Table I. Experimental Results: Molalities of Isopiestic Solutions at $T = 298.15$ K

NaCl	NaGlu	KGlu	NaCl	NaGlu	KGlu
0.2982	0.3011	0.2988	2.295	2.266	2.177
0.615	0.625	0.613	2.579	2.538	2.431
0.930	0.946	0.921	3.243	3.165	3.004
1.135	1.148	1.114	3.778	3.658	
1.466	1.473	1.425	4.194	4.051	
1.788	1.785	1.721			

Table II. Osmotic and Activity Coefficients at 298.15 K

molality,	NaGlu		KGlu	
m	ϕ	γ	ϕ	γ'
0.1	0.928	0.773	0.931	0.776
0.2	0.919	0.725	0.924	0.732
0.3	0.913	0.695	0.921	0.708
0.4	0.909	0.676	0.920	0.691
0.5	0.907	0.661	0.922	0.680
0.6	0.908	0.651	0.926	0.674
0.7	0.909	0.642	0.931	0.670
0.8	0.910	0.636	0.936	0.667
0.9	0.915	0.632	0.940	0.665
1.0	0.921	0.630	0.948	0.666
1.2	0.934	0.629	0.964	0.671
1.4	0.945	0.632	0.930	0.680
1.6	0.961	0.636	0.997	0.691
1.8	0.976	0.645	1.015	0.702
2.0	0.992	0.654	1.035	0.718
2.5	1.032	0.682	1.085	0.767
3.0	1.073	0.718	1.146	0.827
3.5	1.120	0.763		
4.0	1.167	0.813		

cation exchange column in the hydrogen form. The results were in agreement with those expected for pure anhydrous salts. The isopiestic equilibrations of solutions of the two salts with sodium chloride solutions were performed in the manner described in detail in a previous paper (*1*).

Results and Discussion

The experimental results of the isopiestic equilibrations are presented in Table I. The osmotic and activity coefficients at rounded concentrations are given in Table II. Osmotic coefficients were calculated from the relationship

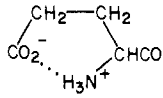
$$\phi = (m_{\text{ref}}/m)\phi_{\text{ref}}$$

Activity coefficients were calculated from the equation (*2*)

$$\ln \gamma = \ln \gamma_{\text{ref}} + \ln (m_{\text{ref}}/m) + 2 \int_0^{m_{\text{ref}}} [(m_{\text{ref}}/m) - 1] \,\mathrm{d} \ln (m_{\text{ref}}\gamma_{\text{ref}})^{1/2}$$

The values of the osmotic and activity coefficients of sodium chloride, the reference salt, are those of Robinson and Stokes (*3*).

A comparison of the coefficients of these salts reveals that the potassium salt has the larger coefficients at any concentration. This is similar to the behavior observed for the salts of monocarboxylic acids. It is different, however, from the behavior of the half-neutralized aliphatic dicarboxylic acids (*4*) where the sodium salts have the larger coefficients. These observations suggest that, whereas there is some type of interaction between the carboxylic acid proton and the carboxylate group of the normal diprotic acid, this does not occur in the glutamate anion. A zwitterionic structure $^-O_2CCH_2CH_2CHNH_3^+CO_2^-$, such as is known to exist in monocarboxylic amino acids, would seem to be reasonable, but the resultant anion would possess *two* negative and one positive charge centers. A cyclical, hydrogen-bonded structure of the type



would leave *one* free carboxylate anion and would seem to be more probable.

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Osmotic and Activity Coefficients of Methyl-Substituted Ammonium Nitrates at 298.15 K

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Osmotic and activity coefficient data are reported for three methyl-substituted ammonium nitrates. A comparison of these data with those for the other two members of the family which have already been reported enables one to note the effect of successive methyl substitution on ion-solvent and ion-ion interactions.

Osmotic and activity coefficient data have been reported for ammonium nitrate (*1*) and tetramethylammonium nitrate (*2*) but not for any of the intermediate methyl-substituted ammonium salts. For the two salts for which data have been reported, the osmotic coefficients of the ammonium salt are larger in dilute solutions while the tetramethylammonium salt has much the larger coefficients in the more concentrated solutions. This observation suggests that data for the remainder of the family might be desirable.

Method

The free bases methylamine and trimethylamine in aqueous solution were obtained from Aldrich Chemical Co. The aqueous solution of dimethylamine was from Eastman Kodak Co. The free bases, as received, were almost neutralized with aqueous nitric acid. The water and excess base from each of the solutions were removed by drying in a vacuum desiccator over

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Table I. Experimental Results. Molalities of Isopiestic Solutions at $T = 298.15$ K[a]

NaCl	TMANO$_3$	MMANO$_3$	NaCl	DMANO$_3$
0.230_2	0.242_3	0.237_6	0.382_3	0.343_1
0.345_8	0.376_8	0.366_5	0.531	0.568
0.799	0.910	0.885	0.633	0.685
1.049	1.229	1.196	0.816	0.897
1.475	1.797	1.764	1.027	1.154
1.848	2.325	2.296	1.294	1.484
2.242	2.881	2.871	1.845	2.214
2.627	3.449	3.479	2.149	2.646
3.058	4.146	4.235	2.463	3.100
3.419	4.730	4.932	2.831	3.663
3.791	5.324	5.639	3.229	4.323
4.243	6.105	6.643	3.648	5.046
4.781	7.108	7.844	3.973	5.649
5.239	7.979	8.998	4.126	5.971
5.506	8.558	9.823	4.273	6.238

[a] MMA = monomethylammonium; DMA = dimethylammonium; TMA = trimethylammonium.

Table II. Osmotic and Activity Coefficients at 298.15 K[a]

molality, m	MMANO$_3$		DMANO$_3$		TMANO$_3$	
	ϕ	γ	ϕ	γ	ϕ	γ
0.1	0.919	0.757	0.920	0.758	0.912	0.747
0.2	0.899	0.697	0.900	0.698	0.886	0.678
0.3	0.886	0.658	0.887	0.659	0.869	0.634
0.4	0.873	0.628	0.876	0.631	0.855	0.601
0.5	0.864	0.605	0.868	0.608	0.844	0.575
0.6	0.857	0.585	0.860	0.589	0.835	0.554
0.7	0.849	0.568	0.854	0.573	0.828	0.536
0.8	0.843	0.553	0.846	0.557	0.821	0.520
0.9	0.837	0.539	0.844	0.546	0.815	0.506
1.0	0.832	0.527	0.841	0.535	0.810	0.494
1.2	0.823	0.506	0.833	0.515	0.802	0.472
1.4	0.814	0.487	0.827	0.499	0.794	0.454
1.6	0.805	0.471	0.823	0.485	0.790	0.440
1.8	0.797	0.457	0.819	0.473	0.784	0.427
2.0	0.791	0.444	0.815	0.463	0.780	0.416
2.5	0.782	0.420	0.808	0.441	0.776	0.394
3.0	0.776	0.401	0.803	0.423	0.775	0.374
3.5	0.771	0.385	0.801	0.410	0.775	0.365
4.0	0.761	0.370	0.796	0.397	0.774	0.354
4.5	0.752	0.358	0.792	0.386	0.775	0.345
5.0	0.745	0.344	0.788	0.376	0.780	0.339
5.5	0.738	0.334	0.783	0.366	0.784	0.333
6.0	0.732	0.324	0.778	0.357	0.789	0.328
6.5	0.726	0.315			0.791	0.323
7.0	0.721	0.307			0.792	0.319
7.5	0.717	0.300			0.792	0.314
8.0	0.713	0.294			0.793	0.310
8.5	0.710	0.287			0.793	0.307
9.0	0.704	0.281				
9.5	0.698	0.275				

[a] MMA = monomethylammonium; DMA = dimethylammonium; TMA = trimethylammonium.

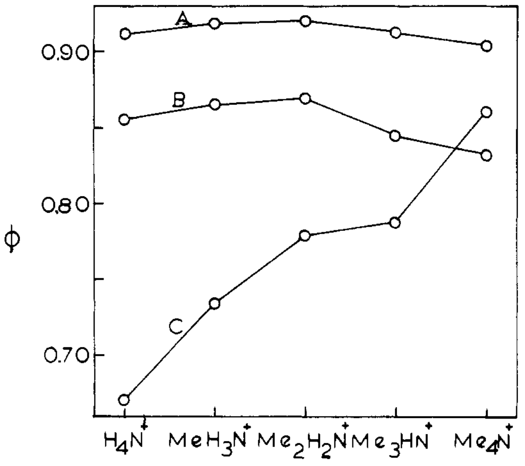

Figure 1. Osmotic coefficients of the methyl-substituted ammonium nitrates at (A) 0.1, (B) 0.5, and (C) 6.0 *m*.

concentrated sulfuric acid. The dried salts were recrystallized several times from methanol-ether solutions and dried in the same manner. They were then stored, under vacuum, over P_2O_5. The molecular weights of the salts as determined by passing solutions of known weights of each salt through ion-exchange columns in the hydrogen form and titration of the eluent gave values agreeing with those calculated for the anhydrous salts within the accuracy of the titration (0.1-0.2%).

The isopiestic equilibration of solutions was carried out in the usual manner with NaCl solutions serving as the reference. Complete experimental details have been previously reported (*3*).

Results and Discussion

The primary results of the isopiestic equilibrations are presented in Table I. The osmotic and activity coefficients at rounded concentrations are given in Table II. Osmotic coefficients were calculated from the relationship

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

Activity coefficients were calculated from the equation (*4*)

$$\ln \gamma = \ln \gamma_{\text{ref}} + \ln R + 2 \int_0^{m_{\text{ref}}} (R - 1) \, \mathrm{d} \ln (m_{\text{ref}}\gamma_{\text{ref}})^{1/2}$$

where $R = m_{\text{ref}}/m$. The values of the osmotic and activity coefficients of sodium chloride, the reference salt, are those of Robinson and Stokes (*5*).

The osmotic coefficient data in concentrated solutions (Figure 1) indicate that the expected ion-ion association, presumably through hydrogen bonding, causes the coefficients to be in the order $NH_4^+ < MeNH_3^+ < Me_2NH_2^+ < Me_3NH^+ < Me_4^+$. The data in dilute solutions where ion-solvent interactions should predominate are indicative of a competition between the two types of interactions. The same order of osmotic coefficients holds for the ammonium, methylammonium, and dimethylammonium salts, suggesting that ion-ion interactions are still important relative to ion-solvent interactions even in dilute solutions. The osmotic coefficients of the tetramethylammonium salt are the least of the family at any concentration less than 1.2 *m*, and the trimethylammonium salt coefficients are next to the least. This is the expected position of the Me_4N^+, Me_3NH^+, and $Me_2NH_2^+$ salts if ion-solvent interactions are the principal ones involved. It thus appears that cation-anion hydrogen bonding is favored over bonding of the two ions to the solvent molecules for the two cations containing three or four protons. The dimethylammonium cation has the largest osmotic coefficients in dilute solutions. It is interesting to speculate, since the nitrate anion contains three oxygen acceptor atoms, that perhaps three protons might be involved in the cation-anion association process.

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