experimental pressures and superimposed to the points as shown in Figure 2. The agreement appears quite satisfactory, which indicates the suitability of the obtained parameters for the prediction of equilibrium conditions over a fairly extended range of total pressures.

Glossary

A, B, C	parameters of Antoine equation for vapor pressure
d	parameters in eq 2
D	parameters in eq 3
H^E	heat of mixing, cal/mol
P	total pressure, mmHg
P°	vapor pressure, mmHg
R	gas constant, cal/(K mol)
t	temperature, °C
T	absolute temperature, K
v	molar volume, cm^3/mol
x	liquid mole fraction
y	vapor mole fraction

Greek

γ	activity coefficient
ν	fugacity coefficient

Subscripts

c	critical
i	index of component
k	index of parameter in eq 2 and 3
L	liquid phase
1	MEK
2	SBA

Literature Cited

(1) Amick, E. H., Weiss, M. A., Kirshenbaum, M. A., *Ind. Eng. Chem.*, **43**, 969 (1951).
(2) API Project 44, "Selected Values of Properties of Hydrocarbons and Related Compounds", Thermodynamic Research Center, Texas 1973.
(3) Hala, E., Pick, J., Fried, V., Vilim, O., "Vapor Liquid Equilibrium", Pergamon, Oxford, 1967.
(4) Miller, K. J., Huang, H. S., *J. Chem. Eng. Data*, **17**, 77 (1972).
(5) Perry, H. R., Chilton C. H., "Chemical Engineers' Handbook", 5th ed, McGraw-Hill, New York, N.Y., 1973.
(6) Prausnitz, J. M., "Computer Calculations for Multicomponent Vapor-Liquid Equilibria", Prentice-Hall, Englewood Cliffs, N.J., 1967.
(7) Sebastiani, E., Carli, A., Lacquaniti, L., *Ann. Chim.* (*Rome*), **60**, 45 (1970).
(8) Sunner, S., Wadso, S., *Sci. Tools*, **13**, 1 (1966).

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Activity Measurements in Aqueous Mixed Electrolyte Solutions. 1. Hydrochloric Acid–Quaternary Ammonium 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 $(CH_3)_4NCl$ and (ii) HCl and $(C_2H_5)_4NCl$, in different proportions, but at constant total ionic strength (μ = 3, 2, 1, 0.5, 0.2, 0.1). Measurements have been carried out at 10 °C intervals, over the temperature ranges 5–35 °C. The Ag|AgCl electrodes used, prepared by the thermoelectrolytic method, gave closely agreeing results. The values for the standard electrode potential E° and the interaction coefficient α_{12} for each constant total ionic strength mixture at all the four temperatures have been evaluated by the computerized least-squares method. Interpretation of the results has been made in the light of the recent work 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 recent spurt in this interest, attributable chiefly to the practical problem of desalination, has stimulated development of the underlying theory and also accumulation of precise experimental results.

The specific ionic interaction principle postulating the existence of short-range interactions among ions of unlike charge was enunciated by Bronsted (*2–4*) and was applied to dilute solutions by Guggenheim (*13–15*). Modifications were suggested for concentrated solutions by Scatchard (*46*, *47*). Pitzer and Brewer (*34*) used the Guggenheim equations with Scatchard modifications (*46*) (BSG theory) to give a simple and compact summary of experimental data. Scatchard et al. (*48*) have subsequently extended and elaborated the Guggenheim equations in several ways leading to very complex formulas for the osmotic and activity coefficients. On this basis Lietzke and Stoughton (*28*) have been able to represent accurately the osmotic coefficients of a number of pure electrolytes; also several systems of mixed electrolytes have been treated. Pitzer (*35*) has recently developed, in a general form, a system of equations for the thermodynamic properties of pure and also mixed electrolytes by using an "electrostatic term" plus a virial coefficient series in which the coefficients may be functions of the ionic strength of the solution. The observed osmotic coefficients of a large number of pure electrolytes of different valence types have been fitted (*36–38*) by using a three-parameter equation; also, a large number of binary electrolyte mixtures have been handled with a two-parameter equation. The work of Reilly, Wood, and Robinson (*41*, *42*) is directed primarily to the process of mixing of pure electrolytes. Finally, Friedman and collaborators (*10*, *11*) have made significant advances in the theory on the basis of rigorous statistical mechanical calculations.

Among the experimental methods for the measurement of the activity and osmotic coefficients in mixed electrolyte solutions, the emf measurement method and the isopiestic vapor pressure measurement have been used most widely. Cells without liquid junction of the type $Pt;H_2(g,\ 1\ atm)|HCl(m_1),MCl(m_2)|AgCl;Ag$

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(I) have found particular favor because the familiar hydrogen and silver-silver chloride electrodes can be used with easy determination of the activity coefficient of hydrochloric acid. For the other electrolyte, 1/1 alkali chlorides, e.g., LiCl (*16*, *25*), NaCl (*16*, *25*, *29*), KCl (*25*, *30*), RbCl (*30*), and CsCl (*16*, *30*), 2/1 alkaline earth chlorides, e.g., $BaCl_2$ (*8*, *19*), $SrCl_2$ (*8*, *19*, *30*), $CaCl_2$ (*6*, *30*, *49*), $MgCl_2$ (*30*, *50*, *51*), and $MnCl_2$ (*6*, *9*), and 3/1 metal chlorides, e.g., $AlCl_3$ (*20*), $LaCl_3$ (*40*), $GdCl_3$ (*31*), etc., have been used. Cation-sensitive glass electrodes have also been used for the study of mixed electrolyte solutions by the emf method (*12*, *27*).

From measurements at constant total ionic strength some simple empirical relationships have been discovered to hold in both dilute and concentrated solutions. It has been found, for the HCl-MCl mixture, for example, that the activity coefficient of the first component ($\log \gamma_1$) 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 molality but not of the mole fraction of the second component y_2 ($=m_2/m$). In many cases the simpler linear equation, the so called Harned rule

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

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 (*33*) and by Harned himself (*21*-*24*).

Among examples of the cases where the simple linear relation (2) has been found to be valid (up to definite concentrations), the following may be cited (*18*, *24*, *43*): (i) $\gamma_{\pm(HCl)}$ in mixtures of HCl with 1/1 electrolytes like LiCl, NaCl, and KCl and $NaClO_4$, $KClO_4$, and higher valent electrolytes like $BaCl_2$, $SrCl_2$, $AlCl_3$, $LaCl_3$, and $CeCl_3$; (ii) $\gamma_{\pm(MCl)}$ in mixtures of MCl and NCl with N given, for M = Na, as K or Cs; for M = K, as H or Cs; for M = Li, as H, etc. The following are among cases where the extended eq 1 is known to be necessary: (i) $\gamma_{\pm(MCl)}$ in MCl-NCl mixtures with N given, for M = Na, as H; (ii) $\gamma_{\pm(MOH)}$ and $\gamma_{\pm(MCl)}$ in MOH-MCl mixtures with M given as Na or K.

Scope of the Present Work

Quaternary ammonium salts have been the subject of research interest for quite some time now because of the information they yield regarding the problem of solute-solvent interactions. Measurements of activity coefficients of quaternary ammonium salts using cells with junction have been reported by Devanathan and Fernando (*7*) but the results were criticized (*52*) as having been vitiated due to spurious junction potentials. Lindenbaum and Boyd (*32*) have reported the osmotic and activity coefficient data for a large number of quaternary salts R_4NX (where R = CH_3, C_2H_5, C_3H_7, and C_4H_9; X = Cl, Br, and I) at different molalities by the gravimetric isopiestic method, at 25 °C only. Data for solutions containing mixtures of quaternary salts with hydrochloric acid obtained from cells without liquid junction, at a constant total molality of 0.1, have been reported by Downes (*8*) at four different temperatures. The results have been interpreted in terms of the specific interaction theory of Guggenheim and also the Harned empirical rule. However, in order to be able to decide between the applicability of either eq 1 or the simple Harned rule eq 2 in the case of either the acid or the salt component, one must have data for the variation of α_{12} with the total mixture molality. It was the object of the present research to investigate this point for mixtures of the quaternary salts [$(CH_3)_4NCl$ and $(C_2H_5)_4NCl$] with HCl.

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 which are available. It therefore appeared worthwhile to secure accurate experimental data regarding the temperature variation of the ionic interaction coefficients for the mixed system HCl-quaternary ammonium salts.

Experimental Section

Hydrochloric acid (AR), diluted to the azeotropic composition, was distilled, and only the middle fraction was retained for use. Tetramethylammonium chloride (Fluka) was dissolved in methanol, filtered hot, and then precipitated by dry ether (*5*). It was dried at 130 °C. Tetraethylammonium chloride (*8*) (Fluka) was similarly dissolved in chloroform and precipitated by dry ether (cooling in freezing mixture ensured nearly complete precipitation). This was dried under vacuum over concentrated sulfuric acid for 7 days. Stock solutions of the electrolytes (HCl, 1.9102 and 5.3643 M; $(CH_3)_4NCl$, 2.8320 M; $(C_2H_5)_4NCl$, 1.7015 and 5.9233 M) were prepared and their molalities determined by gravimetric chloride analysis. Triplicate analyses agreed within 0.01% for HCl, within about 0.14% for $(CH_3)_4NCl$, and within about 0.1% for $(C_2H_5)_4NCl$. No further characterization of the purity of the salts was made.

Four different HCl-$(CH_3)_4NCl$ mixtures in molal ratios (1:4, 2:3, 3:2, 4:1) having total ionic strength μ = 3.0 M were prepared by direct weighing from the stock solutions of known molality. In the case of tetraethylammonium chloride, five different HCl-$(C_2H_5)_4NCl$ mixtures in molal ratios (1:9, 3:7, 1:1, 7:3, 9:1) having total ionic strength μ = 3.0 M were prepared as above. The lower total ionic strength mixtures (μ = 2, 1, 0.5, 0.2, 0.1) were prepared in both cases by weight dilution, from mixtures of just higher ionic strengths.

The cells used for emf measurements were H-shaped all-glass vessels, with two connecting bridges between the two limbs (*44*). A (hydrogen) gas presaturator vessel containing the same solution as that in the electrode vessel was fixed alongside each. The leak-proof Pyrex-platinum joint for the electrodes was made by first spot welding the stout platinum wire (carrying the platinum coil for the Ag|AgCl electrodes, or else the platinum foil for the hydrogen electrode) to fine platinum wire 5 cm in length (0.15 mm), almost the entire length of which including the weld was then fused inside the glass of the Pyrex electrode tube, so that only the stout platinum electrode piece remained protruding below, while the top end of the connecting fine platinum wire remained exposed for mercury contact inside the top end of the electrode tube.

Ag|AgCl electrodes were prepared in batches of six to eight electrodes by the thermoelectrolytic method (*26*). The thoroughly washed electrodes were aged in deoxygenated (0.05 N) HCl for 48 h. The bias potentials were measured in oxygen-free dilute HCl solution with respect to an aged reference electrode; only those electrodes were retained for use for which the values were found to be less than 0.05 mV.

Measurements were carried out in a thermostat bath at 10 °C intervals, over the temperature range 5-35 °C, controlled to ±0.1 °C. An LN Type K2 potentiometer, in conjunction with an LN moving coil galvanometer of sensitivity 1 mm/m at 10^{-5} 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.

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 in any particular run; the flow in each could be conveniently controlled. With the barometric pressure having never been very different from the standard value during the time of the experiments and also the depth of the hydrogen gas inlet below the level of the solution in the vessel also having been very small (only a few millimeters), neither the "barometric pressure correction" nor the "depth correction" was deemed significant and hence was neglected.

For the higher total molality mixtures ($m = 3$, mostly), a whitish gray deposit was usually observed on the platinized platinum electrodes soon after the start of the experiment, leading to erratic functioning of the electrode. (The authors are grateful to Dr. R. N. Roy for a clarification of the nature of this effect, for his suggestion regarding the modified cell design (since adopted) to overcome this, and also for some other very fruitful discussions.) The modified cell design helped greatly in reducing this disturbing effect; also the platinum electrode was changed frequently.

Calculations

Tables I and II give respectively the experimental results for the emf of cell I containing mixtures of (1) HCl (m_1) and $(CH_3)_4NCl$ (m_2) and (2) HCl (m_1) and $(C_2H_5)_4NCl$ (m_2), at six different values of the total molality $m = m_1 + m_2$ in each case, each constant total molality comprising a number of different mole ratio mixtures. Data are recorded for four different temperatures in each case. The emf E of cell I is given by the equation

$$\begin{aligned} E &= E^\circ - \frac{RT}{F} \ln a_{H^+}a_{Cl^-} \\ &= E^\circ - K \log [m_1(m_1 + m_2)\gamma_1{}^2] \end{aligned} \qquad (4)$$

where m_1 and m_2 are the molalities of the acid and the tetraalkyl salt, respectively, $K = (2.303\ RT)/F$, and γ_1 is the mean ionic activity coefficient of hydrochloric acid. On introducing eq 2 into eq 4 one obtains

$$E + K \log m_1 = (E^\circ - K \log m - 2K \log \gamma_1{}^0) + 2K\alpha_{12}m_2 \qquad (5)$$

Values of $\gamma_1{}^0$ for pure HCl solutions of different molalities and at different temperatures have been taken from the literature (*17*) and are given in both Tables I and II. Computerized least-squares calculations were made for calculating E° and α_{12}; these values together with the standard deviations $\sigma(E)$ in E, and $\sigma(\alpha_{12})$ in α_{12}, are also given in Tables I and II.

From Tables I and II for the tetramethyl and tetraethyl salts, respectively, over the range $\mu = 0.1$ to $\mu = 3.0$ (comprising of six different constant total molality mixtures), the deviations of the E° values at the four different temperatures investigated from the corresponding literature values (*17*) are given in Table III (except for an occasional E° value in some of the sets showing some slightly more negative deviation).

The deviation of the E° values in any (constant temperature) set, from an average value for the set (which is generally a few tenths of a millivolt lower than the literature E° value for that temperature), is even lower (except for an occasional E° value in some sets, as mentioned). This is true for both the tetraalkyl salt mixtures. Considering the wide range of variation of the total mixture molality, and the modest range of temperature variation involved, this result may be considered satisfactory, though better constancy of E° has been reported (*44*) for the HCl-NH_4Cl mixture, albeit at one temperature only.

The standard electrode potential of the Ag|AgCl electrode at any temperature is not established to a precision better than 0.2 mV, and it was suggested (*1*) that "the uncertainty is most probably due to small differences in the solid phases.... In measurement of the highest precision each worker could advantageously determine the E° values of his own set of electrodes". We have used in our calculations the specific E° value determined for each electrode, for each set, by least-squares extrapolation as mentioned above, at all the four different working temperatures.

Discussion

The standard deviation in E as found by the computerized least-squares analysis is generally small (average values at the four different temperatures are, for the Me_4NCl salt, 0.15, 0.15, 0.16, and 0.18 mV and, for the Et_4NCl salt, 0.13, 0.17, 0.16, and 0.21 mV respectively), except, generally, for the higher total molality solutions, where the accuracy of the results is a trifle less certain, due to the experimental difficulty mentioned. Thus, within the experimental accuracy secured, it can be concluded that the Harned rule holds for the HCl component in the HCl–quaternary ammonium salt mixtures, over the temperature range studied.

In order to decide whether or not the same holds true for the tetraalkylammonium component in the above mixtures, we make use of Pitzer's treatment (*35–38*). For a mixture of two 1:1 electrolytes MX and NX, at a total molality m, Pitzer's eq 41 (*35*) is

$$\begin{aligned} \ln \gamma_1 = f^\gamma + {} & \\ & m[B_{MX}{}^\gamma + y_2(B_{NX}{}^\phi - B_{MX}{}^\phi + \theta_{MN}) + y_1y_2m\theta_{MN}{}'] + \\ & m^2[C_{MX}{}^\gamma + y_2(C_{NX}{}^\phi - C_{MX}{}^\phi + \tfrac{1}{2}\psi_{MNX}) + \tfrac{1}{2}y_1y_2\psi_{MNX}] \end{aligned} \qquad (6)$$

where the quantities 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 measures of binary and ternary interactions between the ions indicated by the subscripts.

***Analysis for the Case* $\psi_{MNX} = 0$.** In the analysis of their data for the HCl-NH_4Cl mixtures, Robinson, Roy, and Bates (*44*) have made use of Pitzer's contention, derived from the analysis of the experimental results for a large number of single and mixed electrolyte solutions, that the ternary interaction term ψ_{MNX} is generally very small and negligible, and also the concentration dependence of θ_{MN} is only very slight, if any at all. We assume provisionally the same to be true in the case of the present mixtures also. Further, making use of (i) the expression derived from eq 6 for the activity coefficient in solutions containing the first component only, viz., $\ln \gamma_1{}^0 = f^\gamma + mB_{MX}{}^\gamma + m^2C_{MX}{}^\gamma$, and (ii) the fact that the Harned rule is valid for the first component, so that $\ln (\gamma_1/\gamma_1{}^0) = -2.303\alpha_{12}y_2m$, the interaction coefficient α_{12} would be given by

$$-2.303\alpha_{12} = (B_{NX}{}^\phi - B_{MX}{}^\phi) + m(C_{NX}{}^\phi - C_{MX}{}^\phi) + \theta \qquad (7)$$

The interaction coefficient α_{12} is then seen to be the sum of two parts: the first, comprising of B and C terms, given by the properties of the pure electrolyte component 1; the second part consists of the much smaller θ term, characteristic of the mixture. The B quantities in the above equation have been expressed by Pitzer (*35*) in terms of certain β quantities; $B_{MX} = \beta_{MX}{}^0 + \beta_{MX}{}^1 \exp(-2m^{1/2})$, so that eq 7 becomes

$$\begin{aligned} \theta = -2.303\alpha_{12} + (\beta_{MX}{}^0 - \beta_{NX}{}^0) + {} & \\ & (\beta_{MX}{}^1 - \beta_{NX}{}^1)[\exp(-2m^{1/2})] + m(C_{MX}{}^\phi - C_{NX}{}^\phi) \end{aligned} \qquad (8)$$

$$\theta = -2.303\alpha_{12} + f(\phi^0) \qquad (9)$$

where the $f(\phi^0)$ term on the right-hand side is a function of the last six terms on the right of eq 8 which are all characteristic of the respective single electrolyte solutions.

Pitzer and Mayorga (*36*, *37*) have given the following values for the constants β^0, β^1, and C^ϕ for HCl, $(CH_3)_4NCl$, and $(C_2H_5)_4NCl$ at 25 °C: $\beta_{HCl}{}^0 = 0.1775$, $\beta_{Me_4NCl}{}^0 = 0.04305$, $\beta_{Et_4NCl}{}^0 = 0.06175$, $\beta_{HCl}{}^1 = 0.2945$, $\beta_{Me_4NCl}{}^1 = -0.0288$, $\beta_{Et_4NCl}{}^1 = -0.0988$, $C_{HCl}{}^\phi = 0.0008$, $C_{Me_4NCl}{}^\phi = 0.0078$, $C_{Et_4NCl}{}^\phi = 0.01051$;

Table I. Experimental Emf Data for the Cell Pt;H_2 |HCl(m_1),$(CH_3)_4NCl$(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

			5 °C		15 °C		25 °C		35 °C	
parameters	m_1	m_2	E, V	γ_{HCl}	E, V	γ_{HCl}	E, V	γ_{HCl}	E, V	γ_{HCl}
$m = 3.0 \pm 0.02$ mol kg^{-1}										
	2.9711	0.0	0.16449	1.439	0.15850	1.384	0.15201	1.325	0.14442	1.261
	2.3943	0.6059	0.18142	1.120	0.17535	1.093	0.16866	1.062	0.16081	1.026
	1.8011	1.1996	0.19950	0.8856	0.19372	0.8703	0.18727	0.8523	0.17972	0.8287
	1.2043	1.8211	0.22056	0.6950	0.21467	0.6951	0.20836	0.6885	0.20121	0.6733
γ_1^0			1.427		1.373		1.316		1.256	
E°, V			0.23411		0.22871		0.22240		0.21454	
$\sigma(E)$, V			0.00014		0.00021		0.00022		0.00022	
α_{12}			0.1714		0.1625		0.1546		0.1483	
$\sigma(\alpha_{12})$			0.0013		0.0015		0.0015		0.0021	
$m = 2.0 \pm 0.006$ mol kg^{-1}										
	2.0023	0.0	0.19732	1.078	0.19174	1.051	0.18562	1.018	0.17882	0.9829
	1.5991	0.4012	0.21095	0.9078	0.20576	0.8876	0.19920	0.8747	0.19238	0.8524
	1.1893	0.8078	0.22487	0.7880	0.21991	0.7746	0.21431	0.7565	0.20762	0.7424
	0.8005	1.2104	0.24190	0.6709	0.23683	0.6692	0.23130	0.6601	0.22479	0.6526
	0.3969	1.5934	0.26505	0.5908	0.26061	0.5917	0.25543	0.5891	0.24946	0.5854
γ_1^0			1.068		1.039		1.009		0.9755	
E°, V			0.23418		0.22870		0.22219		0.21477	
$\sigma(E)$, V			0.00030		0.00035		0.00034		0.00032	
α_{12}			0.1639		0.1560		0.1498		0.1421	
$\sigma(\alpha_{12})$			0.0054		0.0065		0.0034		0.0031	
$m = 1.0 \pm 0.004$ mol kg^{-1}										
	0.9995	0.0	0.24246	0.8391	0.23799	0.8266	0.23274	0.8135	0.22675	0.7988
	0.7969	0.2090	0.25166	0.7732	0.24745	0.7627	0.24252	0.7507	0.23663	0.7403
	0.6003	0.3998	0.26247	0.7130	0.25834	0.7077	0.25353	0.7001	0.24796	0.6910
	0.4003	0.6054	0.27539	0.6649	0.27159	0.6618	0.26707	0.6568	0.26160	0.6527
	0.1984	0.7967	0.29541	0.6253	0.29206	0.6258	0.28816	0.6221	0.28325	0.6199
γ_1^0			0.8363		0.8229		0.8090		0.7942	
E°, V			0.23403		0.22851		0.22211		0.21479	
$\sigma(E)$, V			0.00024		0.00024		0.00024		0.00029	
α_{12}			0.1623		0.1535		0.1472		0.1392	
$\sigma(\alpha_{12})$			0.0055		0.0048		0.0046		0.0054	
$m = 0.5 \pm 0.002$ mol kg^{-1}										
	0.5008	0.0	0.27865	0.7751	0.27537	0.7657	0.27154	0.7558	0.26648	0.7468
	0.4001	0.1050	0.28663	0.7310	0.28319	0.7287	0.27926	0.7245	0.27444	0.7161
	0.1997	0.3020							0.29651	0.6710
	0.0988	0.3967	0.32602	0.6528	0.32390	0.6520	0.32102	0.6528	0.31727	0.6493
γ_1^0			0.7730		0.7658		0.7571		0.7477	
E°, V			0.23329		0.22778		0.22163		0.21425	
$\sigma(E)$, V			0.00013		0.00003		0.00004		0.00009	
α_{12}			0.1913		0.1812		0.1667		0.1571	
$\sigma(\alpha_{12})$			0.0109		0.0020		0.0030		0.0023	
$m = 0.2 \pm 0.001$ mol kg^{-1}										
	0.1987	0.0	0.32320	0.7789	0.32113	0.7751	0.31850	0.7687		
	0.1601	0.0420	0.32944	0.7554	0.32754	0.7525	0.32485	0.7504	0.32154	0.7454
	0.1200	0.0799					0.33335	0.7390	0.33016	0.7363
	0.0799	0.1209	0.34799	0.7285	0.34666	0.7272	0.34452	0.7268	0.34158	0.7258
	0.0397	0.1594	0.36546	0.7211	0.36466	0.7212				
γ_1^0			0.7756		0.7717		0.7667		0.7604	
E°, V			0.23379		0.22826		0.22198		0.21486	
$\sigma(E)$, V			0.00007		0.00009		0.00009		0.00009	
α_{12}			0.2101		0.1970		0.1885		0.1644	
$\sigma(\alpha_{12})$			0.0061		0.0069		0.0127		0.0105	
$m = 0.1 \pm 0.001$ mol kg^{-1}										
	0.0998	0.0	0.35461	0.8029	0.35369	0.8011	0.35191	0.7986	0.34917	0.7944
	0.0800	0.0210	0.36039	0.7902	0.35970	0.7881	0.35826	0.7837	0.35577	0.7790
	0.0401	0.0607	0.37796	0.7737	0.37776	0.7737	0.37667	0.7736	0.37469	0.7705
γ_1^0			0.8023		0.8000		0.7964		0.7918	
E°, V			0.23362		0.22823		0.22194		0.21456	
$\sigma(E)$, V			0.00002		0.00001		0.00008		0.00010	
α_{12}			0.2295		0.2105		0.1852		0.1740	
$\sigma(\alpha_{12})$			0.0074		0.0023		0.0291		0.0378	

so that the "f" functions for the methyl and ethyl salt at 25 °C are respectively

$$f'(\phi^0) = 0.13445 + 0.3233 \exp(-2m^{1/2}) - 0.00701$$

$$f''(\phi^0) = 0.11575 + 0.3933 \exp(-2m^{1/2}) - 0.00971$$

The values of $f(\phi^0)$, together with those of θ (apparent) obtained by combining $f(\phi^0)$ with $2.303\alpha_{12}$ (eq 9), for the HCl–tetramethyl salt and HCl–tetraethyl salt, respectively, at 25 °C, are given in Table IV (supplementary material). The values of the Pitzer parameters for the pure electrolytes considered are presently not available at the other experimental temperatures. We therefore have to restrict the discussion of our results in terms of Pitzer equations to the data for 25 °C only. (We are grateful

Table II. Experimental Emf Data for the Cell Pt;H_2 |HCl(m_1),$(C_2H_5)_4NCl$(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

			5 °C		15 °C		25 °C		35 °C	
parameters	m_1	m_2	E, V	γ_{HCl}	E, V	γ_{HCl}	E, V	γ_{HCl}	E, V	γ_{HCl}
$m = 3.0 \pm 0.003$ mol kg^{-1}										
	2.7009	0.2997	0.17299	1.246	0.16715	1.206	0.16064	1.161	0.15339	1.122
	2.0851	0.9129	0.19268	0.9408	0.18702	0.9203	0.18065	0.8958	0.17351	0.8746
	1.4996	1.4953	0.21316	0.7239	0.20764	0.7168	0.20153	0.7039	0.19366	0.7060
γ_1^0			1.427		1.373		1.316		1.256	
E°, V			0.23367		0.22840		0.22207		0.21505	
$\sigma(E)$, V			0.00006		0.00008		0.00007		0.00029	
α_{12}			0.1976		0.1894		0.1823		0.1687	
$\sigma(\alpha_{12})$			0.0008		0.0011		0.0009		0.0038	
$m = 2.0 \pm 0.008$ mol kg^{-1}										
	1.7895	0.1985	0.20456	0.9898	0.19846	0.9652	0.19247	0.9398	0.18582	0.9119
	1.0048	1.0019	0.23420	0.7084	0.22921	0.6901	0.22360	0.6810	0.21730	0.6695
	0.5993	1.3974	0.25394	0.6092	0.24924	0.5985	0.24410	0.5932	0.23808	0.5876
γ_1^0			1.068		1.039		1.009		0.9755	
E°, V			0.23448		0.22821		0.22188		0.21461	
$\sigma(E)$, V			0.00013		0.00027		0.00025		0.00028	
α_{12}			0.1756		0.1733		0.1667		0.1593	
$\sigma(\alpha_{12})$			0.0019		0.0038		0.0033		0.0036	
$m = 1.0 \pm 0.002$ mol kg^{-1}										
	0.8968	0.0995	0.24672	0.8094	0.24239	0.7974	0.23748	0.7862	0.23159	0.7740
	0.6949	0.3043	0.25716	0.7384	0.25298	0.7308	0.24814	0.7247	0.24255	0.7143
	0.4997	0.4983	0.26842	0.6889	0.26441	0.6850	0.25991	0.6800	0.25448	0.6732
	0.2997	0.6988	0.28440	0.6372	0.28086	0.6349	0.27661	0.6343	0.27149	0.6309
	0.1001	0.9003	0.31442	0.5888	0.31178	0.5888	0.30822	0.5926	0.30400	0.5912
γ_1^0			0.8363		0.8229		0.8090		0.7942	
E°, V			0.23389		0.22835		0.22223		0.21500	
$\sigma(E)$, V			0.00016		0.00016		0.00015		0.00020	
α_{12}			0.1698		0.1617		0.1512		0.1434	
$\sigma(\alpha_{12})$			0.0092		0.0080		0.0086		0.0110	
$m = 0.5 \pm 0.002$ mol kg^{-1}										
	0.4490	0.0498	0.28263	0.7593	0.27928	0.7507	0.27531	0.7430	0.27026	0.7360
	0.3473	0.1521	0.29073	0.7287	0.28754	0.7223	0.28375	0.7164	0.27914	0.7076
	0.2506	0.2499	0.30094	0.6926	0.29725	0.6986	0.29365	0.6948	0.28929	0.6873
	0.1513	0.3527	0.31490	0.6638	0.31246	0.6595	0.30923	0.6580	0.30522	0.6530
	0.0498	0.4498	0.34310	0.6453	0.34145	0.6440	0.33919	0.6430	0.33604	0.6399
γ_1^0			0.7730		0.7658		0.7571		0.7477	
E°, V			0.23358		0.22790		0.22161		0.21426	
$\sigma(E)$, V			0.00019		0.00023		0.00022		0.00021	
α_{12}			0.1791		0.1699		0.1597		0.1537	
$\sigma(\alpha_{12})$			0.0090		0.0090		0.0090		0.0064	
$m = 0.2 \pm 0.001$ mol kg^{-1}										
	0.1800	0.0200	0.32605	0.7690	0.32410	0.7651	0.32138	0.7607	0.31781	0.7561
	0.1390	0.0609	0.33297	0.7575	0.33116	0.7554	0.32862	0.7520	0.32540	0.7460
	0.0999	0.0996	0.34147	0.7490	0.33990	0.7478	0.33763	0.7449	0.33461	0.7404
	0.0603	0.1407	0.35455	0.7307	0.35346	0.7295	0.35156	0.7281	0.34880	0.7265
γ_1^0			0.7756		0.7717		0.7667		0.7604	
E°, V			0.23379		0.22827		0.22193		0.21470	
$\sigma(E)$, V			0.00009		0.00011		0.00011		0.00007	
α_{12}			0.1700		0.1578		0.1445		0.1301	
$\sigma(\alpha_{12})$			0.0119		0.0180		0.0168		0.0068	
$m = 0.1 \pm 0.0002$ mol kg^{-1}										
	0.0899	0.0100	0.35716	0.7955	0.35619	0.7935	0.35454	0.7903	0.35199	0.7864
	0.0695	0.0304	0.36370	0.7898	0.36293	0.7883	0.36146	0.7860	0.35917	0.7818
	0.0500	0.0499	0.37180	0.7860	0.37126	0.7855	0.37005	0.7837	0.36800	0.7801
	0.0302	0.0704	0.38451	0.7740	0.38435	0.7748	0.38354	0.7738	0.38185	0.7716
	0.0100	0.0900	0.41194	0.7604	0.41280	0.7606	0.41291	0.7606	0.41221	0.7584
γ_1^0			0.8023		0.8000		0.7964		0.7918	
E°, V			0.23328		0.22773		0.22141		0.21414	
$\sigma(E)$, V			0.00021		0.00024		0.00024		0.00024	
α_{12}			0.2310		0.2127		0.1919		0.1774	
$\sigma(\alpha_{12})$			0.0715		0.0744		0.0735		0.0651	

to Professor K. S. Pitzer for this suggestion.)

In order to assess if θ can actually be considered to be total molality independent, as was assumed earlier, it is necessary to see how far an assumed constant value of θ successfully reproduces the value of the interaction coefficient α_{12}. The simple ("unweighted") average θ values for the two salts at 25 °C, at all the different constant total molalities are recorded in

Table III

quaternary ammonium salt	5 °C	15 °C	25 °C	35 °C
ΔE°, mV				
HCl-$(CH_3)_4NCl$	±0.4	±0.3	−0.5	−1.2
HCl-$(C_2H_5)_4NCl$	±0.4	±0.3	−0.6	−1.1
E°, V (lit. values)				
	0.2340	0.2285	0.2224	0.2157

Table IV. Using these average θ (apparent) values, the α_{12} values for the different constant total molality sets at 25 °C have been calculated (eq 7) and compared with the corresponding observed values as obtained from Tables I and II [$\Delta\alpha_{12} = \alpha_{12(\text{exptl})} - \alpha_{12(\text{theor})}$] in Tables V and VI, for the two tetraalkyl salts, respectively (supplementary material).

However, since the emf of the cell I is a measure of θm rather than θ, Pitzer suggests (*44*) that the weighted average of the θ values, each being weighted in proportion to the corresponding total molality, should be taken rather than the unweighted average. For this type of weighted averaging, it is imperative here to leave out in each case the θ value for the highest total molality mixture (m = 3.0 M), because it generally always shows the largest deviation (due possibly to the experimental difficulty mentioned) and therefore would otherwise weight the result (disproportionately) erroneously. Again, the error in the computation of α_{12} is proportional to $1/m$, and hence its evaluation at the lowest molalities may not be of a high enough order of accuracy to yield accurate values of θ (*18*, *44*). For this reason the θ values for the lowest total molality mixture (m = 0.1 M) have also been left out. The average of the θ values for the remaining mixtures (four minimally), which still spans a fairly large concentration range (m = 0.2–2.0 M), then gives the (weighted) average θ (apparent) values for the two salts at 25 °C, which are also recorded in the Table IV. These (weighted) average θ values have also been used to calculate the α_{12} value for each particular mixture, which are also recorded in Tables V and VI.

Table IV shows that the "unweighted" average is closer to the general run of θ values than is the corresponding "weighted" average. α_{12} calculated using the former should therefore agree somewhat better with the $\alpha_{12(\text{exptl})}$ values, than would those calculated using the latter. We are grateful to the first referee for the suggestion that all data be considered in taking averages; this has improved (though marginally) the agreement between $\alpha_{12(\text{calcd})}$ and $\alpha_{12(\text{exptl})}$, in the case of the "unweighted" average. In the case of the weighted average, however, the same suggestion has not been followed, because of the reason mentioned.

If Harned's rule applies also to the activity coefficient of the quaternary ammonium chloride, i.e., $\log \gamma_2 = \log \gamma_2{}^0 - \alpha_{21}m_1$, then an equation similar to eq 7 holds for α_{21} also

$$-2.303\alpha_{21} = (B_{\text{MX}}{}^{\phi} - B_{\text{NX}}{}^{\phi}) + m(C_{\text{MX}}{}^{\phi} - C_{\text{NX}}{}^{\phi}) + \theta \qquad (10)$$

Values of α_{21} for the two systems calculated by using the (unweighted and weighted) average θ (apparent) values at 25 °C are also included in Tables V and VI, respectively.

Finally, the excess Gibbs energy of mixing is given by

$$\Delta G^{\text{E}} = -2.303 y_1 y_2 RTm^2(\alpha_{12} + \alpha_{21}) = 2y_1y_2RTm^2\theta \qquad (11)$$

The values of ΔG^{E} at $y_1 = y_2 = 0.5$, for the two systems at 25 °C, calculated by using the (unweighted) average θ values listed in Table IV, are included in the same table.

Analysis for the Case $\psi_{\text{MNX}} \neq 0$**.** The above analysis using the Pitzer equation (6) with $\psi = 0$ and $\theta' = 0$ and the subsequent calculation of the Harned coefficient α_{21} for the quaternary ammonium component, using a suitably averaged value of θ, gives no clue as to whether or not the higher coefficient β_{21} for the second component can also be considered zero (referee's remark). A glance at Table IV shows a definite tendency of the θ values for both the mixed electrolyte systems to decrease systematically with the total mixture molality m (*39*). It is interesting to explore how far this can be attributed to the neglect of the ternary interaction term.

Table VII. Evaluation of the Average Values of the Parameters θ (actual) and ψ of Eq 12 (by Least-Squaring All the Total Molality Sets Together) for the Systems HCl–$(CH_3)_4NCl$ and HCl–$(C_2H_5)_4NCl$ at 25 °C

tetramethylammonium chloride			tetraethylammonium chloride		
$-\theta$	$-\psi$	σ	$-\theta$	$-\psi$	σ
0.1671	0.0271	0.011	0.1104	0.0846	0.034

We therefore analyzed the results afresh without putting $\psi = 0$, although we assume as before that $\theta' = 0$. Assuming that the experimentally determined γ_{MX} values, calculated from the measured cell emf by means of the usual equation $\ln \gamma_{\text{MX}} = [E^{\circ} - E - (RT/F) \ln m_1(m_1 + m_2)]/(2RT/F)$, using the tabulated E° values, would be reproduced by the complete eq 6 above, for a proper choice of the parameters θ and ψ, one obtains easily

$$\Delta \ln \gamma_{\text{MX}} \equiv \ln \gamma_{\text{MX(exptl)}} - \ln \gamma_{\text{MX(theor, } \theta = \psi = 0)} \equiv \ln \frac{\gamma_{\text{MX(exptl)}}}{\gamma_{\text{MX}}{}^0} - f(\phi^0) = m_2[\theta_{\text{MN}} + 1/2(m + m_1)\psi_{\text{MNX}}] \qquad (12)$$

The values of the binary and ternary interaction coefficients θ (actual) and ψ as calculated by the computerized least-squares handling of eq 12 above, using the experimental activity coefficient values for the HCl component in the HCl–Me_4NCl and HCl–Et_4NCl mixtures at 25 °C are given in Table VII. The results for both salts were first plotted on a suitable scale so as to be able to obtain a more realistic overall assessment, and thus justifiably neglect (if need be) one or more sets of data which show greater scatter or appear to go contrary to the trend otherwise. In the results presented, we have on this basis neglected the results for the 4:1 mixtures in the 0.5, 0.2, and 0.1 M sets for HCl–Me_4NCl and the 1:1 mixtures in the 0.2 and 0.1 M sets for HCl–Et_4NCl.

Using these θ (actual) values the values of the Harned coefficients α_{12} and α_{21} can be calculated afresh using again eq 7 and 10, respectively. These are also listed in Tables V and VI for the methyl and ethyl salt, respectively, at 25 °C.

Also given in Table VII are the values of σ (standard deviation of $(1/m_2)\ \Delta \ln \gamma_{\text{HCl}}$, using the θ and ψ values obtained). The smallness of the standard deviation σ for appropriate θ and ψ is gratifying.

There is an alternative possible method of least-squares analysis of the data according to eq 12, namely, piecemeal least squaring, separately for each "constant total molality set", followed by "weighted" or "unweighted" averaging over the θ and ψ values obtained. We have analyzed the results for both salts by this method also (after neglecting one or two sets of data for each salt on the basis mentioned) and find that the "unweighted" average of the θ and ψ values obtained for solutions of total molality ≥0.5 M are roughly comparable with those obtained by the first method, whereas the corresponding "weighted" averages are markedly different. Solutions of lower total molality lead to progressively higher (and ultimately, almost inadmissible) values of the negative slope. These incongruities of the lower "constant total molality sets" are naturally present also in the case of the first method of least-squares analysis; however, there these get swamped out because data for all different "constant total molality sets" are least squared together. A similar observation regarding the marked departure of the $(\Delta \ln \gamma_1)/m_2$ values, for low values of $^1/_2(m + m_1)$ from the corresponding linear plot for higher $^1/_2(m + m_1)$ values, has been made by Roy et al. (*45*) for the system HBr–Pr_4NBr at 25 °C and has been ignored on the grounds that $\Delta \ln \gamma_1$ is very small in the lower total molality range.

Whereas the analysis for the case $\psi = 0$ (eq 9, above) should lead to θ (apparent) values capable of reproducing, according to Pitzer, the different (constant) Harned slopes α_{12} for the variation of $\log \gamma_1$ at different constant total molalities, the analysis for the case $\psi \neq 0$ (eq 12) should lead to θ (actual) and ψ values capable of reproducing the individual γ_1 values for different compositions at the same (constant) (and also different) total molalities. The extent to which eq 12 or an analogous eq 13 for the second component is successful in doing

$$-2.303\alpha_{21} = f(\phi^0) + \theta + \tfrac{1}{2}(m + m_2) \qquad (13)$$

this is measured by the magnitude of the standard deviation σ of Table VII. Further, the magnitude of the parameter ψ as found for any particular electrolyte in a binary mixture measures how far the more elaborate eq 12 is necessary for reproducing the observed γ values for the electrolyte component showing deviations from Harned rule behavior (eq 9) in mixtures, in contrast to the Harned rule obeying component, whose behavior is adequately described by eq 9 (for which $\psi = 0$). (See first referee's remark at beginning of section.)

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Literature Cited

(1) Bates, R. G., Guggenheim, E. A., Harned, H. S., Ives, D. J. G., Janz, G. J., Monk, C. B., Prue, J. E., Robinson, R. A., Stokes, R. H., Wynne-Jones, W. F. K., *J. Chem. Phys.*, **25**, 361 (1956).
(2) Bronsted, J. N., *K. Dan. Vidensk. Selsk., Mat.-Fys. Medd.*, **4**(4) (1921).
(3) Bronsted, J. N., *J. Am. Chem. Soc.*, **44**, 877 (1922).
(4) Bronsted, J. N., *J. Am. Chem. Soc.*, **45**, 2898 (1923).
(5) Conway, B. E., Verral, R. E., Desnoyers, J. E., *Trans. Faraday Soc.*, **62**, 2738 (1966).
(6) Covington, A. K., *J. Chem. Soc.*, 4906 (1965).
(7) Devanathan, M. A. V., Fernando, M. J., *Trans. Faraday Soc.*, **58**, 784 (1962).
(8) Downes, C. J., *J. Phys. Chem.* **74**, 2153 (1970).
(9) Downes, C. J., *J. Chem. Soc., Faraday Trans.*, **68**, 1964 (1972).
(10) Friedman, H. L., Ramanathan, P. S., *J. Phys. Chem.*, **74**, 3756 (1970).
(11) Friedman, H. L., Krishnan, C. V., *J. Phys. Chem.*, **78**, 1927 (1974).
(12) Gieskes, J. M. T. M., *Z. Phys. Chem. (Frankfurt am Main)*, **50**, 78 (1966).
(13) Guggenheim, E. A., *Philos. Mag.*, **19**, 588 (1935).
(14) Guggenheim, E. A., Turgeon, J. C., *Trans. Faraday Soc.*, **51**, 747 (1955).
(15) Guggenheim, E. A., "Application of Statistical Mechanics", Clarendon Press, Oxford, England, 1966, pp 166–170.
(16) Guntelberg, E., *Z. Phys. Chem., Abt. A*, **123**, 199 (1926).
(17) Harned, H. S., Owen, B. B., "The Physical Chemistry of Electrolyte Solutions", 3rd ed, Reinhold, New York, N.Y., 1958, pp 456, 716.
(18) Harned, H. S., Owen, B. B., "The Physical Chemistry of Electrolyte Solutions", 3rd ed, Reinhold, New York, N.Y., 1958, pp 595, 608.
(19) Harned, H. S., Geary, C. C., *J. Am. Chem. Soc.*, **59**, 2032 (1937).
(20) Harned, H. S., Mason, C. M., *J. Am. Chem. Soc.*, **53**, 3377 (1931).
(21) Harned, H. S., *J. Phys. Chem.*, **63**, 1299 (1954).
(22) Harned, H. S., *J. Phys. Chem.*, **64**, 112 (1960).
(23) Harned, H. S., *J. Phys. Chem.*, **67**, 1739 (1963).
(24) Harned, H. S., Robinson, R. A., "Multicomponent Electrolyte Solutions", Pergamon, Oxford, England, 1968, p 438.
(25) Hawkins, J. E., *J. Am. Chem. Soc.*, **54**, 4480 (1932).
(26) Ives, D. J. G., Janz, G. J., "Reference Electrodes", Academic Press, New York, N.Y., 1961, p 209.
(27) Lanier, R. D., *J. Phys. Chem.*, **69**, 3992 (1965).
(28) Lietzke, M. H., Stoughton, R. W., *J. Phys. Chem.*, **66**, 508 (1962).
(29) Lietzke, M. H., *J. Phys. Chem.*, **69**, 2395 (1965).
(30) Lietzke, M. H., *J. Phys. Chem.*, **72**, 4408 (1968).
(31) Lietzke, M. H., *J. Phys. Chem.*, **72**, 257 (1968).
(32) Lindenbaum, S., Boyd, G. E., *J. Phys. Chem.*, **68**, 911 (1964).
(33) McKay, H A., *Trans. Faraday Soc.*, **51**, 903 (1955).
(34) Pitzer, K. S., Brewer, L., "Thermodynamics", 2nd ed, G. N. Lewis and M. Randal, Ed., Kogakusha, Tokyo, 1961, p 569.
(35) Pitzer, K. S., *J. Phys. Chem.*, **77**, 268 (1973).
(36) Pitzer, K. S., Mayorga, G., *J. Phys. Chem.*, **77**, 2300 (1973).
(37) Pitzer, K. S., Mayorga, G., *J. Phys. Chem.*, **78**, 2698 (1974).
(38) Pitzer, K. S., Kim, J. J., *J. Am. Chem. Soc.*, **96**, 5701 (1974).
(39) Pitzer, K. S., *J. Solution Chem.*, **4**, 249 (1975).
(40) Randall, M., Breckenridge, G. D., *J. Am. Chem. Soc.*, **49**, 1435 (1927).
(41) Reilly, P. J., Wood, R. H., *J. Phys. Chem.*, **73**, 4292 (1969).
(42) Reilly, P. J., Wood, R. H., Robinson, R. A., *J. Phys. Chem.*, **75**, 1305 (1971).
(43) Robinson, R. A., Stokes, R. H., "Electrolyte Solutions", 2nd ed, Butterworths, London, 1959, p 50.
(44) Robinson, R. A., Roy, R. N., Bates, R. G., *J. Solution Chem.*, **3**, 837 (1974).
(45) Roy, R. N., Gibbons, J. J., Snelling, R., Moeller, J., White, T., *J. Phys. Chem.*, **81**, 391 (1977).
(46) Scatchard, G., *Chem. Rev.*, **19**, 309 (1936).
(47) Scatchard, G., in "The Structure of Electrolytic Solutions", W. J. Hamer, Ed., Wiley, New York, N.Y., 1959, p 9.
(48) Scatchard, G., Rush, R. M., Johnson, J. S., *J. Phys. Chem.*, **74**, 3786 (1970).
(49) Sengupta, M., Mukherjee, A., communicated for publication.
(50) Sengupta, M., Mahapatra, P., Proceedings of the 14th Seminar on Electrochemistry, CECRI, Karaikudi, India, Nov 1973, p 290.
(51) Smith, R. F., Ph.D. Thesis, University of Otago, 1962, cited in ref 8.
(52) Stokes, R. H., *Trans. Faraday Soc.*, **59**, 761 (1963).

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Supplementary Material Available: Table IV, concerning the evaluation of $f(\phi^0)$, θ, and ΔG^E, and Tables V and VI, containing the values of α_{12} and α_{21} for the systems HCl–$(CH_3)_4NCl$ and HCl–$(C_2H_5)_4NCl$ at 25 °C (2 pages). Ordering information is given on any current masthead page.

Vapor–Liquid Equilibria of the Ternary System Chloroform–Methanol–Benzene

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New data of the vapor–liquid equilibria of the system chloroform–methanol–benzene were obtained at 760 mmHg. The activity coefficients were satisfactorily correlated according to the Redlich–Kister equation and could be predicted by considering only the binary data. Boiling points of the ternary mixture were predicted by an empirical correlation with a mean error of ±1.12%. The system probably exhibits azeotropic behavior.

Table I. Physical Constants of Compounds at 25 °C

Compound	Density	Refractive index
Chloroform	1.485	1.440
	1.480[a]	1.443[a]
Methanol	0.791	1.360
	0.787[b]	1.326[b]
Benzene	0.880	1.497
	0.874[a]	1.498[a]

[a] Reference 4. [b] Reference 5.

Introduction

This ternary system for which no vapor equilibrium data are available was chosen for two reasons: (a) to confirm whether the ternary system exhibits an azeotrope, as the binary chloroform–methanol and the methanol–benzene form a minimum boiling point azeotrope, and (b) to examine whether ternary