verified for the free MEA ligand in the presence of dioxane only with the $j = 2$ and with a slope of 1.36 (Figure 2). Best-fit straight lines were obtained for the Co-MEA (Figure 3), Ni-MEA (Figure 3), Ni-MEA (Figure 4), and Cu-MEA (Figure 5) systems in the four solvents used in this study for $j = 2$, with slopes ranging from 0.79 to 2.20. The trial with $j = 3$ gave straight lines for Co-MEA and Cu-MEA in the presence of methanol, dioxane and acetonitrile solvents, but with slopes approaching 2. This confirms that the best results were obtained in most of these systems for $j = 2$. Therefore, solvation by the cosolvent can be assumed to be of major importance. This is readily apparent when the variation between W and j is large. However, it is obvious that, when $W \approx j$, solvation by the cosolvent is of minor importance. The W values obtained are calculated and written on the linear plots in the figures. In summary, the ΔG values for these systems were found to be dependent on the solvent composition (except for Ni-MEA in the presence of methanol, where the ΔG value amounts to 0.929 ± 0.005 kcal/mol). In general, these values decreased with increasing solvent concentration.

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Received for review June 3, 1980. Revised manuscript received February 23, 1981. Accepted July 27, 1981.

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

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Osmotic and activity coefficient data are reported for three methyl-substituted ammonium perchlorates. New data to replace the literature values of the coefficients of ammonium perchlorate are also included. A comparison of the coefficients of the various members of the family illustrates the effect of successive methyl substitution on ion-solvent and ion-ion interactions.

Osmotic and activity coefficient data have been reported for ammonium perchlorate (*1*). Tetramethylammonium perchlorate is soluble to the extent of less than 0.1 *m*, and there have been no colligative property data reported for the other methyl-substituted members of the family. I have recently reported (*2*, *3*) activity coefficients of the methyl-substituted ammonium chlorides and nitrates, and these data should be useful for comparisons of the contributions of the anions to the various ion-ion and ion-solvent interactions.

Method

Aqueous solutions of the free amine bases, as received from Aldrich Chemical Co. or Eastman Kodak Co., were almost neutralized with aqueous perchloric acid. The water and the excess base from each of the solutions were removed by drying in a vacuum desiccator over concentrated sulfuric acid. The dried salts were recrystallized several times from methanol-ether solution and were again dried in the same manner. They were then stored, under vacuum, over P_2O_5. The salts were found to contain no water of hydration, and the molecular weights as determined by ion exchange (*3*) agreed with those calculated for the anhydrous salts within 0.1-0.2%. Certified ammonium perchlorate was used as received from Fisher Scientific Co.

The isopiestic equilibration of solutions, using sodium chloride as the reference solution, was carried out in the usual manner. Complete details of the experimental procedure have been previously reported (*4*).

Results and Discussion

The isopiestic solutions of sodium chloride and the perchlorate salts are listed in Table I. The osmotic and activity coefficients ar rounded concentrations are given in Table II. The osmotic coefficients were calculated from the molality ratios by the relation

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

Activity coefficients were calculated from the equation (*5*)

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

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

NaCl	NH_4^+	NaCl	$CH_3NH_3^+$	NaCl	$(CH_3)_2NH_2^+$	NaCl	$(CH_3)_3NH^+$
0.1857	0.1921	0.3716	0.4040	0.3716	0.4134	0.1857	0.2021
0.3807	0.4061	0.712	0.819	0.6213	0.7285	0.3716	0.4321
0.3925	0.4182	0.747	0.865	0.712	0.847	0.712	0.927
0.5582	0.6106	0.989	1.185	0.815	0.988	0.747	0.991
0.753	0.847	1.189	1.466	1.024	1.289	0.989	1.419
0.989	1.148	1.256	1.571	1.283	1.692	1.189	1.830
1.295	1.562	1.295	1.634	1.535	2.117		
1.592	1.987	1.636	2.149	1.818	2.627		
		2.010	2.763	2.012	3.018		
		2.396	3.444	2.242	3.477		
		2.660	3.974	2.499	4.050		
		2.818	4.293	2.696	4.521		
				2.965	5.163		
				3.121	5.574		
				3.410	6.423		
				3.830	7.610		

Table II. Osmotic and Activity Coefficients at 298.15 K

molality,	NH_4ClO_4		$MeNH_3ClO_4$		$Me_2NH_2ClO_4$		Me_3NHClO_4	
m	ϕ	γ	ϕ	γ	ϕ	γ	ϕ	γ
0.1	0.916	0.754	0.905	0.739	0.902	0.730	0.891	0.712
0.2	0.895	0.693	0.881	0.668	0.871	0.655	0.854	0.627
0.3	0.879	0.648	0.863	0.622	0.848	0.605	0.824	0.572
0.4	0.864	0.615	0.848	0.588	0.830	0.567	0.800	0.528
0.5	0.852	0.590	0.835	0.560	0.813	0.536	0.778	0.494
0.6	0.843	0.568	0.825	0.538	0.801	0.512	0.759	0.464
0.7	0.834	0.549	0.816	0.518	0.791	0.491	0.741	0.439
0.8	0.826	0.532	0.807	0.501	0.782	0.473	0.726	0.417
0.9	0.819	0.517	0.800	0.485	0.773	0.456	0.711	0.398
1.0	0.814	0.505	0.792	0.472	0.765	0.442	0.706	0.381
1.2	0.802	0.482	0.780	0.448	0.750	0.416	0.676	0.352
1.4	0.791	0.462	0.766	0.427	0.736	0.395	0.655	0.327
1.6	0.783	0.445	0.757	0.410	0.723	0.376	0.636	0.306
1.8	0.776	0.431	0.749	0.395	0.711	0.359	0.617	0.287
2.0	0.771	0.418	0.741	0.382	0.701	0.328		
2.5			0.726	0.354	0.678	0.315		
3.0			0.713	0.333	0.659	0.291		
3.5			0.700	0.314	0.643	0.271		
4.0			0.688	0.297	0.627	0.254		
4.5					0.612	0.240		
5.0					0.600	0.227		
5.5					0.589	0.216		
6.0					0.578	0.206		
6.5					0.569	0.197		
7.0					0.561	0.190		
7.5					0.556	0.183		

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 (*6*).

Tetramethylammonium perchlorate is too insoluble for a meaningful isopiestic study. The osmotic and activity coefficients of the other methyl-substituted salts at all concentrations are in the order $MeH_3N^+ > Me_2H_2N^+ > Me^3HN^+$. This simple sequence is in contrast to the recently reported chloride and nitrate data (*2*, *3*). It is also noted that the order of coefficients for any cation is $Cl^- > NO_3^- > ClO_4^-$. These observations when taken together confirm that solvation decreases as the size of the anion increases and that there is much less cation–anion interaction in the perchloride solutions than was observed for the chlorides and nitrates.

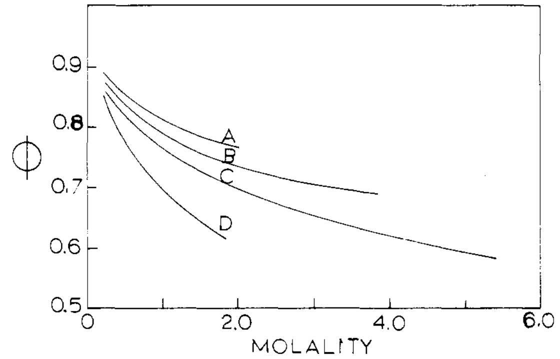

Figure 1. Osmotic coefficient of methyl-substituted ammonium perchlorates at 25 °C: (A) NH_4^+, (B) $MeNH_3^+$, (C) $MO_2NH_2^+$, (D) Me_3NH^+.

It would be anticipated that the ammonium perchlorate solutions would uniformly have the highest coefficients at any concentration. The literature values (*1*) were consistent with this expectation only at concentrations greater than 0.5 *m*. An inspection of the paper reveals that the concentrations of the isopiestic solutions were reported to only three significant figures for the more dilute solutions. This results in an uncertaintly of 0.2–1.0% in the concentration range 0.5–0.1 *m*. Furthermore, a plot of the molality ratios as calculated from these data exhibited some scatter, and too much weight was apparently given to the more dilute measurements (which had the largest uncertainty) in the extrapolation to infinite dilution. As a matter of fact, it appears that the data for concentrations above 0.7 *m* were for one solution and those for concentrations less than 0.7 *m* were observed for a different solution with the dilute-solution data lying on a curve about 1–1.5% below the extrapolated curve for the concentrated-solution data. It seemed desirable,therefore, to repeat the measurements on this system, and these data are included in Tables I and II. Osmotic coefficients of the four salts are presented graphically in Figure 1.

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Received for review May 13, 1981. Accepted November 2, 1981.

Vapor–Liquid Equilibrium with Association in Both Phases. Multicomponent Systems Containing Acetic Acid

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The vapor–liquid equilibrium behavior of the quaternary system methyl acetate–methanol–water–acetic acid was modeled by using the Margules equation in combination with Marek's method for the association of acetic acid. The constants in the Margules equation were obtained from existing or experimentally determined equilibrium composition of the constituent binary and ternary mixtures. The final equation was experimentally verified on the quaternary system in the presence and the absence of the catalyst.

Introduction

Chemical reaction with simultaneous distillation in a column is an operation of particular interest. The practical evaluation of such a process requires the formulation of a model which describes the complete operation of the column (*1*). For this purpose, data on the vapor–liquid equilibria of the multicomponent system must be available.

The usual equations used in process calculations for the determination of vapor–liquid equilibrium data are the Wohl, Margules, Van Laar, Wilson, and lately the NRTL equations. Sabylin and Aristovich (*2*) concluded that the best predictions for multicomponent systems were given by the Wilson equation, while the Wohl equation produced the worst results. The NRTL equation is superior to the Wilson equation since it can also describe systems with immiscible components. Simulation of the vapor–liquid equilibria of systems that contain associating components is, however, difficult. Owing to the complexity of the system under investigation, Sabylin and Aristovich's conclusions do not necessarily apply, and also simulation cannot be established alone by these relationships.

In the past a model was developed by Marek and Standart (*3*) and used by Marek (*4*) to correlate data of acetic acid mixtures. Jenkins and Gibson-Robinson (*5*, *6*) developed a new model based on that of Marek and Standart, but they also took into account a concentration-dependent factor for the association of acetic acid in the liquid phase. These models only require the calculation of adjustable parameters as those for the integrated form of the Gibbs–Duhem equation which correlate activity coefficients to component mole fractions. They also use correction-factor expressions to include the effect of association of acetic acid.

In the present work the model developed by Marek and Standart was used (*3*, *4*). The model is applied to the quaternary system of acetic acid with water, methanol, and methyl acetate. It is, however, established that alcohols in solution (*7*) as well as water alone and in mixture associate to form dimers and polymers (*8*). This model assumes that only acetic acid forms dimers or higher polymers and does not take into account the association behavior of the other components but only of acetic acid. In the case of systems containing acetic acid and methanol, there is a further complication that the components react to form methyl acetate, although very slowly in the absence of the catalyst. The vapor–liquid equilibrium data for these systems were therefore obtained in a flow still in order to minimize this complication. This does not, however, exclude the possibility that acetic acid does not reach the monomer-dimer equilibrium mixture. Having described the complications, we studied the use of this model for these systems.

Data Sets Examined

The following vapor–liquid equilibrium data at 760 mmHg must be known: (a) methyl acetate–methanol, (b) methyl acetate–water, (c) methyl acetate–acetic acid, (d) methanol–water, (e) methanol–acetic acid, (f) water–acetic acid, (g) methyl acetate–methanol–water, (h) methyl acetate–methanol–acetic acid, (i) methyl acetate–water–acetic acid, (j) methanol–water–acetic acid, and (k) methyl acetate–methanol–water–acetic acid. Existing data for systems given in the literature were considered to be correct and therefore were not repeated. System a has already been investigated by Teshima et al. (*9*), Crawford et al. (*10*), Bushmakin and Kish (*11*), and Bredig and Bayer (*12*). Complete data for system b have been presented only by Teshima et al. (*9*). Similarly, system d has been investigated by Fastovskij and Petrovskij (*13*), Bennett (*14*), Bredig and Bayer (*15*), Dunlop (*16*), Huges and Maloney (*17*), Ramalho et al. (*18*), and many others; system (f) by Rivenc (*19*), Brown and Ewald (*20*), Garwin and Hutchinson (*21*), Othmer et al. (*22*), and others; and finally system g by Crawford et al. (*10*), Kogan (*23*), and Teshima et al. (*9*). Data for system e have been given in the literature by Rius et al. (*24*) at pressures of ~706 mmHg and had to be repeated at atmospheric pressure. System f (water–acetic acid) has been presented by Rivenc (*19*) in weight fraction in the liquid and vapor phases. To convert it into molar fraction, we used a constant weight of monomeric acetic acid. Systems c, e, and h–k were not available and had to be experimentally determined. All of the experimentally determined vapor–liquid equilibrium data are contained in Tables I–VI.

Thermodynamic relations are used extensively for the interpolation and extrapolation of experimental data for systems with two and more components. The commonly used expressions are valid only for an ideal, or slightly nonideal, behavior of the vapor phase, but they fail completely for substances with highly

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0021-9568/82/1727-0064$01.25/0