of percent errors in predicted *K* values, the sum being taken over all components.

Tables III and IV present the results of the final correlation. Average errors in predicted *K* values of methane, ethane, propane, toluene, and 1-methylnaphthalene range from 4.5 to 7.0%. The predicted *K* values of methane, ethane, and propane are generally low at low pressure and high at high pressure for each isotherm using the interaction parameters obtained in this work. The predicted *K* values of toluene are low at high pressures and high at low pressures. The predicted *K* values of 1-methylnaphthalene show somewhat larger errors, as expected, and no consistent error trends.

Conclusion

Equilibrium liquid and vapor compositions and *K* values have been obtained in a five-component light hydrocarbon-aromatic solvent system. The data of this work have been represented by the Soave equation of state. The correlating parameters should be of use in the prediction of phase behavior in systems containing light hydrocarbons in aromatic solvents.

Glossary

a, b	parameters in Soave equation of state
C	interaction parameter
K_i	phase equilibrium ratio for component i, y_i/x_i
x	liquid mole fraction
y	vapor mole fraction
z	mole fraction
ϵ	mean value of average absolute percent deviation

Subscripts

i, j	components in a mixture
m	mixture property

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Activity Measurements in Aqueous Mixed Electrolyte Solutions. 2. Hydrochloric Acid–Choline Chloride and Hydrochloric Acid–Acetylcholine Chloride Mixtures of Constant Total Ionic Strength

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Emf measurements have been made in cells without liquid junction of the type Pt,H_2(1 atm)|HX(m_1),MX(m_2)|AgCl,Ag, containing mixtures of (I) HCl and $CH_2(OH)CH_2N(CH_3)_3Cl$ and (II) HCl and $CH_2(OOCCH_3)CH_2N(CH_3)_3Cl$ in different proportions, but at constant total ionic strength (μ = 3, 2, 1, 0.5, 0.25, 0.1). Measurement have been carried out at 10 °C intervals, over the temperature range 5–35 °C. The Ag–AgCl electrodes, prepared by the thermoelectrolytic method, used in pairs for each measurement, gave results which closely agreed. The values for the standard electrode potential, $E°$, and the interaction coefficient, α_{12}, for each constant total ionic strength mixture at all of the four temperatures have been evaluated by the computerized least-squares method. Interpretation of the results has been made in terms of the multicomponent ionic equilibrium theory of Scatchard ("neutral electrolyte as components" treatment) and of Pitzer.

Introduction

The determination of the activity coefficient of one electrolyte in the presence of another has evoked interest for a fairly long time. The specific ionic interaction principle postulating the existence of short-range interactions among ions of unlike sign of charge was enunciated by Brönsted (*1*, *2*) and was applied to dilute solutions by Guggenheim (*3–5*). Modifications were suggested for concentrated solutions by Scatchard (*6*, *7*). Pitzer and Brewer (*8*) used the Guggenheim equations with Scatchard modifications (*6*) (BSG theory) to give a simple and compact summary of experimental data.

From emf measurements at constant total ionic strength, some simple empirical relationships have been discovered to hold in both dilute and concentrated solutions (*9*). It has been found, for the HCl–MCl mixture, for example, that the activity coefficient of the first component (log γ_1) can, in general, be expressed as

$$\log \gamma_1 = \log \gamma_1{}^0 - \alpha_{12} m_2 - \beta_{12} m_2{}^2 \qquad (1)$$

where $\gamma_1{}^0$ is the activity coefficient of hydrochloric acid in its own solution (without MCl) at a molality equal to the total molality of the solution to which γ_1 refers. The quantities α_{12}, β_{12}, ... are functions of the total ionic strength but not of the ionic strength fraction of the second component y_2 (=m_2/m). In many cases the simple linear equation, the so-called Harned rule (*9*)

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$$\log \gamma_1 = \log \gamma_1{}^0 - \alpha_{12} m_2 \qquad (2)$$

is found to express sufficiently accurately the activity coefficient γ_1. For the other electrolyte, MCl, one can similarly write

$$\log \gamma_2 = \log \gamma_2{}^0 - \alpha_{21} m_1 - \beta_{21} m_1{}^2 \qquad (3)$$

though it does not follow, even if eq 2 holds, that $\beta_{21} = 0$; this has been recognized by McKay (*10*) and by Harned himself (*11*, *12*).

Scatchard (*13*, *14*) has subsequently extended and elaborated the Guggenheim equations in several ways. The Brönsted principle of specific ion interaction has been abandoned, and terms are introduced for short-range interaction of ions of like signs. Further, arrays of third and fourth virial coefficients are added, in addition to the second virial coefficient terms (corresponding to the β quantities). Also, the Debye–Hückel term in the expression for the excess Gibbs energy (to correspond to the Debye–Hückel term in the expression for activity coefficients) is elaborated to take into account the different distances of closest approach for the solute components. Appropriate derivatives then yield very complex formulas for the osmotic and activity coefficients. On this basis Lietzke (*15*) has been able to represent accurately the osmotic coefficients of a number of pure electrolytes; also, several systems of mixed electrolytes have been treated. The earlier (*13*) "neutral electrolyte molecules as components" treatment of Scatchard was subsequently (*14*) developed into the "ions as components" treatment. Equations for the excess free energy, the osmotic coefficient, and the activity coefficients were derived and were applied to the reciprocal salt system Na–Mg–Cl–SO_4. The ion-component treatment was found to provide a better estimate of the osmotic and activity coefficients when only data on the two-ion (single-salt) systems are available and to provide a means of calculating values for the four-ion (non-common-ion) systems using only parameters derived from the three-ion data.

Rush and Johnson (*16*) have used the equations of Scatchard (*13*) (neutral electrolytes as components) for calculating the activity coefficients of solutes from isopiestic data of mixed electrolyte solutions. Their method can be adapted to the calculation of activity coefficients of the second solute, if activity coefficients of the first solute are available. Their expression for the activity coefficient of solute A in mixed solutions with B is (*17*)

$$\log \gamma_A = \log \gamma_A{}^0 + [I_A/(2.3026\nu_A m_A)][(\alpha_B - \alpha_A)y_B + \beta_{AB}{}^{(0)}y_B + (B_{AB}{}^{(0)} - \beta_{AB}{}^{(0)})y_B{}^2 + \beta_{AB}{}^{(1)}y_B + 3(B_{AB}{}^{(1)} - \beta_{AB}{}^{(1)})y_B{}^2 - 2(2B_{AB}{}^{(1)} - \beta_{AB}{}^{(1)})y_B{}^3] \qquad (4)$$

where

$$B_{AB}{}^{(0)} = b_{AB}{}^{(0,1)}I + \tfrac{1}{2}b_{AB}{}^{(0,2)}I^2 + \tfrac{1}{3}b_{AB}{}^{(0,3)}I^3$$

$$B_{AB}{}^{(1)} = \tfrac{1}{2}b_{AB}{}^{(1,2)}I^2 + \tfrac{1}{3}b_{AB}{}^{(1,3)}I^3$$

$$\beta_{AB}{}^{(0)} = b_{AB}{}^{(0,1)}I + b_{AB}{}^{(0,2)}I^2 + b_{AB}{}^{(0,3)}I^3$$

$$\beta_{AB}{}^{(1)} = b_{AB}{}^{(1,2)}I^2 + b_{AB}{}^{(1,3)}I^3 \qquad (5)$$

$$\alpha_J = (\nu_J m_J/I_J)(\phi_J - 1) \qquad (6)$$

In these equations ν_J is the number of moles of ions per mole of component J, and ϕ_J is the osmotic coefficient of a solution of pure J at the total ionic strength of the mixture. The analogous expression for the activity coefficient of component B in mixed solutions with A can be obtained from eq 4 by replacing the A subscripts by B and changing the sign of the terms in $\beta_{AB}{}^{(1)}$ and $B_{AB}{}^{(1)}$, i.e.

$$\log \gamma_B = \log \gamma_B{}^0 + [I_B/(2.3026\nu_B m_B)][(\alpha_A - \alpha_B)y_A + \beta_{AB}{}^{(0)}y_A + (B_{AB}{}^{(0)} - \beta_{AB}{}^{(0)})y_A{}^2 - \beta_{AB}{}^{(1)}y_A - 3(B_{AB}{}^{(1)} - \beta_{AB}{}^{(1)})y_A{}^2 + 2(2B_{AB}{}^{(1)} - \beta_{AB}{}^{(1)})y_A{}^3] \qquad (7)$$

Identical b_{AB} parameters apply to each expression.

More recently, Pitzer (*18*) has worked out the idea that the properties of electrolyte solutions can be expressed by an "electrostatic" term (which may be an improved version of the Debye–Hückel term) plus a virial coefficient series in which the coefficients may be functions of the ionic strength of the solution. Development is then made, in a general form, of a system of equations for the thermodynamic properties of pure as well as mixed electrolytes. The observed osmotic coefficients of a large number of pure electrolytes of different valence types have been fitted by using a three-parameter ($\beta^{(0)}$ and $\beta^{(1)}$, both corresponding to the second virial coefficient, and C^ϕ, corresponding to the third) equation. Also, a large number of binary electrolyte mixtures have been handled with a two-parameter equation.

For a mixture of two 1:1 electrolytes MX and NX, at a total molality m, Pitzer's equation (eq 41, ref *18*) is

$$\ln \gamma_{MX} = f^\gamma + m[B_{MX}{}^\gamma + y_2(B_{NX}{}^\phi - B_{MX}{}^\phi + \theta_{MN}) + y_1 y_2 m\theta'_{MN}] + m^2[C_{MX}{}^\gamma + y_2(C_{NX}{}^\phi - C_{MX}{}^\phi + \tfrac{1}{2}\psi_{MNX}) + \tfrac{1}{2}y_1 y_2 \psi_{MNX}] \qquad (8)$$

where

$$B = \beta^{(0)} + \beta^{(1)} \exp(-2m^{1/2}) \qquad (9)$$

In eq 8, the quantitites θ_{MN} and ψ_{MNX} arise in the case of mixtures only in contrast to the B and C terms, which can be determined from the activity (γ) or osmotic (ϕ) properties of pure MX and NX solutions, and are respectively the measures of binary and ternary interactions between the ions indicated by the suffixes. Pitzer has indicated that the concentration dependence of θ is generally very small, and hence θ'_{MN} ($= \partial\theta_{MN}/\partial m$) can be neglected. Further, when one makes use of the expression derived from eq 8 for the activity coefficient in solutions containing the first component only, viz., $\ln \gamma_{MX}{}^0 = f^\gamma + mB_{MX}{}^\gamma + m^2 C_{MX}{}^\gamma$, and eq 9, eq 8 changes to

$$\ln \gamma_{MX} = \ln \gamma_{MX}{}^0 + m_2[\{(\beta_{NX}{}^{(0)} - \beta_{MX}{}^{(0)}) + (\beta_{NX}{}^{(1)} - \beta_{MX}{}^{(1)}) \exp(-2m^{1/2}) + \theta_{MN}\} + m(C_{NX}{}^\phi - C_{MX}{}^\phi) + \tfrac{1}{2}(m + m_1)\psi_{MNX}] \qquad (10)$$

Scope of the Present Work

In an earlier paper (*19*) the results from emf studies in cells without liquid junction containing mixed electrolyte solutions of hydrochloric acid and quaternary ammonium chlorides at four different temperatures have been reported. The experimental results, which showed that the Harned rule is obeyed by the activity-coefficient values of the acid component in the different mixtures, were interpreted in terms of the Pitzer theory.

The choline and acetylcholine ions, which are structurally very similar to the tetramethylammonium ion, are of biochemical interest from the standpoint of carbohydrate and lipid metabolism. They have achieved considerable importance in recent years due to their property of producing a marked vasodilation and also because it has been shown that they are normally present in the serous coat of the intestine and probably are the normal peristaltic hormones. The acetyl derivative is especially interesting since it has been found that it possesses a depressor effect 10^5 times as great as that produced by choline itself, and yet it is only 3 times as toxic as this substance. Moreover, acetylcholine is of great importance physiologically as the neurohormone of the parasympathetic nervous system and produces a lowering of the blood pressure.

Boyd, Schwarz, and Lindenbaum (*20*) have made isopiestic studies of choline chloride solutions and determined its osmotic- and activity-coefficient values. These have been utilized subsequently for calculating the Pitzer coefficients $\beta^{(0)}$, $\beta^{(1)}$, and C^ϕ for this compound. Baum (*21*) has used cation-sensitive electrodes for the study of choline chloride and acetylcholine chloride solutions. Very recently, Bates et al. (*22*) have also made further isopiestic measurements in choline chloride solutions up to high molalities, and the derived activity-coefficient values have been compared with those obtained directly from emf measurements on cells without liquid junction, using a choline ion electrode. With such an amount of precise information available regarding the thermodynamic property of activity coefficients of choline chloride and acetylcholine chloride solutions, it is very tempting to investigate the properties of these two electrolytes in binary mixed solutions with hydrochloric acid and to see how far the Pitzer theory, or the alternatively available Scatchard–Rush–Johnson theory, is successful in interpreting the results.

Further, data regarding the temperature variation of the interaction coefficient α_{12} (and β_{12}) are meager and not well interpreted even for the few mixed systems for which they are available. It therefore appeared worthwhile to secure accurate experimental data regarding the temperature variation of the ionic interaction coefficient for the mixed systems (i) HCl–$CH_2(OH)CH_2N(CH_3)_3Cl$ and (ii) HCl–$CH_2(OOCCH_3)CH_2N(CH_3)_3Cl$.

Experimental Section

Hydrochloric acid (AR), diluted to the azeotropic composition, was distilled, and only the middle fraction was retained for use. Both choline chloride (E. Merck, pro analysi) and acetylcholine chloride (E. Merck) were dissolved in absolute alcohol and then precipitated by dry ether (*23*, *24*). The fine white crystals were filtered, washed with ether, and dried under vacuum. Stock solutions of the electrolytes (HCl, 4.0243 M; $CH_2(OH)CH_2N(CH_3)_3Cl$, 3.5202 M; $CH_2(OOCCH_3)CH_2N(CH_3)_3Cl$, 4.6167 M) were prepared, and their molalities determined by gravimetric chloride analysis. Triplicate analyses agreed within 0.01% for hydrochloric acid and acetylcholine chloride and within ~0.1% for choline chloride. No further characterization of the purity of the salts was made.

Five different HCl–$CH_2(OH)CH_2N(CH_3)_3Cl$ mixtures in molal ratios 1:9, 3:7, 1:1, 7:3, and 9:1 having total ionic strength μ = 3.0 M were prepared by direct weighing from the stock solutions of known molality. The lower total ionic strength mixtures (μ = 2, 1, 0.5, 0.25, and 0.1) were prepared by weight dilution from the highest ionic strength mixture (μ = 3.0). The same procedure was followed for the HCl–acetylcholine chloride.

The cell and electrode design have been described earlier (*19*). Ag–AgCl electrodes prepared in batches of six to eight by the thermoelectrolytic method (*25*), washed thoroughly, and then aged in 0.05 N hydrochloric acid for 3–4 days were tested with respect to an aged reference electrode; only those were retained for use for which the bias potentials were ≤0.05 mV.

Electrolytic hydrogen gas was freed from any oxygen and then washed by bubbling through distilled water. The gas stream was divided into four parts to feed each of the four electrode vessels (containing duplicate sets of each of two different mixture compositions) in any particular run; the flow in each could be conveniently controlled. Neither the "barometric pressure correction" nor the "correction for the depth of the gas inlet below the level of the solution in the electrode vessel" was applied, because both were estimated to be small (ca. a few hundredths of a millivolt) compared to the accuracy and reproducibility level of the emf measurements attained. The disturbing effect due to the appearance of a whitish grey deposit of silver on the platinized platinum electrodes soon after the start of the experiment, particularly in the highest total molality mixtures, leading to erratic functioning of the electrode, was less here than during the earlier measurements (*19*) and was further reduced as before through adoption of the modified cell design with two connecting bridges between the two limbs.

Table I. Experimental Emf Data for the Cell Pt,H_2(1 atm)|HCl(m_1),$CH_2(OH)CH_2N(CH_3)_3Cl$(m_2)|AgCl,Ag for Various Values of m_1 and m_2 at Six Different Constant Total Molalities ($m = m_1 + m_2$) and at Four Different Temperatures

parameters	m_1	m_2	E, V 5 °C	E, V 15 °C	E, V 25 °C	E, V 35 °C
			m = 3.0 ± 0.001 mol kg^{-1}			
	2.6990	0.3020	0.171 86	0.165 92	0.159 40	0.152 56
	2.1520	0.8495	0.188 45	0.182 39	0.175 85	0.168 70
	1.5019	1.4993	0.209 42	0.203 49	0.196 30	0.189 17
γ_1°			1.427	1.373	1.316	1.256
E°, V			0.233 24	0.227 89	0.221 96	0.215 07
$\sigma(B)$, v			0.000 19	0.000 15	0.000 30	0.000 24
α_{12}			0.177 8	0.168 0	0.154 0	0.143 6
$\sigma(\alpha_{12})$			0.003 0	0.002 3	0.004 5	0.003 4
			m = 2.0 ± 0.001 mol kg^{-1}			
	1.7986	0.2013	0.204 28	0.198 01	0.191 94	0.185 26
	1.4246	0.5775	0.216 77	0.211 31	0.205 28	0.198 03
	1.0015	0.9997	0.232 63	0.227 30	0.221 57	
	0.6226	1.3971	0.251 03	0.246 14	0.240 64	0.234 41
γ_1°			1.068	1.039	1.009	0.975 5
E°, V			0.234 89	0.228 62	0.222 26	0.214 66
$\sigma(B)$, V			0.000 27	0.000 42	0.000 42	0.000 12
α_{12}			0.156 0	0.153 0	0.145 5	0.137 2
$\sigma(\alpha_{12})$			0.005 8	0.010 5	0.009 9	0.002 9
			m = 1.0 ± 0.001 mol kg^{-1}			
	0.8995	0.1007	0.246 85	0.242 55	0.237 60	0.231 82
	0.5007	0.4998	0.268 00	0.263 89	0.259 31	0.253 70
	0.3018	0.6997	0.283 50	0.279 80	0.275 39	0.270 25
	0.1181	0.8803	0.309 24	0.306 23	0.302 57	0.297 75
γ_1°			0.836 3	0.822 9	0.809 0	0.794 2
E°, V			0.234 00	0.228 53	0.222 37	0.215 28
$\sigma(B)$, V			0.000 05	0.000 03	0.000 07	0.000 09
α_{12}			0.159 2	0.148 7	0.138 4	0.126 7
$\sigma(\alpha_{12})$			0.001 2	0.000 4	0.001 5	0.002 7
			m = 0.5 ± 0.004 mol kg^{-1}			
	0.4488	0.0502	0.282 65	0.279 35	0.275 37	0.270 46
	0.3438	0.1477	0.291 35	0.288 14	0.284 19	0.279 55
	0.2507	0.2503	0.301 23	0.297 50	0.293 88	0.289 44
	0.1513	0.3509	0.314 88	0.312 35	0.309 10	0.304 99
	0.0591	0.4406	0.338 67	0.336 81	0.334 27	0.330 90
γ_1°			0.773 0	0.765 8	0.757 1	0.747 7
E°, V			0.233 88	0.228 24	0.221 91	0.214 65
$\sigma(B)$, V			0.000 31	0.000 22	0.000 21	0.000 22
α_{12}			0.172 9	0.161 1	0.150 4	0.140 6
$\sigma(\alpha_{12})$			0.028 6	0.014 5	0.010 2	0.013 5
			m = 0.25 ± 0.002 mol kg^{-1}			
	0.2241	0.0251	0.316 10	0.313 81	0.310 88	0.307 14
	0.1724	0.0741	0.323 61	0.321 50	0.318 67	0.314 90
	0.1269	0.1267	0.331 46	0.329 59	0.326 95	0.323 56
	0.0753	0.1745	0.345 05	0.343 57	0.341 44	0.338 51
	0.0295	0.2196	0.367 94	0.367 32	0.365 85	0.363 51
γ_1°			0.770 1	0.765 4	0.759 8	0.752 9
E°, V			0.234 28	0.228 75	0.222 50	0.215 28
$\sigma(B)$, V			0.000 18	0.000 16	0.000 17	0.000 18
α_{12}			0.148 5	0.139 0	0.124 2	0.110 8
$\sigma(\alpha_{12})$			0.031 5	0.028 0	0.022 7	0.012 8
			m = 0.1 ± 0.0005 mol kg^{-1}			
	0.0901	0.0101	0.357 08	0.356 21	0.354 60	0.352 05
	0.0495	0.0494	0.372 61	0.372 16	0.371 02	0.368 81
	0.0303	0.0703	0.384 50	0.384 55	0.383 90	0.382 04
	0.0118	0.0882	0.407 77	0.408 52	0.408 51	0.407 62
γ_1°			0.802 3	0.800 0	0.796 4	0.791 8
E°, V			0.233 45	0.228 01	0.221 75	0.214 42
$\sigma(B)$, V			0.000 14	0.000 10	0.000 07	0.000 09
α_{12}			0.223 2	0.204 7	0.186 7	0.166 0
$\sigma(\alpha_{12})$			0.025 1	0.018 4	0.020 3	0.011 3

Table II. Experimental Emf Data for the Cell Pt,H_2(1 atm)|HCl(m_1),$CH_2(OCOCH_3)CH_2N(CH_3)_3Cl$($m_2$)|AgCl,Ag for Various Values of m_1 and m_2 at Six Different Constant Total Molalities ($m = m_1 + m_2$) and Four Different Temperatures

parameters	m_1	m_2	E, V 5 °C	15 °C	25 °C	35 °C
$m = 3.0 \pm 0.002$ mol kg^{-1}						
	2.6974	0.2998	0.171 45	0.165 35	0.158 64	0.151 01
	2.1012	0.9005	0.186 40	0.180 31	0.173 57	0.166 34
	1.4987	1.5021	0.203 70	0.197 06	0.190 36	0.182 97
γ_1°			1.427	1.373	1.316	1.256
E°, V			0.234 03	0.228 80	0.222 38	0.214 72
$\sigma(B)$, V			0.000 05	0.000 10	0.000 10	0.000 25
α_{12}			0.136 9	0.124 5	0.116 9	0.111 3
$\sigma(\alpha_{12})$			0.000 8	0.001 4	0.001 4	0.003 3
$m = 2.0 \pm 0.005$ mol kg^{-1}						
	1.7942	0.1994	0.203 00	0.197 49	0.191 46	0.184 56
	1.3994	0.5997	0.214 34	0.209 03	0.203 06	0.196 51
	0.5975	1.3961	0.245 96	0.241 06	0.235 59	0.229 29
γ_1°			1.068	1.039	1.009	0.975 5
E°, V			0.233 93	0.228 36	0.222 05	0.214 65
$\sigma(B)$, V			0.000 08	0.000 03	0.000 05	0.000 07
α_{12}			0.126 0	0.119 1	0.112 4	0.106 0
$\sigma(\alpha_{12})$			0.002 1	0.000 9	0.001 1	0.001 7
$m = 1.0 \pm 0.002$ mol kg^{-1}						
	0.9999	0.0	0.242 45	0.237 98	0.232 84	0.226 90
	0.8988	0.0999	0.246 44	0.242 04	0.236 95	0.230 98
	0.6999	0.3000	0.255 15	0.250 91	0.245 99	0.239 95
	0.4994	0.5005	0.265 95	0.261 81	0.257 10	0.251 59
	0.2987	0.6980	0.280 93	0.277 20	0.272 75	0.267 51
	0.0998	0.9037	0.310 08	0.307 20	0.303 75	0.298 84
γ_1°			0.836 3	0.822 9	0.809 0	0.794 2
E°, V			0.233 91	0.228 35	0.222 00	0.214 72
$\sigma(B)$, V			0.000 03	0.000 05	0.000 07	0.000 11
α_{12}			0.123 8	0.115 5	0.108 4	0.098 3
$\sigma(\alpha_{12})$			0.001 4	0.001 9	0.001 9	0.001 7
$m = 0.5 \pm 0.004$ mol kg^{-1}						
	0.4999	0.0	0.279 04	0.275 63	0.271 54	0.266 74
	0.4494	0.0499	0.282 43	0.279 07	0.275 02	0.270 09
	0.3501	0.1500	0.289 64	0.286 44	0.282 53	0.277 87
	0.2488	0.2493	0.299 36	0.296 29	0.292 64	0.288 25
	0.0500	0.4524	0.340 52	0.338 89	0.336 50	0.333 40
γ_1°			0.773 0	0.765 8	0.757 1	0.747 7
E°, V			0.233 54	0.227 99	0.221 65	0.214 42
$\sigma(B)$, V			0.000 06	0.000 05	0.000 06	0.000 04
α_{12}			0.125 3	0.116 6	0.107 6	0.100 5
$\sigma(\alpha_{12})$			0.007 1	0.007 6	0.007 1	0.002 5
$m = 0.25 \pm 0.0005$ mol kg^{-1}						
	0.2489	0.0	0.313 34	0.310 96	0.307 96	0.304 01
	0.2247	0.0250	0.316 04	0.313 73	0.310 82	0.307 00
	0.1753	0.0751	0.322 57	0.320 38	0.317 49	0.313 90
	0.1245	0.1248	0.331 35	0.329 40	0.326 84	0.323 46
	0.0751	0.1755	0.343 90	0.342 35	0.340 14	0.337 10
	0.0248	0.2249	0.371 08	0.370 32	0.369 05	0.367 01
γ_1°			0.770 1	0.765 4	0.759 8	0.752 9
E°, V			0.234 26	0.228 75	0.222 50	0.215 25
$\sigma(B)$, V			0.000 04	0.000 03	0.000 05	0.000 06
α_{12}			0.100 2	0.083 6	0.070 6	0.063 3
$\sigma(\alpha_{12})$			0.003 5	0.002 3	0.006 6	0.007 3
$m = 0.1 \pm 0.001$ mol kg^{-1}						
	0.0977	0.0	0.354 91	0.353 89	0.352 17	0.349 69
	0.0900	0.0100	0.357 48	0.356 60	0.354 90	0.352 43
	0.0699	0.0299	0.363 75	0.362 97	0.361 48	0.359 21
	0.0499	0.0501	0.371 90	0.371 38	0.370 24	0.368 22
γ_1°			0.802 3	0.800 0	0.796 4	0.791 8
E°, V			0.233 95	0.228 46	0.222 12	0.214 94
$\sigma(B)$, V			0.000 03	0.000 04	0.000 02	0.000 01
α_{12}			0.077 8	0.052 8	0.050 2	0.029 4
$\sigma(\alpha_{12})$			0.010 5	0.028 8	0.015 5	0.003 5

Table III. Standard Deviations of the Experimental E° Values from the Corresponding Literature Values for the Two Mixtures at the Four Different Temperatures

substituted quaternary ammonium salt	σ, mV 5 °C	15 °C	25 °C	35 °C
choline chloride	±0.54	±0.36	±0.38	±0.87
acetylcholine chloride	±0.22	±0.28	±0.39	±0.95
	E°, V 5 °C	15 °C	25 °C	35 °C
lit. values	0.2340	0.2285	0.2224	0.2157

Measurements were carried out in a thermostat bath at 10 °C intervals, over the temperature range 5–35 °C, controlled to ±0.05 °C. An LN type K2 potentiometer, in conjunction with an LN moving coil galvanometer of sensitivity 1 mm/m at 10^{-6} V, was used. Duplicate emf measurements were carried out for each of the above mixtures, and the emf values from the two electrodes almost always agreed within experimental error.

Calculations

Table I gives the experimental results for the emf of the cell containing mixtures of HCl (m_1) and choline chloride (m_2), at six different values of the total molality $m = m_1 + m_2$, each constant total molality comprising a number of different mole-ratio mixtures. Data are recorded for four different temperatures in each case. If one assumes that the mean ionic activity-coefficient values of the hydrochloric acid component in the mixture obeys Harned's rule, at all of the four different temperatures, the emf of the cell is given by eq 11, where k

$$E + k \log m_1 = (E^\circ - k \log m - 2k \log \gamma_1^0) + 2k\alpha_{12}m_2 \tag{11}$$

= (2.3026RT)/F and α_{12} is the Harned coefficient of the acid component in the mixture. Values of γ_1^0 for pure HCl solutions of different molalities and at different temperatures were taken from the literature (*9*) and are included in Table I. Computerized least-squares calculations were made for calculating E° and α_{12}, together with the standard deviations $\sigma(E)$ in E, and $\sigma(\alpha_{12})$ in α_{12}, which are also given in Table I. Table II summarizes exactly similarly the experimental data for the HCl–acetylcholine chloride system.

It is seen from Tables I and II that, over the range μ = 3.0–0.1 M (comprising six different constant total molality mixtures), the standard deviations of the E° values at the four different temperatures investigated from the corresponding literature values (*26*) are as given in Table III. When one considers the wide range of variation of the total mixture molality, and the modest range of temperature variation involved, this result may be considered satisfactory. We have used in our further calculations the specific E° value determined for each electrode, for each set, in the manner shown above, at all of the four different working temperatures (rather than the literature E° values at these temperatures), for the same reason (*26*) as mentioned earlier (*19*).

Discussion

The standard deviation in E as found by the computerized least-squares analysis is generally less than (i) 0.1 mV for acetylcholine chloride, except for the 3.0 M mixture at 35 °C, and (ii) 0.3 mV for choline chloride, except for the 2.0 M mixtures at 15 and 25 °C only, where it is 0.4 mV. Thus, it can be concluded that the Harned rule holds for the HCl component in both the HCl–choline chloride and HCl–acetylcholine chloride mixtures, over the temperature range studied, at least within the experimental accuracy secured.

The compositions of the solutions and the experimental values of log γ_1 for the HCl–choline chloride and HCl–acetylcholine chloride systems are given respectively in Tables IV and V, which also show the closeness of fit obtained when the values of log γ_1 at each total ionic strength are fitted to the eq

Table IV. Activity Coefficients of Hydrochloric Acid in the System $HCl-CH_2(OH)CH_2N(CH_3)_3Cl-H_2O$ at All of the Four Different Temperatures[a]

		5 °C			15 °C			25 °C			35 °C		
m	y_2	γ_{HCl}	$10^4\Delta_1$	$10^4\Delta_2$	γ_{HCl}	$10^4\Delta_1$	$10^4\Delta_2$	γ_{HCl}	$10^4\Delta_1$	$10^4\Delta_2$	γ_{HCl}	$10^4\Delta_1$	$10^4\Delta_2$
3.0	0.100 67	1.2647	14	0	1.2242	10	0	1.1875	20	0	1.1403	15	0
	0.283 16	1.0019	−25	0	0.9839	−19	0	0.9654	−36	0	0.9422	−28	0
	0.499 76	0.7743	11	0	0.7700	9	0	0.7762	17	0	0.7671	13	0
2.0	0.100 63	0.9985	23	−2	0.9767	40	3	0.9513	38	1	0.9173	10	0
	0.288 73	0.8641	−18	6	0.8391	−44	−8	0.8240	−39	−3	0.8100	−15	0
	0.499 84	0.7404	−36	−5	0.7254	−30	8	0.7159	−35	3			
	0.698 54	0.6505	26	2	0.6401	34	−3	0.6370	36	−1	0.6281	5	0
1.0	0.100 65	0.8063	3	1	0.7949	1	0	0.7838	3	1	0.7720	6	−1
	0.499 83	0.6950	−8	−3	0.6931	−2	−1	0.6883	−9	−5	0.6852	−7	4
	0.699 73	0.6475	3	5	0.6476	0	1	0.6480	5	7	0.6459	−11	−6
	0.880 26	0.6059	2	−2	0.6089	1	0	0.6113	1	−3	0.6161	12	2
0.5	0.100 42	0.7638	19	−13	0.7549	2	−8	0.7465	−2	−12	0.7387	1	−11
	0.295 48	0.7333	15	32	0.7280	7	12	0.7237	15	20	0.7165	12	18
	0.500 58	0.6921	−53	−20	0.6993	3	14	0.6951	0	10	0.6899	−3	9
	0.701 80	0.6693	−19	−5	0.6666	−37	−33	0.6645	−39	−35	0.6617	−37	−32
	0.881 10	0.6536	38	6	0.6535	25	15	0.6532	26	17	0.6517	27	15
0.25	0.100 28	0.7676	13	−6	0.7630	11	−5	0.7575	8	−7	0.7503	3	−13
	0.296 28	0.7524	2	12	0.7492	4	13	0.7463	7	16	0.7432	19	27
	0.506 64	0.7339	−24	−5	0.7315	−24	−7	0.7298	−21	−5	0.7255	−24	−8
	0.698 08	0.7230	−15	−7	0.7220	−11	−4	0.7201	−17	−10	0.7161	−24	−18
	0.878 48	0.7179	24	4	0.7164	20	3	0.7167	22	6	0.7158	27	11
0.1	0.100 80	0.7980	−5	0	0.7959	−6	−1	0.7929	−4	−1	0.7879	−9	−1
	0.493 90	0.7839	7	−1	0.7841	12	3	0.7824	13	7	0.7806	18	5
	0.702 60	0.7751	6	2	0.7741	0	−4	0.7715	−8	−10	0.7709	−1	−6
	0.881 90	0.7654	−8	−1	0.7665	−6	2	0.7668	0	4	0.7642	−8	3

[a] $\Delta_{1,2}$ = log (experimental activity coefficient) − log (value calculated by least-squares fit to eq 1), Δ_1 with $\beta_{12} = 0$, Δ_2 with $\beta_{12} \neq 0$.

Table V. Activity Coefficients of Hydrochloric Acid in the System $HCl-CH_2(OCOCH_3)CH_2N(CH_3)_3Cl-H_2O$ at All of the Four Different Temperatures[a]

		5 °C			15 °C			25 °C			35 °C		
m	y_2	γ_{HCl}	$10^4\Delta_1$	$10^4\Delta_2$	γ_{HCl}	$10^4\Delta_1$	$10^4\Delta_2$	γ_{HCl}	$10^4\Delta_1$	$10^4\Delta_2$	γ_{HCl}	$10^4\Delta_1$	$10^4\Delta_2$
3.0	0.099 93	1.2979	−3	0	1.2622	7	0	1.2162	7	0	1.1675	15	0
	0.300 16	1.0757	5	0	1.0573	−13	0	1.0297	−13	0	0.9904	−30	0
	0.500 70	0.8879	−3	0	0.8936	7	0	0.8795	7	0	0.8575	15	0
2.0	0.099 70	1.0080	−4	0	0.9847	0	0	0.9590	−1	0	0.9318	8	0
	0.299 86	0.8997	6	0	0.8825	0	0	0.8652	1	0	0.8413	−12	0
	0.698 06	0.7128	−2	0	0.7095	0	0	0.7039	0	0	0.6954	4	0
1.0	0.0	0.8369	1	4	0.8238	2	5	0.8099	2	6	0.7950	2	−3
	0.099 89	0.8127	−3	−2	0.8011	−3	−3	0.7890	−3	−2	0.7770	1	0
	0.299 95	0.7675	−3	−5	0.7588	−7	−9	0.7494	−9	−12	0.7432	5	10
	0.500 54	0.7252	1	−2	0.7213	5	2	0.7146	3	−1	0.7066	−16	−10
	0.697 98	0.6871	12	11	0.6852	11	10	0.6824	18	17	0.6781	0	2
	0.903 74	0.6448	−8	−5	0.6455	−9	−6	0.6435	−13	−9	0.6480	6	1
0.5	0.0	0.7741	2	4	0.7664	0	6	0.7574	−2	5	0.7467	−10	−2
	0.099 86	0.7612	−7	−7	0.7547	−8	−7	0.7470	−7	−6	0.7398	1	3
	0.300 08	0.7412	5	3	0.7364	4	−1	0.7306	6	−1	0.7233	6	−2
	0.498 68	0.7194	2	0	0.7179	11	4	0.7133	11	3	0.7072	10	0
	0.904 76	0.6773	−2	0	0.6764	−7	−1	0.6749	−7	−1	0.6714	−8	0
0.25	0.0	0.7718	5	2	0.7673	6	2	0.7615	4	3	0.7552	8	5
	0.099 88	0.7665	0	0	0.7624	0	−1	0.7567	−4	−5	0.7450	−5	−6
	0.300 56	0.7559	−8	−6	0.7537	−7	−3	0.7511	0	2	0.7443	−5	−3
	0.499 28	0.7485	0	3	0.7474	0	4	0.7446	−1	1	0.7393	−1	1
	0.702 08	0.7399	2	3	0.7395	−2	−1	0.7382	−1	0	0.7344	4	5
	0.899 64	0.7310	1	−2	0.7334	4	0	0.7325	2	0	0.7284	0	−3
0.1	0.0	0.8042	6	2	0.8023	8	4	0.7981	5	4	0.7931	3	3
	0.100 00	0.8004	−6	−4	0.7978	−10	−8	0.7948	−8	−7	0.7910	−5	−5
	0.299 40	0.7981	−2	3	0.7975	0	5	0.7946	3	5	0.7912	3	3
	0.500 60	0.7956	2	−1	0.7956	2	−2	0.7918	0	−1	0.7890	−1	−1

[a] $\Delta_{1,2}$ = log (experimental activity coefficient) − log (value calculated by least-squares fit to eq 1), Δ_1 with $\beta_{12} = 0$, Δ_2 with $\beta_{12} \neq 0$.

1 by the method of least squares, the case where $\beta_{12} = 0$ being considered first. There is an improvement in fit when the term in m_2^2 is included, and such a term is possibly warranted at the higher ionic strengths, but Harned's rule is a good approximation, as can be gauged from the Δ_1 values in Tables IV and V. Tables VI and VII give respectively the results of the above fit, for the two systems considered.

Analysis of the Results by the Scatchard Method. In order to be able to calculate the b_{AB} coefficients characteristic of the mixture, one must know the values of the α_J parameters for the two components of the mixture (α_1, α_2) at each constant total ionic strength. To obtain α_1, for example, the values of γ_1 (pure first component activity coefficients) must first be fitted (least squares) to an extended Debye–Hückel equation of the type

$$2.3026\nu_J m_J/I_J \log \gamma_1 = -2SI^{1/2}/(1 + a_J I^{1/2}) + 2a_J^{(1)}I + {}^3\!/_2 a_J^{(2)}I^2 + {}^4\!/_3 a_J^{(3)}I^3 + {}^5\!/_4 a_J^{(4)}I^4 + \ldots \quad (12)$$

Table VI. Parameters of Eq 1 Obtained by the Method of Least Squares for the System $HCl-CH_2(OH)CH_2N(CH_3)_3Cl-H_2O$ at All of the Four Different Temperatures

	5 °C			15 °C			25 °C			35 °C		
m	α_{12}	$-\beta_{12}$	$\log \gamma_1^\circ$	α_{12}	$-\beta_{12}$	$\log \gamma_1^\circ$	α_{12}	$-\beta_{12}$	$\log \gamma_1^\circ$	α_{12}	$-\beta_{12}$	$\log \gamma_1^\circ$
3.0	0.1778	0.0^a	0.1543	0.1681	0.0^a	1.1376	0.1540	0.0^a	0.1192	0.1436	0.0^a	0.0989
	0.1970	0.0105	0.1605	0.1826	0.0080	0.1423	0.1820	0.0154	0.1282	0.1648	0.0116	0.1057
2.0	0.1559	0.0^a	0.0285	0.1529	0.0^a	0.0165	0.1455	0.0^a	0.0038	0.1371	0.0^a	−0.0109
	0.1812	0.0158	0.0354	0.1909	0.0237	0.0269	0.1831	0.0235	0.0141	0.1495	0.0075	−0.0077
1.0	0.1590	0.0^a	−0.0778	0.1484	0.0^a	−0.0848	0.1382	0.0^a	−0.0922	0.1265	0.0^a	−0.1002
	0.1635	0.0048	−0.0772	0.1498	0.0014	−0.0846	0.1428	0.0049	−0.0916	0.1390	0.0131	−0.0984
0.5	0.1783	0.0^a	−0.1099	0.1665	0.0^a	−0.1140	0.1558	0.0^a	−0.1189	0.1460	0.0^a	−0.1244
	0.2609	0.1683	−0.1030	0.1941	0.0562	−0.1117	0.1801	0.0495	−0.1169	0.1776	0.0644	−0.1217
0.25	0.1548	0.0^a	−0.1123	0.1453	0.0^a	−0.1150	0.1305	0.0^a	−0.1182	0.1171	0.0^a	−0.1221
	0.2547	0.4090	−0.1082	0.2335	0.3611	−0.1113	0.2117	0.3326	−0.1148	0.1988	0.3343	−0.1188
0.1	0.2279	0.0^a	−0.0952	0.2094	0.0^a	−0.0965	0.1914	0.0^a	−0.0984	0.1707	0.0^a	−0.1009
	0.1339	−0.9841	−0.0966	0.1164	−0.9728	−0.0978	0.1335	−0.6057	−0.0993	0.0291	−1.4823	−0.1030

[a] Set equal to zero.

Table VII. Parameters of Eq 1 Obtained by the Method of Least Squares for the System $HCl-CH_2(OCOCH_3)CH_2N(CH_3)_3Cl-H_2O$ at All of the Four Different Temperatures

	5 °C			15 °C			25 °C			35 °C		
m	α_{12}	$-\beta_{12}$	$\log \gamma_1^\circ$	α_{12}	$-\beta_{12}$	$\log \gamma_1^\circ$	α_{12}	$-\beta_{12}$	$\log \gamma_1^\circ$	α_{12}	$-\beta_{12}$	$\log \gamma_1^\circ$
3.0	0.1371	0.0^a	0.1546	0.1248	0.0^a	0.1379	0.1171	0.0^a	0.1195	0.1115	0.0^a	0.0992
	0.1331	−0.0023	0.1533	0.1347	0.0055	0.1410	0.1269	0.0054	0.1226	0.1339	0.0125	0.1063
2.0	0.1259	0.0^a	0.0290	0.1189	0.0^a	0.0170	0.1122	0.0^a	0.0043	0.1059	0.0^a	−0.0104
	0.1210	−0.0030	0.0277	0.1187	−0.0001	0.0170	0.1111	−0.0007	0.0040	0.1155	0.0058	−0.0079
1.0	0.1243	0.0^a	−0.0774	0.1159	0.0^a	−0.0844	0.1088	0.0^a	−0.0918	0.0988	0.0^a	−0.0998
	0.1216	−0.0030	−0.0777	0.1131	−0.0031	−0.0847	0.1053	−0.0040	−0.0922	0.1033	0.0052	−0.0994
0.5	0.1274	0.0^a	−0.1114	0.1186	0.0^a	−0.1155	0.1096	0.0^a	−0.1205	0.1026	0.0^a	−0.1259
	0.1240	−0.0073	−0.1116	0.1071	−0.0253	−0.1161	0.0969	−0.0279	−0.1211	0.0870	−0.0341	−0.1267
0.25	0.1032	0.0^a	−0.1130	0.0866	0.0^a	−0.1156	0.0736	0.0^a	−0.1188	0.0663	0.0^a	−0.1228
	0.1133	0.0454	−0.1127	0.1023	0.0711	−0.1152	0.0797	0.0274	−0.1186	0.0767	0.0469	−0.1225
0.1	0.0865	0.0^a	−0.0952	0.0614	0.0^a	−0.0964	0.0588	0.0^a	−0.0984	0.0380	0.0^a	−0.1009
	0.1508	1.2763	−0.0949	0.1356	1.4712	−0.0961	0.0790	0.4001	−0.0983	0.0386	0.0118	−0.1009

[a] Set equal to zero.

Table VIII. Best-Fitting Parameters of Eq 12 for HCl and $CH_2(OH)CH_2N(CH_3)_3Cl$ at 25 °C

parameters	HCl	$CH_2(OH)CH_2N(CH_3)_3Cl$
a_J	1.465 07	0.684 52
$10^2 a_J^{(1)}$	25.202 9	4.632 74
$10^3 a_J^{(2)}$	15.797	9.231 6
$10^4 a_J^{(3)}$	−5.646 5	−0.941 644
$10^5 a_J^{(4)}$	−7.667 63	−0.857 94

Table IX. Values of b_{AB} Coefficients Obtained by Least-Squares Fit of Eq 4 (Written in Terms of b_{AB} Coefficients) to the Measured Activity Coefficients of Hydrochloric Acid for the System $HCl-CH_2(OH)CH_2N(CH_3)_3Cl-H_2O$ at 25 °C

$b_{AB}^{(0,1)}$	−0.165 67
$b_{AB}^{(0,2)}$	−0.114 75
$b_{AB}^{(0,3)}$	0.010 51
$b_{AB}^{(1,2)}$	0.0^a
$b_{AB}^{(1,3)}$	0.0^a

[a] Set equal to zero.

S is the value of the limiting Debye–Hückel slope for the appropriate experimental temperature, and a_J is the "distance of closest approach" parameter. Such fits have already been made by Downes (*17*) for hydrochloric acid and by Bates (*22*) for choline chloride, both at 25 °C. We have used their values of the parameters a_J and $a_J^{(i)}$, which are listed in Table VIII.

Knowing the best fitting values of a_J and $a_J^{(i)}$, one can calculate α_J by using the following relation which is thermodynamically related to eq 12:

$$\alpha_J = \frac{-2S}{a_J^3 I}\left[1 + a_J I^{1/2} - \frac{1}{1 + a_J I^{1/2}} - 2 \ln (1 + a_J I^{1/2})\right] + a_J^{(1)} I + a_J^{(2)} I^2 + a_J^{(3)} I^3 + a_J^{(4)} I^4 + \ldots \tag{13}$$

Having obtained the parameters for the single-electrolyte solutions, we first evaluated the values of $B_{AB}^{(0)}$ and $\beta_{AB}^{(0)}$ at a particular ionic strength by subjecting eq 4, after neglecting $B_{AB}^{(1)}$ and $\beta_{AB}^{(1)}$ terms, to the method of least squares. These values of either $B_{AB}^{(0)}$ or $\beta_{AB}^{(0)}$, obtained at different total ionic strengths, were then subjected to the least-squares analysis of eq 5 for calculating the b_{AB} parameters, which are listed in Table IX.

The magnitude of the $\Delta_3^{(S)}$ values listed in Table X shows the success with which eq 4 with $B_{AB}^{(1)}$ and $\beta_{AB}^{(1)}$ set equal to zero can be applied for reproducing the experimental results (γ_{HCl}). The activity coefficients of choline chloride in the mixtures can be obtained from the analogous equation (eq 7) for γ_{ChCl} by using the same b_{AB} values; these are also listed in Table X. (Since the actual experimental values are not known, the deviation functions cannot be given (like $\Delta_3^{(S)}$ and $\Delta_4^{(P)}$ for the first component.)

Analysis of the Results by the Pitzer Method. For the analysis of our results according to Pitzer's treatment of mixed electrolyte solutions, we make use of the equations given earlier (with $\theta'_{MN} = 0$). Pitzer and Mayorga (*27*) have given the following values for the parameters for HCl and ChCl at 25 °C, which we use in our calculation: $\beta_{HCl}^{(0)} = 0.1775$; $\beta_{HCl}^{(1)} = 0.2945$; $C_{HCl}^{\phi} = 0.0008$; $\beta_{ChCl}^{(0)} = 0.0457$; $\beta_{ChCl}^{(1)} = -0.196$; $C_{ChCl}^{\phi} = 0.0008$.

Table X. Activity Coefficients of Choline Chloride Calculated by Using Scatchard and Pitzer Equations, and the Deviations of the Calculated Values of log γ_{HCl} from the Corresponding Experimental log γ_{HCl} Values at 25 °C[a]

m, mol kg^{-1}	y_1	$-\log \gamma_2{}^{(S)}$	$-\log \gamma_2{}^{(P)}$	$10^4\Delta_3{}^{(S)}$	$10^4\Delta_4{}^{(P)}$	$\sigma^{(S)}$	$\sigma^{(P)}$
3.0	0.899 66	0.3317	0.3084	11	55	0.0109	0.0043
	0.717 33	0.3382	0.2938	−95	1		
	0.500 64	0.3398	0.2875	−163	−52		
2.0	0.899 31	0.2977	0.2743	37	41	0.0104	0.0126
	0.712 30	0.3061	0.3061	−67	−65		
	0.500 73	0.3125	0.2807	−127	−143		
	0.301 29	0.3153	0.2906	−146	−194		
1.0	0.899 50	0.2503	0.2333	2	−1	0.0045	0.0076
	0.500 71	0.2652	0.2508	−32	−53		
	0.301 79	0.2714	0.2612	−42	−76		
	0.118 10	0.2763	0.2718	−75	−123		
0.5	0.897 60	0.2073	0.1958	10	11	0.0036	0.0036
	0.687 66	0.2134	0.2037	15	15		
	0.501 46	0.2187	0.2109	−16	−16		
	0.302 68	0.2240	0.2190	−73	−73		
	0.118 20	0.2288	0.2267	−26	−27		
0.25	0.896 36	0.1671	0.1598	26	27	0.0048	0.0057
	0.689 48	0.1712	0.1653	38	43		
	0.507 56	0.1748	0.1703	23	32		
	0.301 08	0.1787	0.1760	39	50		
	0.117 84	0.1822	0.1811	88	102		
0.1	0.901 00	0.1207	0.1171	0	2	0.0008	0.0011
	0.494 80	0.1250	0.1230	14	20		
	0.303 00	0.1271	0.1258	−9	8		
	0.118 30	0.1290	0.1285	−3	0		

[a] Δ_3 = log (experimental activity coefficient) − log (value calculated by least-squares fit to eq 4, with $B_{AB}{}^{(1)}$ and $\beta_{AB}{}^{(1)}$ set equal to zero). Δ_4 = log (experimental activity coefficient) − log (value calculated by least-squares fit to eq 10).

Assuming that eq 10 would reproduce correctly (for a proper choice of the θ and ψ values) the experimentally determined γ_{MX} values (calculated from the measured cell emf's by means of the usual equation: $\ln \gamma_{MX} = [E° - E - (RT/F) \ln m_1(m_1 + m_2)]/(2RT/F)$, using the tabulated $E°$ values (Table I)), one obtains

$$\Delta \ln \gamma_{MX} = \ln \gamma_{MX}(\text{exptl}) - \ln \gamma_{MX}(\text{theor}, \theta = \psi = 0) = m_2[\theta_{MN} + \tfrac{1}{2}(m + m_1)\psi_{MNX}] \tag{14}$$

The values of the binary and ternary interaction coefficients θ and ψ were calculated by the computerized least-squares handling of eq 14, using the experimental activity-coefficient values of hydrochloric acid in $HCl-CH_2(OH)CH_2N(CH_3)_3Cl$ mixtures at 25 °C only. (Since the values of the pure-electrolyte parameters at the other experimental temperatures are not so far available in the literature, the analysis is restricted to this temperature only.) These values, together with that of the standard deviation σ of the fit, are $\theta = -0.0520$, $\psi = -0.0644$, and $\sigma = 0.032$.

The rather large values of the standard deviation in comparison with the values of the Pitzer parameters might appear to raise some doubt regarding the meaningfulness of the latter. An actual plot of this fit shows that, though the overall standard deviation σ is indeed somewhat large, this can be attributed mostly to the sets of lower total molality data which show the largest scatter, very likely because of the somewhat lower experimental accuracy attained there. A very similar situation was noted earlier by us (*19*) for the HCl–quaternary ammonium chloride mixtures and by Roy et al. (*28*) for the $HBr-(C_3H_7)_4NBr$ mixtures. The conclusion to be drawn would be that the Pitzer coefficients are significant, but that the unambiguous experimental establishment of their values would require exceptionally accurate data in the lower molality range.

The magnitude of the $\Delta_4{}^{(P)}$ values listed in Table X shows the success of the Pitzer equation (eq 10) for reproducing the activity coefficients of hydrochloric acid. Also given in the same table are the activity coefficients of choline chloride, calculated by using the Pitzer equation (an equation analogous to eq 10, for γ_{ChCl}) and the same values of interaction parameters θ and ψ.

The standard deviations of the fits of the log γ_{HCl} values in Scatchard's and Pitzer's analyses are also given in Table X ($\sigma^{(S)}$ and $\sigma^{(P)}$, respectively).

Comparison of Scatchard and Pitzer Equations. It is seen from Table X for the $HCl-CH_2(OH)CH_2N(CH_3)_3Cl$ system at 25 °C that $\sigma^{(S)}$ is less than $\sigma^{(P)}$ for the total molalities m = 2, 1, 0.25, and 0.1, while, for m = 3.0, $\sigma^{(P)}$ is less than $\sigma^{(S)}$, and, for m = 0.5, $\sigma^{(S)} = \sigma^{(P)}$.

Scatchard's equation as used here contains three interaction parameters whose physical meaning is somewhat vague. On the other hand, Pitzer's equations have effectively only two parameters (e.g., θ and ψ) which characterize specific types of ionic interactions in the mixtures and should on this count be preferable to the Scatchard equations. However, for the $HCl-CH_2(OH)CH_2N(CH_3)_3Cl$ mixture, Pitzer's equation is found not to be quite as successful as Scatchard's.

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Binary Vapor–Liquid Equilibria of Iso Alcohol–Tetrachloroethene Systems

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Vapor–liquid equilibrium data for two binary iso alcohol–tetrachloroethene systems are measured at 760 mmHg pressure. these two systems are nonideal in behavior and show positive deviations from Raoult's law. The data are correlated by the Margules, Van Laar, Wilson, NRTL, and UNIQUAC equations.

In order to develop predictive methods for vapor–liquid equilibria, a continuing study on various binary systems is in progress at this laboratory. As part of this, two binary systems comprising either 2-methyl-1-propanol or 3-methyl-1-butanol in a common solvent, tetrachloroethene, were studied at 760 ± 1 mmHg pressure.

Experimental Section

Purity of Chemicals. The iso alcohols and tetrachloroethene were of reagent grade and were further purified in a laboratory-packed distillation column. The physical properties of these chemicals are presented in Table I. These values compare well with the literature values (*16*).

Equilibrium Still and Analytical Method. An equilibrium still of Jones, Schoenborn, and Colburn as modified by Ward (*15*) was used for the determination of the vapor–liquid equilibria. The details of the still and its operation were described elsewhere (*11*). Equilibrium in the still was attained in 45–60 min depending on the temperature range of the binary mixture. Equilibrium was assumed to be attained when the boiling temperature was constant. In all of the runs, the still was allowed to operate for an additional 60–90 min after getting the equilibrium temperature to ensure complete attainment of equilibrium.

The equilibrium vapor and liquid samples were analyzed by refractive index. For this purpose, mixtures of known composition were prepared at intervals of ~10 mol %, and their refractive indexes were measured. The refractive index vs. composition data for the two binary mixtures are given in Table II. A standard calibration chart of the refractive index vs. composition was prepared for each system on 75 × 50 cm graph paper. Refractive-index measurements were taken at 30 °C for sodium light by using an Abbe's precision refractometer which gave direct readings to three significant figures and had an accuracy to the nearst 0.0005. This corresponds to a maximum error of 0.0055 mole fraction. The equilibrium temperature was measured by a standard mercury in glass thermometer having an accuracy of 0.1 °C.

Table I. Physical Properties of Chemicals

compd	normal bp, °C exptl	normal bp, °C lit.^{13}	refractive index at 30 °C exptl	refractive index at 30 °C lit.^{13}
2-methyl-1-propanol	107.9	107.89	1.3920	1.391 63
3-methyl-1-butanol	131.7	132.0	1.4035	1.402 84
tetrachloroethene	121.3	121.20	1.5019	1.5018

Table II. Refractive Index vs. Composition Data

2-Methyl-1-propanol (1)–Tetrachloroethene (2)

mole fraction of 2-methyl-1-propanol	refractive index	mole fraction of 2-methyl-1-propanol	refractive index
0.0000	1.5019	0.6261	1.4339
0.1071	1.4889	0.7000	1.4230
0.2191	1.4769	0.8000	1.4129
0.3252	1.4662	0.9000	1.4025
0.4305	1.4540	1.0000	1.3920
0.5259	1.4442		

Tetrachloroethene (1)–3-Methyl-1-butanol (2)

mole fraction of tetrachloroethene	refractive index	mole fraction of tetrachloroethene	refractive index
0.0000	1.4035	0.6142	1.4619
0.1062	1.4142	0.7055	1.4710
0.2096	1.4232	0.7854	1.4810
0.3130	1.4327	0.9131	1.4913
0.4130	1.4424	1.0000	1.5019
0.5111	1.4519		

Table III. Antoine Constants and Constants for Molar Volumes

constant	2-methyl-1-propanol	3-methyl-1-butanol	tetrachloroethene
A	8.53516	7.38170	7.62930
B	1950.940	1373.780	1803.96
C	237.147	174.333	258.976
a	90.56	106.92	85.75
b	0.07237	0.1006	0.0853
c	0.409×10^{-3}	0.0	0.889×10^{-4}

Results and Discussion

The liquid-phase activity coefficient of a component in a highly nonideal mixture is related to the liquid- and vapor-phase mole fractions of the component at equilibrium conditions as follows:

$$\gamma_i = \frac{\phi_i \pi y_i}{x_i \phi_i^{s} P_i^{0} \exp[\bar{V}_i^{L}(\pi - P_i^{0})/(RT)]} \qquad (1)$$

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