440 J. Chem. Eng. Data 1991, 36, 440-446

Activity Measurements in Aqueous Mixed Electrolyte Solutions. 5. Ternary Mixtures of (i) Hydrochloric Acid, (ii) Mono-, Di-, or Trimethylammonium Chloride, and (iii) Water of Constant Total Molality

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Electromotive force measurements have been made in cells without liquid junction of the type $Pt,H_2(1\ atm)|HCl\ (m_A),MCl\ (m_B)|AgCl,Ag$, containing mixtures of (i) HCl and $CH_3NH_2\cdot HCl$, (ii) HCl and $(CH_3)_2NH\cdot HCl$, and (iii) HCl and $(CH_3)_3N\cdot HCl$ in different proportions, but at constant total molality (m = 3, 2, 1, 0.75, 0.5, 0.25, 0.1). Measurements have been carried out at 10 °C intervals, over the temperature range 5–35 °C. The values of the standard electrode potential, $E°$, and the Harned interaction coefficient, Q_A for each constant total molality mixture at all four temperatures have been evaluated by the computerized least-squares method. The measured activity coefficients of HCl in all the mixtures at all four temperatures have been found to obey Harned's rule. Interpretation of the results has been made in terms of the multicomponent ionic equilibrium theory of Lim ("all mixing coefficients"). Activity coefficients of all three substituted ammonium chlorides in the different mixtures at all four temperatures are derived.

Introduction

The study of the thermodynamic properties of mixed electrolyte solutions continues to attract attention, and the recent spurt in this interest, attributable mainly to the practical problem of desalination, has stimulated further development of the underlying theory and accumulation of precise experimental data. At constant total molality m ($=m_A + m_B$) of a binary mixture of two electrolytes A and B, the variation of the activity coefficient of component A, for example, with composition can, in general, be expressed by an equation of the type

$$\log \gamma_A = \log \gamma_A° + Q_A y_B + R_A y_B^2 \qquad (1)$$

where γ_A and $\gamma_A°$ are respectively the activity coefficients of the component A in the mixture and in pure solution, at the same total molality m, y_B is the molality fraction m_B/m of the second component, and Q_A and R_A are constants at a given total molality independent of the mixture composition. A similar equation holds for component B. Frequently, the linear form obtained by considering $R_A = 0$ in eq 1 has been found to express sufficiently accurately the measured activity coefficients of A; the electrolyte is then said to obey Harned's rule (*1*).

There exist a number of theories to calculate the activity coefficient values of the second-component electrolyte in the mixture after that of the first one has been determined (*2–4*).

Lim's treatment ("all mixing coefficients") of mixed electrolyte solutions uses extended Harned equations (*5*) like

$$\log\left(\frac{\gamma_A}{\gamma_A°}\right) = \frac{z_1 z_3}{2 \ln 10} yI \sum_{n=0}^{M-1} A_n(-IY)^n \qquad (2)$$

A_n's (functions of I only) being the nth order modified Harned coefficients. Restricting the order of the equations M to 2, one obtains for the two component electrolytes A (ions 1 and 3) ar B (ions 2 and 3)

$$\frac{2 \ln 10}{z_1 z_3} \log\left(\frac{\gamma_A}{\gamma_A°}\right) = yI(A_0 - A_1 IY)$$

$$\frac{2 \ln 10}{z_2 z_3} \log\left(\frac{\gamma_B}{\gamma_B°}\right) = (1 - y)I(B_0 + B_1 IY)$$

Here y is the fraction of the total ionic strength I due to tl component electrolyte B, and $Y = 1 - 2y$. The change excess free energy (per kilogram of solvent) upon formation the mixture from the components, viz.,

$$\Delta_m G^{ex}(y,I) = G^{ex}(y,I) - [(1 - y)G^{ex}(0,I) + yG^{ex}(1,I)]$$

which is expressed analogously to eq 2 ("g_n" (function of I onl being the nth order mixing coefficient)

$$\Delta_m G^{ex}(y,I) = I^2 RTy(1 - y)\sum_{n=0}^{M-1} g_n(IY)^n$$

takes the simpler form for this case

$$\Delta_m G^{ex}(y,I) = I^2 RTy(1 - y)(g_0 + g_1 IY)$$

Also, the general expressions for the mixing coefficient g_n, ar its derivative $g_n' = \partial g_n/\partial I$, namely,

$$g_n = \sum_{k=n}^{M-1} \frac{[(-1)^n A_k + B_k]}{(n + 2 + 2e(k - n))} I^{k-n}$$

where $e(0) = e(1) = 0$, and

$$g_n' = [B_n + (-1)^n A_n - (n + 2)g_n]/I$$

give in this case

$$g_0 = \frac{A_0 + B_0}{2} + \frac{A_1 + B_1}{2} I$$

$$g_1 = \frac{B_1 - A_1}{3}$$

$$g_0' = (B_0 + A_0 - 2g_0)/I = -(A_1 + B_1)$$

$$g_1' = (B_1 - A_1 - 3g_1)/I = 0$$

The coefficient g_1 is implicitly zero in the Scatchard metho and generally small in the other methods; so Lim puts g_1 = and consequently $B_1 = A_1$. The activity coefficients of the tw electrolytes are interrelated:

$$\frac{2 \ln(\gamma_A/\gamma_A°)}{z_1 z_2} + \frac{2 \ln(\gamma_B/\gamma_B°)}{z_2 z_3} = YI\Phi + \frac{Y}{IRT}\frac{\partial}{\partial y}\Delta_m G^{ex} + \frac{2}{RT}\frac{\partial}{\partial I}\Delta_m G^{ex}$$

0021-9568/91/1736-0440$02.50/0

Table I. Values of $\gamma°$ and $\phi°$ for HCl, $CH_3NH_2{\cdot}HCl$, $(CH_3)_2NH \bullet HCl$, and $(CH_3)_3N \bullet HCl$

		273.15 K		278.15 K		288.15 K		298.15 K		308.15 K	
electrolyte	m/(mol kg^{-1})	$\gamma°$	$\phi°$	$\gamma°$	$\phi°$	$\gamma°$	$\phi°$	$\gamma°$	$\phi°$	$\gamma°$	$\phi°$
HCl	0.1			0.8023	0.947	0.8000	0.945	0.7964	0.943	0.7918	0.942
	0.25			0.7695	0.954	0.7656	0.951	0.7598	0.949	0.7531	0.946
	0.50			0.7730	0.981	0.7658	0.978	0.7571	0.974	0.7477	0.970
	0.75			0.7994	1.014	0.7888	1.010	0.7774	1.005	0.7653	1.001
	1.0			0.8363	1.049	0.8229	1.044	0.8090	1.039	0.7942	1.034
$CH_2NH_2{\cdot}HCl$	0.1	0.741	0.911	0.740	0.910	0.738	0.910	0.735	0.909	0.732	0.908
	0.25	0.662	0.890	0.661	0.890	0.658	0.889	0.656	0.889	0.653	0.888
	0.50	0.611	0.888	0.610	0.888	0.608	0.887	0.605	0.887	0.602	0.886
	0.75	0.586	0.892	0.586	0.892	0.584	0.892	0.581	0.891	0.578	0.891
	1.0	0.568	0.891	0.567	0.891	0.566	0.891	0.563	0.891	0.560	0.891
$(CH_3)_2NH{\cdot}HCl$	0.1	0.723	0.901	0.723	0.901	0.721	0.900	0.719	0.900	0.717	0.899
	0.25	0.637	0.876	0.636	0.877	0.635	0.876	0.633	0.876	0.631	0.876
	0.50	0.583	0.875	0.583	0.876	0.582	0.876	0.580	0.876	0.578	0.875
	0.75	0.559	0.882	0.558	0.882	0.557	0.882	0.556	0.882	0.554	0.882
	1.0	0.540	0.882	0.540	0.882	0.539	0.882	0.537	0.882	0.535	0.882
$(CH_3)_3N{\cdot}HCl$	0.1	0.687	0.880	0.687	0.880	0.687	0.881	0.687	0.881	0.686	0.881
	0.25	0.588	0.850	0.589	0.850	0.590	0.852	0.590	0.853	0.590	0.854
	0.50	0.531	0.853	0.532	0.854	0.534	0.856	0.536	0.858	0.537	0.860
	0.75	0.506	0.862	0.507	0.863	0.510	0.866	0.512	0.868	0.513	0.870
	1.0	0.484	0.857	0.485	0.858	0.488	0.861	0.490	0.863	0.492	0.864

with

$$I\Phi = \frac{2(1 - \phi_B°)}{z_2 z_3} - \frac{2(1 - \phi_A°)}{z_1 z_3}$$

Using eqs 4 and 6 and putting in the values of g_1', g_1, g_0, and g_0', one obtains finally

$$\log (\gamma_A/\gamma_A°) = \frac{z_1 z_3}{2 \ln 10}\left[YI\Phi + A_0\frac{I}{2} + A_1\frac{I^2}{2}Y(Y - 1) - B_0\frac{I}{2}Y \right] \quad (12)$$

The values of the modified Harned coefficients A_0, A_1, and B_0 are then obtained by solving eq 12 in the form of a 3 × 3 matrix, using literature values of $\gamma_A°$ for different I, and experimental values of γ_A for the same I but varying y. These values of A_0, A_1, and B_0 are then used in eqs 3 and 4 to calculate the theoretical values of γ_A and γ_B for different values of y and I.

Alternatively, for the case of mixtures of two 1-1 electrolytes, eq 12 may be converted into a 2 × 2 matrix equation and solved for A_0 and A_1. B_1 and B_0 are then obtained respectively from the relation $B_1 = A_1$ and the following

$$2\Phi = B_0 - A_0 + Ig_1 \quad (13)$$

with $g_1 = 0$ and

$$\Phi = \frac{2}{I}(\phi_A° - \phi_B°) \quad (14)$$

Scope, Object, and Method of the Present Work

In earlier papers we have reported the results of electromotive force (emf) studies on binary mixtures of HCl and (i) quaternary ammonium chlorides (tetramethyl and tetraethyl) (*6*), (ii) substituted quaternary ammonium chlorides (choline and acetylcholine) (*7*), and (iii) guanidinium chloride (*8*). Similar studies on binary mixtures of HCl with methyl-, dimethyl-, and trimethylammonium chlorides would be interesting and could be expected to throw light on the nature of the variation of ion–ion interaction with the progressive replacement of H atom by methyl groups in the NH_4^+ cation. Further, studies at different temperatures would be yet more interesting as these would show the effect of temperature on the values of the interaction parameters of the different theories mentioned. We report below the results of such a study.

Jones, Spuhler, and Felsing (*9*) have used a differential freezing point apparatus to determine the freezing point depressions of aqueous solutions of mono-, di-, and trimethylammonium chlorides over the concentration range 0.0025–1.0 m from which the activity coefficients were calculated at the freezing temperature of the solvent (water). The values over the molality range 0.2–1 m (which minimizes the standard deviation of fit) have been utilized by us for calculating (eq 15) the Pitzer coefficients ($\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ}) at 0 °C for each of the three substituted ammonium chlorides mentioned.

The Pitzer equations (*3*) for the activity and osmotic coefficients of a pure electrolyte are

$$\ln \gamma° + A_{\phi}\left[\frac{m^{1/2}}{1 + 1.2m^{1/2}} + \frac{5}{3}\ln (1 + 1.2m^{1/2})\right] = 2\beta^{(0)}m + \frac{1}{2}\beta^{(1)}[1 - \exp(-2m^{1/2})(1 + 2m^{1/2} - 2m)] + \frac{3}{2}C^{\phi}m^2 \quad (15)$$

$$\phi° - 1 + A_{\phi}\frac{m^{1/2}}{1 + 1.2m^{1/2}} = \beta^{(0)}m + \beta^{(1)}\exp(-2m^{1/2})m + C^{\phi}m^2 \quad (16)$$

where A_{ϕ} is the Debye–Hückel limiting slope of the plot of ϕ vs $m^{1/2}$ and the β and C terms are pure electrolyte parameters, which can be determined by least-squares fit of the experimental data to the above equations.

Then by use of the values of the respective temperature derivatives, as tabulated by Silvester and Pitzer (*10*) (molality range up to 0.5), we obtain the parameter values at the required temperatures (5, 15, 25, and 35 °C). We are then able to calculate the activity and osmotic coefficient values (eqs 15 and 16, respectively) of these three substituted ammonium chlorides at any molality up to 1.0 m at the four different temperatures mentioned (Table I).

[The calculation over this slightly extended range is justified, since (i) the calculated values change less markedly over the extended range of 0.5–1.0 m (hence any possible errors resulting from possibly slightly different actual values of the Pitzer coefficients are also likely to be small) and (ii) the deviations of fit with the experimental values, of the finally calculated log γ_{HCl} values in the mixtures, remain almost comparable in magnitude for constant total molalities over the extended range of 0.5–1.0 m, as over the restricted range of 0.1–0.5 m, implying the calculated γ_{HCl} values with use of the surmised Pitzer coefficient values to be essentially correct.]

For the other component in the mixtures mentioned, viz., HCl, a similar procedure has been followed: while the values of the osmotic coefficient at 25 °C is available from literature (*11*),

Table II. Experimental Emf Data and γ_{HCl} Values for Various Values of m_A and m_B at Total Molalities m (= $m_A + m_B$)

		278.15 K		288.15 K		298.15 K		308.15 K	
m/(mol kg^{-1})	m_A/(mol kg^{-1})	E/V	γ_{HCl}	E/V	γ_{HCl}	E/V	γ_{HCl}	E/V	γ_{HCl}
(a) Cell: Pt,H_2(1 atm)|HCl (m_A),$CH_3NH_2\cdot HCl$ (m_B)|AgCl,Ag									
3.00	2.9995	0.164 27	1.428	0.158 20	1.375	0.152 11	1.312	0.145 12	1.260
	2.6970	0.169 77	1.342	0.163 91	1.293	0.157 81	1.239	0.151 37	1.181
	1.4994	0.195 82	1.045	0.190 42	1.016	0.184 77	0.983	0.178 78	0.945
	0.2993	0.246 80	0.808	0.242 71	0.794	0.238 49	0.774	0.233 33	0.757
2.00	1.7981	0.202 27	1.022	0.196 94	0.997	0.191 09	0.972	0.184 90	0.942
	0.9999	0.224 29	0.866	0.219 70	0.845	0.214 30	0.830	0.208 49	0.810
	0.5988	0.240 80	0.793	0.236 29	0.782	0.231 39	0.769	0.226 01	0.753
1.00	1.0002	0.242 79	0.832	0.238 39	0.820	0.233 55	0.806	0.228 06	0.793
	0.9011	0.246 03	0.819	0.241 93	0.805	0.237 08	0.793	0.231 70	0.780
	0.7006	0.254 18	0.784	0.250 26	0.772	0.245 92	0.757	0.240 74	0.746
	0.5000	0.264 23	0.752	0.260 72	0.740	0.256 33	0.732	0.251 55	0.720
	0.3000	0.278 28	0.724	0.275 10	0.715	0.271 43	0.704	0.267 10	0.694
	0.0999	0.307 24	0.686	0.304 87	0.680	0.301 96	0.674	0.298 30	0.668
0.75	0.6732	0.261 88	0.786	0.258 03	0.777	0.253 71	0.767	0.248 85	0.754
	0.3739	0.279 07	0.737	0.275 72	0.730	0.271 91	0.722	0.267 52	0.712
	0.0749	0.320 74	0.690	0.318 78	0.686	0.316 33	0.679	0.313 30	0.672
0.50	0.4501	0.282 55	0.765	0.279 30	0.759	0.275 47	0.752	0.271 26	0.741
	0.3496	0.289 69	0.748	0.286 66	0.742	0.283 11	0.735	0.279 01	0.726
	0.2500	0.298 67	0.733	0.296 09	0.726	0.292 84	0.719	0.288 84	0.714
	0.0500	0.339 58	0.699	0.338 18	0.695	0.336 19	0.692	0.333 82	0.684
0.25	0.2242	0.315 89	0.765	0.313 57	0.762	0.310 85	0.756	0.307 52	0.750
	0.1240	0.331 21	0.747	0.329 40	0.745	0.327 17	0.740	0.324 34	0.734
	0.0249	0.370 81	0.729	0.370 38	0.728	0.369 52	0.724	0.368 05	0.719
0.10	0.1000	0.354 90	0.802	0.353 90	0.801	0.352 61	0.794	0.350 41	0.791
	0.0899	0.357 68	0.798	0.356 88	0.796	0.355 43	0.793	0.353 35	0.790
	0.0700	0.363 98	0.793	0.363 43	0.790	0.362 14	0.789	0.360 44	0.784
	0.0499	0.372 11	0.793	0.371 88	0.789	0.370 99	0.786	0.369 41	0.783
	0.0299	0.384 76	0.787	0.384 79	0.787	0.384 47	0.782	0.383 31	0.779
(b) Cell: Pt,H_2(1 atm)|HCl (m_A),$(CH_3)_2NH\cdot HCl$ (m_B)|AgCl,Ag									
3.00	2.1003	0.184 05	1.129	0.178 31	1.096	0.172 26	1.058	0.165 77	1.020
	1.4995	0.199 31	0.972	0.194 12	0.943	0.188 27	0.917	0.182 06	0.888
	0.9000	0.219 22	0.828	0.214 13	0.813	0.208 88	0.792	0.202 84	0.775
2.99	1.7845	0.202 82	1.014	0.197 36	0.992	0.191 69	0.963	0.185 46	0.935
	0.9999	0.226 30	0.830	0.221 08	0.822	0.215 85	0.804	0.210 09	0.786
	0.5955	0.243 07	0.758	0.238 57	0.749	0.233 72	0.735	0.228 17	0.724
1.00	0.9002	0.246 23	0.816	0.242 05	0.803	0.237 20	0.791	0.231 61	0.781
	0.6994	0.254 28	0.783	0.250 48	0.769	0.245 64	0.761	0.240 69	0.746
	0.5000	0.265 18	0.738	0.261 47	0.729	0.256 60	0.727	0.251 68	0.718
	0.2994	0.279 35	0.709	0.276 06	0.702	0.271 87	0.698	0.267 48	0.689
	0.1000	0.308 37	0.670	0.305 99	0.664	0.302 99	0.659	0.299 02	0.658
0.75	0.6740	0.262 02	0.784	0.258 22	0.774	0.253 80	0.764	0.248 86	0.753
	0.5231	0.269 95	0.754	0.266 25	0.747	0.262 01	0.739	0.257 31	0.729
	0.3751	0.279 73	0.726	0.276 35	0.720	0.272 36	0.713	0.267 88	0.705
	0.2245	0.293 91	0.698	0.290 79	0.696	0.287 18	0.691	0.283 09	0.685
	0.0748	0.322 09	0.672	0.320 01	0.669	0.317 41	0.664	0.314 14	0.661
0.50	0.4501	0.282 72	0.762	0.279 45	0.756	0.275 69	0.747	0.271 28	0.740
	0.3498	0.290 08	0.742	0.286 98	0.736	0.283 43	0.729	0.279 20	0.723
	0.2500	0.299 46	0.722	0.296 68	0.717	0.293 34	0.711	0.289 30	0.707
	0.1499	0.313 14	0.700	0.310 81	0.696	0.307 84	0.692	0.304 19	0.689
	0.0500	0.340 56	0.684	0.339 03	0.683	0.336 96	0.680	0.334 34	0.677
0.25	0.1750	0.322 64	0.752	0.320 49	0.750	0.317 98	0.744	0.314 82	0.739
	0.1247	0.331 50	0.740	0.329 59	0.740	0.327 39	0.734	0.324 47	0.730
	0.0749	0.344 38	0.730	0.343 02	0.729	0.341 12	0.725	0.338 59	0.722
	0.0250	0.371 46	0.718	0.370 89	0.719	0.369 98	0.715	0.368 42	0.712
0.10	0.0900	0.357 63	0.799	0.356 64	0.799	0.355 26	0.794	0.353 33	0.789
	0.0701	0.363 91	0.794	0.363 31	0.791	0.362 08	0.788	0.360 25	0.785
	0.0500	0.372 19	0.791	0.371 82	0.789	0.370 86	0.786	0.369 43	0.781
	0.0100	0.411 56	0.778	0.412 46	0.778	0.412 92	0.775	0.412 78	0.772
(c) Cell: Pt,H_2(1 atm)|HCl (m_A),$(CH_3)_3N\cdot HCl$ (m_B)|AgCl,Ag									
3.00	2.0972	0.186 75	1.070	0.180 94	1.041	0.174 78	1.010	0.168 32	0.974
	1.5012	0.204 23	0.878	0.198 12	0.871	0.192 23	0.850	0.185 56	0.832
	0.8994	0.225 63	0.726	0.220 22	0.721	0.214 71	0.709	0.208 58	0.696
2.00	1.8003	0.203 06	1.006	0.197 72	0.982	0.191 80	0.959	0.185 50	0.931
	1.0001	0.228 08	0.801	0.223 37	0.786	0.217 80	0.775	0.211 59	0.764
	0.5997	0.246 13	0.710	0.241 43	0.705	0.236 14	0.701	0.230 49	0.691
1.00	0.6999	0.255 25	0.768	0.251 58	0.725	0.247 03	0.742	0.241 69	0.733
	0.4997	0.266 36	0.721	0.262 55	0.714	0.258 16	0.707	0.252 68	0.705
	0.3000	0.281 48	0.679	0.278 02	0.675	0.274 09	0.669	0.269 44	0.664
	0.1000	0.310 42	0.643	0.308 26	0.636	0.305 13	0.634	0.301 09	0.634
0.75	0.5251	0.270 34	0.747	0.266 87	0.737	0.262 45	0.733	0.257 71	0.723
	0.3750	0.280 85	0.710	0.276 96	0.712	0.273 24	0.703	0.268 65	0.696
	0.2248	0.295 10	0.681	0.291 98	0.680	0.288 25	0.678	0.284 07	0.672
	0.0751	0.323 58	0.651	0.321 49	0.649	0.318 78	0.647	0.315 53	0.643

Table II (Continued)

		278.15 K		288.15 K		298.15 K		308.15 K	
m/(mol kg^{-1})	m_A/(mol kg^{-1})	E/V	γ_{HCl}	E/V	γ_{HCl}	E/V	γ_{HCl}	E/V	γ_{HCl}
0.50	0.4500	0.282 84	0.762	0.279 58	0.755	0.275 89	0.746	0.271 35	0.739
	0.3498	0.290 58	0.735	0.287 09	0.736	0.283 74	0.726	0.279 45	0.720
	0.2498	0.300 22	0.711	0.296 80	0.717	0.293 94	0.705	0.289 76	0.702
	0.1499	0.313 85	0.691	0.311 35	0.690	0.308 33	0.688	0.304 94	0.681
	0.0500	0.341 61	0.671	0.339 95	0.672	0.338 21	0.666	0.335 22	0.666
0.25	0.2248	0.315 98	0.763	0.313 70	0.760	0.310 91	0.755	0.307 63	0.747
	0.1751	0.322 71	0.752	0.320 57	0.750	0.317 98	0.746	0.314 87	0.739
	0.1247	0.331 65	0.739	0.329 93	0.736	0.327 60	0.733	0.324 65	0.728
	0.0749	0.344 73	0.726	0.343 30	0.725	0.341 39	0.723	0.339 03	0.716
0.10	0.0699	0.364 17	0.792	0.363 45	0.791	0.362 33	0.787	0.360 61	0.781
	0.0498	0.372 64	0.786	0.372 26	0.785	0.371 36	0.782	0.369 95	0.776
	0.0299	0.385 24	0.781	0.385 24	0.780	0.384 84	0.777	0.383 84	0.771

Table III. $E°$ (V) Values of the Ag/AgCl Electrode

	$E°$		
temperature	HCl + $CH_3NH_2 \cdot HCl$	HCl + $(CH_3)_2NH \cdot HCl$	HCl + $(CH_3)_3N \cdot HCl$
278.15 K	0.233 98 ± 0.000 07	0.233 98 ± 0.000 09	0.234 06 ± 0.000 08
288.15 K	0.228 56 ± 0.000 08	0.228 54 ± 0.000 05	0.228 60 ± 0.000 11
298.15 K	0.222 50 ± 0.000 09	0.222 43 ± 0.000 09	0.222 53 ± 0.000 14
308.15 K	0.215 72 ± 0.000 09	0.215 67 ± 0.000 09	0.215 72 ± 0.000 13

Table IV. Harned Interaction Parameters Q_A of Equation 1 for the Three Amine Chloride–Hydrochloric Acid Mixtures Together with the "Closeness of Fit $\sigma(\Delta)$" of log γ_{HCl}(expt) to Equation 1 with $R_A = 0$

	278.15 K		288.15 K		298.15 K		308.15 K	
m/(mol kg^{-1})	$-Q_A$	$\sigma(\Delta) \times 10^4$	$-Q_A$	$\sigma(\Delta) \times 10^4$	$-Q_A$	$\sigma(\Delta) \times 10^4$	$-Q_A$	$\sigma(\Delta) \times 10^4$
HCl + $CH_3NH_2 \cdot HCl$								
3.0	0.2748	8	0.2648	6	0.2551	9	0.2442	13
2.0	0.1841	7	0.1768	6	0.1707	4	0.1632	2
1.0	0.0921	17	0.0891	11	0.0862	11	0.0829	8
0.75	0.0706	0	0.0681	0	0.0656	1	0.0628	0
0.5	0.0491	6	0.0471	1	0.0448	5	0.0428	5
0.25	0.0257	0	0.0247	0	0.0236	0	0.0225	0
0.1	0.0106	7	0.0103	10	0.0099	2	0.0094	5
HCl + $(CH_3)_2NH \cdot HCl$								
3.0	0.3374	12	0.3239	1	0.3145	4	0.2986	1
2.0	0.2136	8	0.2055	3	0.1969	2	0.1873	4
1.0	0.1076	18	0.1020	14	0.0979	20	0.0918	7
0.75	0.0840	2	0.0789	4	0.0752	6	0.0705	4
0.5	0.0596	6	0.0564	10	0.0521	11	0.0490	6
0.25	0.0329	3	0.0310	2	0.0284	2	0.0264	2
0.1	0.0144	5	0.0134	6	0.0125	5	0.0114	1
HCl + $(CH_3)_3N \cdot HCl$								
3.0	0.4215	7	0.3996	10	0.3846	9	0.3639	20
2.0	0.2521	9	0.2399	5	0.2275	7	0.2154	1
1.0	0.1291	10	0.1221	7	0.1148	7	0.1081	19
0.75	0.0989	9	0.0931	13	0.0885	8	0.0832	9
0.5	0.0688	8	0.0650	12	0.0616	7	0.0575	8
0.25	0.0368	3	0.0348	5	0.0326	5	0.0307	5
0.1	0.0154	0	0.0146	2	0.0138	1	0.0131	0

those at 5, 15, and 35 °C have been calculated (eq 16) from the literature value (*11*) of the activity coefficient at 25 °C via (i) first the calculation of $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} values at 25 °C (eq 15) and (ii) then the calculation of the values of the same at the three other temperatures mentioned by use of the respective temperature derivatives. Also, the activity coefficients at all the molalities considered (except 0.25 and 0.75 m) at the three other temperatures are directly available from literature (*1*) [the values at the remaining two concentrations, at all four different temperatures, were obtained by using the method followed by Downes (*12*)]. The HCl data are also shown in Table I.

The calculation of the modified Harned coefficients A_0, A_1 ($=B_1$), and B_0 (eq 12), and thereafter of γ_{HX} and γ_{MX} in the mixtures (eqs 3 and 4) has already been described. The modified method, involving solution of eq 12 in conjunction with eq 13 and the condition $g_1 = 0$, has also been described.

Experimental Details

Hydrochloric acid of analytical reagent grade was distilled to the azeotropic composition and only the middle fraction retained. Methylammonium chloride (E. Merck), dimethylammonium chloride (Aldrich), and trimethylammonium chloride (E. Merck) were recrystallized from ethanol and dried under vacuum (*13*).

Stock solutions of the electrolytes (HCl 3.0968 m, $CH_3NH_2 \cdot HCl$ 3.7039 m; HCl 3.0960 m, $(CH_3)_2NH \cdot HCl$ 3.6576 m; and HCl 3.1157 m, $(CH_3)_3N \cdot HCl$ 3.2806 m) were prepared by using double-distilled water (specific conductance = 5.6 × 10^{-6} mho cm^{-1}) and their molalities (as given above) determined by gravimetric chloride analysis. The results agreed within (i) ±0.19% for HCl (quadruplicate analyses) and ±0.001% for $CH_3NH_2 \cdot HCl$ (duplicate) in the HCl–$CH_3NH_2 \cdot HCl$ system, (ii) ±0.05% for HCl (duplicate) and ±0.01% for $(CH_3)_2NH \cdot HCl$ (triplicate) in the HCl–$(CH_3)_2NH \cdot HCl$ system, and (iii) ±0.08% for HCl (triplicate) and ±0.01% for $(CH_3)_3N \cdot HCl$ (triplicate) in the HCl–$(CH_3)_3N \cdot HCl$ system. No further characterization of the purity of the salts was made. Other details of experimental procedure, such as the preparation of solutions, preparation of electrodes (thermoelectrolytic), cell design, bath temperature control (±0.2 °C), etc., have been described elsewhere (*6*). Duplicate electrodes

Table V. Activity Coefficients of Methylammonium Chlorides in Mixtures with HCl, Calculated by the Lim Equation

		278.15 K		288.15 K		298.15 K		308.15 K	
$m/(\mathrm{mol\ kg^{-1}})$	y_A	$-\log \gamma_B^{(L)}$	$-\log \gamma_B^{(L)*}$	$-\log \gamma_B^{(L)}$	$-\log \gamma_B^{(L)*}$	$-\log \gamma_B^{(L)}$	$-\log \gamma_B^{(L)*}$	$-\log \gamma_B^{(L)}$	$-\log \gamma_B^{(L)*}$
				$CH_3NH_2{\cdot}HCl$					
1.0	1.0002	0.203	0.204	0.204	0.205	0.207	0.208	0.210	0.210
	0.9011	0.206	0.208	0.208	0.209	0.211	0.212	0.215	0.215
	0.7006	0.213	0.215	0.216	0.218	0.219	0.221	0.224	0.224
	0.5000	0.221	0.223	0.224	0.226	0.228	0.230	0.232	0.233
	0.3000	0.230	0.232	0.233	0.234	0.236	0.238	0.240	0.241
	0.0999	0.241	0.242	0.242	0.243	0.245	0.246	0.248	0.248
0.75	0.8975	0.199	0.200	0.202	0.202	0.206	0.205	0.208	0.209
	0.4986	0.214	0.214	0.216	0.216	0.219	0.218	0.222	0.222
	0.0998	0.228	0.229	0.230	0.230	0.233	0.232	0.235	0.235
0.50	0.9002	0.185	0.186	0.188	0.187	0.192	0.189	0.193	0.193
	0.6991	0.191	0.191	0.195	0.193	0.199	0.196	0.198	0.199
	0.5000	0.198	0.198	0.201	0.200	0.205	0.202	0.204	0.205
	0.0999	0.211	0.211	0.213	0.213	0.216	0.215	0.217	0.217
0.25	0.8970	0.153	0.153	0.156	0.155	0.157	0.157	0.161	0.160
	0.4960	0.165	0.165	0.167	0.167	0.169	0.168	0.172	0.171
	0.0996	0.177	0.177	0.179	0.179	0.180	0.180	0.182	0.182
0.1	1.0003	0.108	0.107	0.106	0.106	0.114	0.114	0.114	0.114
	0.8989	0.110	0.111	0.110	0.110	0.116	0.116	0.117	0.117
	0.6999	0.116	0.116	0.118	0.118	0.120	0.121	0.121	0.122
	0.4992	0.120	0.121	0.124	0.123	0.124	0.125	0.126	0.126
	0.2987	0.125	0.125	0.128	0.128	0.127	0.129	0.130	0.130
				$(CH_3)_2NH{\cdot}HCl$					
1.0	0.9002	0.233	0.233	0.233	0.234	0.233	0.235	0.235	0.234
	0.6994	0.239	0.239	0.240	0.241	0.238	0.241	0.243	0.242
	0.5000	0.247	0.247	0.248	0.249	0.245	0.247	0.251	0.250
	0.2994	0.254	0.255	0.256	0.256	0.253	0.255	0.259	0.258
	0.1000	0.263	0.263	0.264	0.264	0.264	0.265	0.267	0.267
0.75	0.8986	0.226	0.226	0.225	0.225	0.226	0.227	0.227	0.227
	0.6975	0.232	0.232	0.231	0.232	0.232	0.233	0.233	0.233
	0.5002	0.238	0.238	0.237	0.238	0.238	0.239	0.240	0.240
	0.2993	0.244	0.244	0.244	0.244	0.244	0.245	0.246	0.246
	0.0998	0.250	0.250	0.250	0.251	0.251	0.251	0.253	0.253
0.50	0.9001	0.206	0.206	0.207	0.206	0.207	0.207	0.209	0.208
	0.6996	0.213	0.212	0.215	0.213	0.215	0.215	0.216	0.215
	0.4999	0.219	0.219	0.221	0.220	0.222	0.222	0.223	0.222
	0.2999	0.225	0.225	0.227	0.226	0.228	0.228	0.229	0.228
	0.1000	0.231	0.231	0.233	0.232	0.234	0.234	0.235	0.235
0.25	0.7000	0.173	0.173	0.173	0.173	0.174	0.175	0.175	0.176
	0.4989	0.179	0.180	0.180	0.180	0.181	0.182	0.181	0.183
	0.2995	0.186	0.186	0.187	0.187	0.188	0.189	0.189	0.190
	0.1001	0.193	0.193	0.194	0.194	0.195	0.195	0.196	0.197
0.10	0.9000	0.117	0.118	0.120	0.119	0.121	0.107	0.121	0.125
	0.7006	0.121	0.123	0.123	0.124	0.125	0.108	0.126	0.127
	0.5004	0.126	0.128	0.130	0.129	0.130	0.112	0.131	0.132
	0.1000	0.138	0.138	0.140	0.139	0.141	0.135	0.142	0.142
				$(CH_3)_3N{\cdot}HCl$					
1.0	0.6999	0.297	0.288	0.280	0.287	0.287	0.286	0.273	0.281
	0.4997	0.304	0.295	0.287	0.294	0.286	0.293	0.281	0.289
	0.3000	0.310	0.303	0.296	0.301	0.294	0.300	0.291	0.297
	0.1000	0.313	0.310	0.306	0.308	0.304	0.307	0.302	0.304
0.75	0.7002	0.278	0.273	0.259	0.270	0.266	0.268	0.264	0.268
	0.5001	0.285	0.280	0.265	0.276	0.271	0.274	0.270	0.274
	0.2997	0.290	0.286	0.274	0.282	0.278	0.280	0.277	0.280
	0.1001	0.294	0.292	0.286	0.289	0.286	0.287	0.285	0.287
0.50	0.9001	0.238	0.236	0.234	0.235	0.235	0.235	0.356	0.235
	0.6995	0.248	0.246	0.241	0.242	0.242	0.243	0.244	0.242
	0.4996	0.257	0.255	0.249	0.249	0.250	0.251	0.251	0.250
	0.2998	0.265	0.263	0.258	0.258	0.258	0.259	0.259	0.258
	0.1000	0.271	0.271	0.267	0.267	0.266	0.267	0.266	0.266
0.25	0.8991	0.182	0.182	0.184	0.184	0.183	0.183	0.186	0.187
	0.7004	0.191	0.192	0.193	0.193	0.193	0.193	0.194	0.195
	0.4989	0.201	0.202	0.203	0.203	0.203	0.202	0.202	0.204
	0.2998	0.212	0.213	0.213	0.213	0.213	0.213	0.212	0.214
0.10	0.6994	0.135	0.134	0.136	0.135	0.135	0.136	0.137	0.138
	0.4979	0.143	0.143	0.145	0.143	0.143	0.144	0.144	0.146
	0.2986	0.152	0.151	0.152	0.151	0.151	0.125	0.125	0.153

were used for emf measurements for each solution at each of four different temperatures (5, 15, 25, and 35 °C), and the results always agreed within experimental error (±0.1 mV). An LN type K2 potentiometer with an LN galvanometer of sensitivity 1 mm/m at 10^{-5} V was used.

Calculation and Results

Table II gives the experimental (i) emf and (ii) γ_{HCl} values (eq 1 with R_A = 0) for seven different constant total molalities (m) of the mixtures, with varying HCl molalities (m_A) for each. The

Table VI. Standard Deviations of Fit of the log γ_{HCl} Values Calculated by the Lim Method (Two Different Treatments) with the Experimental log γ_{HCl} Values

		$\sigma \times 10^4$							
		278.15 K		288.15 K		298.15 K		308.15 K	
binary mixture	m/(mol kg^{-1})	L	L*	L	L*	L	L*	L	L*
$HCl-CH_3NH_2{\cdot}HCl$	0.10	8	8	4	4	8	6	5	5
	0.25	0	0	3	2	1	1	4	3
	0.50	3	3	6	4	15	8	5	4
	0.75	2	1	2	1	5	3	1	1
	1.00	17	15	15	13	14	13	7	7
$HCl-(CH_3)_2NH{\cdot}HCl$	0.10	8	5	8	7	87	47	3	2
	0.25	3	2	2	2	4	1	7	2
	0.50	7	7	12	10	6	5	9	7
	0.75	2	2	5	4	7	6	5	5
	1.00	16	16	15	14	16	12	10	9
$HCl-(CH_3)_3N{\cdot}HCl$	0.10	2	0	4	1	3	1	5	1
	0.25	3	2	5	5	5	5	7	5
	0.50	11	6	11	11	8	7	9	7
	0.75	23	8	49	13	14	8	20	7
	1.00	41	10	31	8	34	9	38	18

emf values are corrected to a hydrogen partial pressure of 1 atm. Data are recorded for four different temperatures in each case. Assuming that the HCl component in the mixture obeys Harned's rule, the cell emf can be written as

$$E + K \log m_A = (E^\circ - K \log m - 2K \log \gamma_A^\circ) - 2KQ_A y_B \qquad (17)$$

where $K = 2.3026RT/F$. Values of γ_A° ($=\gamma_{HCl}^\circ$) were taken from literature (*1*), and the least-squares method was applied for calculating E° and Q_A together with the standard deviations $\sigma(E)$ and $\sigma(Q_A)$. The E° values obtained for all the seven different total molalities at any particular temperature were found to be very close to the literature values (*1*). In our further calculations, we have used the average E° value of all different total molalities, for any particular temperature; these, together with their standard deviations, are given in Table III.

Table IV contains the values of the Harned coefficients Q_A, together with the values of "closeness of fit" $\sigma(\Delta)$ [Δ = log (experimental activity coefficient value of HCl) − log (value calculated by least-squares fit to eq 1 with $R_A = 0$ and the Q_A value obtained for the set)], for all compositions at each constant total molality. The fit is found to improve on inclusion of the quadratic term (eq 1); however, the smallness of Δ values show that the Harned rule itself is adequately valid for the HCl component in the mixtures, at all four temperatures, at least within the experimental accuracy secured.

Analysis of the Results by the Lim Method. The values of the modified Harned coefficients A_0, $A_1 = B_1$, and B_0 were computed by fitting the experimental log γ_{HCl} values together with the literature values of γ_{HCl}° for different constant total molalities (both at four different temperatures) to eq 12 using a 3 × 3 matrix. The log γ values of the two components in the mixtures were then calculated by using eqs 3 and 4. While for all three substituted ammonium chlorides the calculated log $\gamma^{(L)}$ values are directly shown in Table V, for the HCl component the deviations $\Delta^{(L)}$ [=log (experimental activity coefficient) − log (value calculated by least-squares fit to eq 3] were calculated and found to be small; the standard deviations at each constant total molality $\sigma^{(L)}$ are shown in Table VI.

In the alternative method of calculation (for mixtures of two 1–1 electrolytes, as in the present case) eq 12, in conjunction with eq 13 and the condition $g_1 = 0$, has been solved for A_0 and A_1 in the form of a 2 × 2 matrix; B_0 and B_1 are then obtained from eqs 13 and 8, respectively. The log γ values of the two components were then calculated, as before, by using eqs 3 and 4, respectively. The values for the substituted ammonium chloride component log $\gamma^{(L)*}$ are shown directly in Table V, while for the HCl component the deviations from the experimental log γ values $\Delta^{(L)*}$ were calculated; the standard deviations $\sigma^{(L)*}$ are shown in Table VI.

Discussion

We begin by mentioning some points with regard to (i) the securing of the pure first component (i.e. HCl) ϕ and γ values and the method used for (ii) data processing, and (iii) evaluation of the performance of the Lim model.

(i) The pure first component (i.e. HCl) ϕ values have not been calculated directly from the corresponding literature γ values, at all temperatures. The reason was that, though this could have been done for the HCl component, the same would not have been possible for the salt component where for the γ values, being not available at temperatures other than 0 °C, the method of estimating the same by use of the Pitzer coefficients and their temperature derivatives was imperative; for consistency the latter method has also been adopted for the HCl component. However, the fact that our experimental pure HCl γ values (for concentrations for which they are available, Table II) agree pretty well with the corresponding literature values (which again agree exactly with the calculated values (through use of Pitzer coefficients and their temperature derivatives, Table I) at all temperatures) fully testifies to the soundness of our program.

(ii) The parameters of the Lim model (in the case of each mixture studied) have been evaluated separately at the four different temperatures. An alternative procedure would have been to assume the said parameters to be temperature dependent, and by suitably modifying the computerization program to handle data for all temperatures and concentrations simultaneously. However, the method of separate data treatment for each temperature is not in error in itself; we have therefore reported the results as obtained, particularly in view of the fact that the study of the temperature dependence of the said parameters was beyond the scope of the present work.

(iii) The extent to which the chosen activity coefficient model (Lim) fits the experimental data has been estimated by calculating the deviations between the experimental and calculated values of γ_{HCl}. An alternative procedure would have been to back-calculate the emf values using the converged values of the parameters and then to compare the same with the experimental emf values. We have however retained and reported the results obtained by the first method of evaluation, particularly in view of the fact that the performance of only one model has been considered.

We now discuss the results obtained.

(iv) As mentioned earlier, the Scatchard (*2*) and Pitzer (*3*) treatments, in addition to that of Lim, are also available for calculating the γ values of the two components in a mixture. We have actually employed all three methods, though the results given here are only for Lim's treatment. It is interesting to compare the results obtained by the three different methods.

It has been found that the closeness of fit, with the experimental values, of the log γ_{HCl} values calculated according to the different treatments at all four different temperatures are (a) larger for the Pitzer method as compared to the other methods, (b) almost comparable in magnitude in the case of the Scatchard and the Lim methods, and (c) slightly better from the "alternative method" as compared to the "original method" of Lim.

However, "it has been amply shown in the literature that any of the models mentioned give about equally good fits to aqueous electrolyte mixture data. Slight differences in the derived values of the activity coefficients of the components of the mixtures are due to differences in the weighting of the parameters in the various models" (comments of reviewer 4; authors concur). The fact that "the Pitzer approach gives different activity coefficient values for the salts at 1 *m* and substantially higher deviations between experimental and computed values of γ_{HCl} in comparison with the other schemes (may be due to the fact that) the procedure of estimating coefficients does not blank out the two-component contributions in the Pitzer treatment as well as with other approaches. In any case, the information gaps preclude inferences about the validity of the different approaches, which are fairly well established already over the limited concentration range here" (comments of reviewer 2; authors concur).

(v) The variation of the Friedman-Lim mixing coefficients g_0 and g_0' with increasing total molality, at all four temperatures (data not recorded here) for all three binary mixtures mentioned, show the same trend as found earlier in the case of hydrochloric acid-guanidinium chloride mixtures (which again is similar to that in the case of the HCl-KCl mixtures studied by Lim (*4*): g_0 decreases with increasing total molality, becoming increasingly more negative, either (*i*) from an initial positive value at 0.1 *m* or else (ii) after initially increasing from higher negative values. This limiting behavior for vanishingly low ionic strengths is in both cases (calculations by the original as also the alternative method) contradictory to that predicted by the theoretical calculations (*14*).

(vi) The Pitzer binary interaction term (Θ_{HM}) obtained for all three alkylammonium chloride mixtures studied, at 25 °C (results not shown here), follow the order $\Theta_{H^+-CH_3NH_3^+}$ (−0.028) > $\Theta_{H^+-(CH_3)_2NH_2^+}$ (−0.058) > $\Theta_{H^+-(CH_3)_3NH^+}$ (−0.081). Our earlier reported (*8*) $\Theta_{H^+-(CH_3)_4N^+}$ value (−0.167) at the same temperature, and the value reported by Robinson, Ray, and Bates also at the same temperature (*15*), $\Theta_{H^+-NH_4^+} = -0.0165$, are consistent with the above values. These values clearly show that as the size of the cation in the series increases, together with a gradual decrease of the net surface charge density, the binary interaction term becomes increasingly more negative.

Acknowledgment

We are thankful to Swami Satyapriyananda of the R. K. Mission Vivekananda Centenary College, Rahara, India, for help in the computer processing of data.

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Received for review May 7, 1990. Revised January 22, 1991. Accepted June 24, 1991.

Phase Equilibria in the System Poly(ethylene glycol) + Dextran + Water

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Tie lines in the system poly(ethylene glycol) 3000 + dextran 500 000 + water have been measured at 0, 20, and 40 °C. The concentration and molecular weight distributions of the polymers in coexisting liquid phases were determined by using size exclusion chromatography (SEC).

Introduction

Aqueous polymer-polymer two-phase systems are used for the separation of complex mixtures of biomolecules (*1*). The design of such separation processes requires accurate and reliable thermodynamic data of the basis phase equilibria. Phase compositions of some polymer-polymer systems have been determined in previous studies (*2*, *3*). But, for the consistent correlation of these phase equilibria, molecular weight distributions of the polymers in the coexsting phases have to be taken into account (*4*).

Experimental Section

Materials. The components were used in the highest purity commercially available without further purification. Poly(ethylene glycol) (PEG) was supplied by Hüls AG, Marl, Germany, and dextran by Pfeifer & Langen, Dormagen, Germany; water was triply distilled. The number- and weight-average molecular weights of the polymers were determined by using size exclusion chromatography (SEC) and compared with the data of the manufacturers, as given in Table I. The dextran molecular weight standards were supplied by Pharmacosmos, Viby Sj., Denmark; the PEG standards, by Polymer Laboratories, Church Stretton, Shropshire, U.K.

Analytical Methods. The PEG and dextran concentrations in each phase were measured by size exclusion chromatogra-

0021-9568/91/1736-0446$02.50/0