4GuNO_3 lies far above all of the ammonium nitrate curves, and, more significantly, far above the Me_4MNO_3 curve although the volume of the Me_4Gu^+ ion is intermediate between the volumes of the Me_4N^+ and Et_4N^+ ions [9].

The excess entropies (Table 2) also follow a regular order; $NH_4^+ < MeNH_3^+ < MeNH_2^+ < Me_3NH^+ > Me_4N^+$, with the entropies of all the salts

TABLE 2

Relative partial molal heat content and excess entropy

$\bar{L}_2$ values in J mole^{-1}; $\bar{S}_2^E$ values in J K^{-1} mole^{-1}.

m	NH_4NO_3 [a]		$MeNH_3NO_3$		$Me_2NH_2NO_3$		Me_3NHNO_3 [a]		Me_4NNO_3 [b]		Me_4GUNO_3	
	$\bar{L}_2$	$\bar{S}_2^E$	$\bar{L}_2$	$\bar{S}_2^E$	$\bar{L}_2$	$\bar{S}_2^E$	$\bar{L}_2$	$\bar{S}_2^E$	$\bar{L}_2$	$\bar{S}_2^E$	$\bar{L}_2$	$\bar{S}_2^E$
1.0	−2550	+2.9	−1670	5.1	−1090	6.7	−1500	6.7	−2220	5.1	−525	10.7
2.0	−4770	−1.5	−3000	3.5	−1890	6.5	−2370	6.6	−3420	3.5	−840	13.3
3.0	−5900	−3.1	−3850	2.3	−2480	6.0	−2900	6.6	−4110	2.3	−1030	15.7
4.0	−7110	−5.5	−4590	1.1	−2980	5.4	−3250	6.4	−4590	1.2	−1070	18.2
4.5	−7660	−6.6	−4920	0.6	−3200	5.1	−3380	6.4				
5.0									−4950	0.4	−1030	20.3
6.0											−980	21.1
7.0											−950	21.5

[a] Calculated from data in refs. 1 and 10.

[b] From ref. 5.

except NH_4NO_3 being positive. The values of $\overline{S_2^{E}}$ for Me_4GuNO_3 are also positive but much larger than any of the ammonium nitrates. On examining the contributions of $\overline{L}_2$ and $T\overline{S_2^{E}}$ to the $\overline{G_2^{E}}$ values, it is observed that the $\overline{L}_2$ values make the greater contribution for most of the substituted ammonium salts while the $T\overline{S_2^{E}}$ values control the $\overline{G_2^{E}}$ values for the Me_4Gu salt. It was observed in the perchlorate studies [9] that the thermodynamic properties of Me_4GuClO_4 solutions were not predictable from the data available for tetraalkylammonium salts of comparable size and a similar statement may be made for the corresponding nitrates. Again, the ability of the Me_4Gu^+ ion to form strong hydrogen-bonded ion pairs with certain anions in aqueous solutions furnishes a reasonable explanation for its unexpected behavior.

REFERENCES

1 B.F. Wishaw and R.H. Stokes, Trans. Faraday Soc., 49 (1953) 27.
2 O.D. Bonner, J. Chem. Eng. Data, 21 (1976) 498.
3 O.D. Bonner, J. Chem. Eng. Data, 26 (1981) 148.
4 O.D. Bonner, J. Phys. Chem., 83 (1979) 1218.
5 O.D. Bonner and J. Juillard, J. Solution Chem., 10 (1981) 163.
6 O.D. Bonner, J.M. Bednarek and R.K. Arisman, J. Am. Chem. Soc., 99 (1977) 2898.
7 B.E. Conway and R.G. Barradas, Chemical Physics of Ionic Solutions, Wiley, New York, 1966, p. 58.
8 R.H. Wood, J. Phys. Chem., 63 (1959) 1347.
9 O.D. Bonner and J. Juillard, J. Chim. Phys., 78 (1981) 107.
10 V.B. Parker, NSRDS-NBS2, U.S. Dep. Commerce, Nat. Bur. Stand., Washington, DC, 1965.