Thermochimica Acta, 63 (1983) 157–161
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

EXCESS ENTHALPY AND ENTROPY OF AQUEOUS TETRAMETHYLGUANIDINIUM METHANESULFONATE AND TRIFLUOROMETHANESULFONATE SOLUTIONS

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(Received 28 September 1982)

ABSTRACT

Relative apparent molal heat contents, ϕ_L, are reported for the tetramethylguanidinium salts of methanesulfonic (MS) and trifluoromethanesulfonic (TFMS) acids. Relative partial molal heat contents, $\bar{L}_2$, are calculated and combined with previously reported activity coefficient data, to yield excess entropies. It is found that the values of $\bar{L}_2$ make the principal contribution to the excess entropies of Me_4GuMS solutions while the excess free energies, as calculated from activity coefficients, make the greatest contribution to the excess entropies of $Me_4GuTFMS$ solutions.

INTRODUCTION

Trifluoromethanesulfonic acid (triflic acid) has been referred to [1] as the strongest of all acids. This statement is similar to those frequently found when perchloric acid is discussed. The majority of the evidence for these statements is based on the properties of the acids in non-aqueous media. In dilute aqueous solutions, it is observed [2,3] that both acids exhibit a considerable degree of association as evidenced by their colligative properties and heat capacity in solution. This behavior has been postulated [3] to be due to a very stable hydrogen-bonded ion pair involving the hydrated proton and the anion. The association decreases in more concentrated aqueous solutions where the proton is hydrated to a lesser extent. It is significant that in all systems where this type of association occurs there is even greater association of the anion with the tetramethylguanidinium (Me_4Gu^+) cation. The H_3O^+ ion and the Me_4Gu^+ ion can both form bifurcated hydrogen bonds with the anions but only the proton can covalently bond to the anion to form a non-ionic molecule. The Me_4Gu^+ salts are therefore useful in the study of these unusual ion pairs. A comparison of the heats of dilution of Me_4Gu^+ chlorides and perchlorates has been reported [4] as a part of the study to determine why the perchlorate salt associates strongly in aqueous solution while the chloride salt does not. A similar situation exists regarding the methanesulfonate and trifluoromethanesulfonate systems and calorimetric data on these salts should be of equal interest.

EXPERIMENTAL

The best grades of methanesulfonic acid and trifluoromethanesulfonic acid available from Aldrich Chemical Co. were vacuum distilled and the center fraction retained. Anhydrous ether solutions of these acids were then neutralized with the free base, tetramethylguanidine (Pfaltz and Bauer). The salts were separated by filtration, recrystallized twice from methanol-ether solutions and dried under vacuum over concentrated H_2SO_4 and finally over P_4O_{10}. The molecular weight of each salt was obtained by passing an aqueous solution through the acid form of a cation exchange resin. Titration of the eluent showed that neither of the salts was a hydrate (or solute). In each instance the molecular weight agreed with the calculated value within the experimental error of the titration (0.1–0.2%).

The heats of dilution of the salts were measured using the "broken ampoule" technique. The experimental technique was the same as that used in the earlier heat of dilution measurements [4]. The apparatus was that used for previously reported [5] heat capacity measurements. The sets of dilution data are given in Table 1 for the two tetramethylguanidine salts.

RESULTS AND DISCUSSION

The apparent relative molal heat content of a solution, ϕ_L, is obtained by measuring the heat of dilution of that solution to infinite dilution. Since this is not experimentally possible 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 [6] that the limiting Debye–Huckel slope is 1975 J $mole^{-1}$ for 1,1 electrolytes. After obtaining ϕ_L values for the solutions, it is possible to calculate relative partial molal heat contents, $\bar{L}_2$, from the equation

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

The plot (Fig. 1) of ϕ_L vs. $m^{1/2}$ shows that the Me_4Gu MS curve is slightly S-shaped and the Me_4Gu TFMS curve is considerably more so. This is due, in part, to the fact that the concentration axis is expanded below 1.0 *m* and compressed above this concentration when the square root is extracted. Because of the nature of the curves, it was found that the most accurate slopes could be obtained from expanded plots. The partial molal excess

TABLE 1

Heats of dilution data

Me$_4$GuMs					Me$_4$GuTFMS				
m_1	$m_2 \times 10^2$	q/n	ϕ_L (J)	ϕ_L(ave) (J)	m_1	$m_2 \times 10^2$	q/n	ϕ_L (J)	ϕ_L(ave) (J)
0.997	0.701	1267	1427	1407	0.929	0.511	1797	1936	1913
	0.862	1208	1385			0.969	1736	1927	
	0.954	1228	1414			1.103	1708	1913	
	1.375	1162	1384			1.537	1705	1947	
1.497	1.042	1724	1918	1936	1.694	1.184	2781	2994	3001
	1.892	1693	1955			1.508	2725	2965	
	1.968	1657	1923			1.654	2802	3054	
	2.287	1660	1947			2.304	2694	2990	
2.464	1.935	2563	2827	2868	2.529	0.957	3391	3582	3608
	2.143	2596	2873			1.291	3395	3617	
	2.256	2586	2871			1.453	3422	3658	
	2.597	2605	2911			1.814	3315	3578	
	3.143	2520	2856			1.945	3281	3552	
						2.420	3319	3623	
3.491	1.706	3541	3790	3746	3.439	1.910	3840	4109	4064
	2.083	3473	3747			2.188	3747	4036	
	2.447	3448	3745			2.557	3758	4070	
	2.881	3385	3708			3.055	3700	4041	
	3.225	3368	3710						
	4.455	3378	3779						
4.508	1.370	4279	4501	4508	4.181	1.404	4150	4380	4347
	1.876	4239	4499			1.542	4094	4336	
	4.150	4162	4525			1.604	4114	4362	
						1.809	4065	4326	
						2.044	4067	4346	
						2.486	4025	4333	
						2.576	4031	4343	

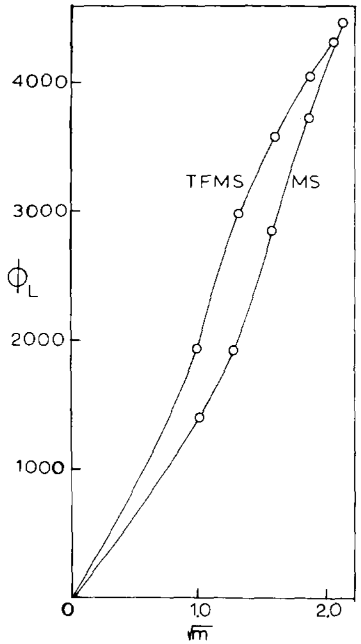

Fig. 1. Apparent relative molal heat contents of tetramethylguanidinium methanesulfonate and trifluoromethanesulfonate solutions.

entropies as given in Table 2, were calculated [7] from

$$TS^E = \bar{L}_2 - vRT \ln \gamma \pm$$

using known activity coefficient data [2].

In a previous study [4], it was noted that the values of $\bar{L}_2$ for Me_4GuCl were not too different from those of NaCl or KCl. Actually, the values of ϕ_L for Me_4GuCl are almost identical to those of Me_3NHCl up to the limit of

TABLE 2

Partial relative molal heat contents and excess entropies

m	Me_4GuMS		$Me_4GuTFMS$	
	$\bar{L}_2$ (J)	TS^E (JK^{-1})	$\bar{L}_2$ (J)	TS^E (JK^{-1})
1.0	2510	4620	3280	8890
2.0	4430	6290	4840	12630
3.0	5900	7310	5400	14680
4.0	7060	7850	5790	16140

the reported values [8] for the latter compound. They are quite different from the large positive values of ϕ_L for HCl. No other salts of Me_4Gu^+, including the nitrate which will be reported later, have been found to have positive values of ϕ_L. The large positive values of Me_4GuMS and $Me_4GuTFMS$ indicate that both of the sulfonate anions make a large contribution to the positive value of ϕ_L. These values of ϕ_L are similar in sign and magnitude to those of HCl at comparable concentrations.

The original purpose of these studies was to compare the relative molal heat contents of the two sulfonate salts. In dilute solutions the values of both ϕ_L and $\bar{L}_2$ for the trifluoro-salt are the larger. The ϕ_L curves cross at about 4.0 m and the $\bar{L}_2$ curves at about 2.5 *m* with the relative molal heat content values of the methanesulfonate salt being larger in the more concentrated solutions. Colligative property data had indicated [2] appreciable association of the TFMS salt. These calorimetric data are consistent with the activity coefficient values if one assumes that the dilute $Me_4GuTFMS$ data are representative of the heat content of the undissociated salt and that the flattening of the curve, with a resultant crossing of the Me_4GuMS curve is a result of association in the more concentrated solutions.

Large positive values of excess entropy for a solute may be due either to large positive values of $\bar{L}_2$ or large negative values of $\bar{G}_2^E$ (resulting from small activity coefficients). It is seen that for Me_4GuMS the principal contribution to TS^E is the heat content, $\bar{L}_2$. For $Me_4GuTFMS$, on the other hand, it is observed that the contribution of $\bar{G}^E$ to TS^E is almost three times that of $\bar{L}_2$. The excess entropy is thus essentially free energy controlled, as was the case for Me_4GuClO_4.

REFERENCES

1 R.D. Howells and J.D. McCown, Chem. Rev., 77 (1977) 69.
2 O.D. Bonner, J. Am. Chem. Soc., 103 (1981) 3262.
3 O.D. Bonner and N.M. Nunn, J. Solution Chem., 10 (1981) 189.
4 O.D. Bonner and J. Juillard, J. Solution Chem., 10 (1981) 163.
5 O.D. Bonner, J.M. Bednarek and R.K. Arisman, J. Am. Chem. Soc., 99 (1977) 2898.
6 B.E. Conway and R.G. Barradas, Chemical Physics of Ionic Solutions, New York, 1966, p. 58.
7 R.H. Wood, J. Phys. Chem., 63 (1959) 1347.
8 V.B. Parker, NSRDS-NBS, 2, U.S. Department of Commerce, National Bureau of Standards, Washington, DC, 1965.