Activity Coefficients in Aqueous Mixtures of Hydrochloric Acid with "Tris" Hydrochloride or *t*-Butylammonium Chloride at 25°C

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Electromotive force measurements of cells containing mixtures of hydrochloric acid with tris(hydroxymethyl)aminomethane hydrochloride (Tris·HCl) or *t*-butylammonium chloride are made at 25°C and ionic strengths from 0.1 to 1.0 mol kg^{-1}. The results are considered in terms of Harned's rule for the variation of activity coefficients in mixtures of electrolytes. The added salts have much the same effect on the activity coefficient of HCl at constant ionic strength as does ammonium chloride.

As part of an investigation of acid-base behavior in seawater, we are studying the properties of common buffer substances in mixed electrolyte solutions. We report here measurements of the activity coefficients of hydrochloric acid in mixture with the chlorides of the protonated bases tris(hydroxymethyl)aminomethane ("Tris") and *t*-butylamine at ionic strengths 0.1, 0.5, and 1.0 mol kg^{-1}. The activity coefficients were derived from the emf of cells of the type

$$\mathrm{Pt;H_2(g,\ 1\ atm)\,|\,HCl}(m_1),\ \mathrm{MCl}(m_2)\,|\,\mathrm{Ag;AgCl} \qquad \text{(A)}$$

where *m* represents molality. An attempt is made to infer the behavior of the salts in mixed electrolyte solutions from their influence on the activity coefficient of hydrochloric acid.

The emf (E) of cell A is related to the solution composition by

$$E = E^{\circ} - \frac{RT \ln 10}{F} \log m_{\mathrm{H}} m_{\mathrm{Cl}} \gamma_{\mathrm{HCl}}^{2} \qquad (1)$$

where E° is the standard emf, and γ is the activity coefficient on the scale of molality. The values of $\log \gamma_{\mathrm{HCl}}$ obtained from the cell measurements were fitted to the familiar Harned expression (6)

$$\log \gamma_{\mathrm{HCl}} = \log \overset{\circ}{\gamma}_{\mathrm{HCl}} - \alpha_1 m_2 - \beta_1 m_2^2 \qquad (2)$$

where $\overset{\circ}{\gamma}_{\mathrm{HCl}}$ represents the activity coefficient of hydrochloric acid alone at the ionic strength of the mixture. The Harned coefficients α and β are specific to the mixture at a given temperature and ionic strength and are a measure of the effect of MCl on γ_{HCl}. The term in m_2^2 usually makes an insignificant contribution to $\log \gamma_{\mathrm{HCl}}$.

Experimental

Hydrochloric acid was distilled twice and standardized as chloride by gravimetric AgCl analysis. Tris hydrochloride of reagent grade was obtained from Sigma Chemical Co. It was recrystallized twice from aqueous ethanol acidified with hydrochloric acid and was dried in vacuum at 70°C. The pH of a 0.1*M* solution was 4.65, as compared with 4.83 for the unrecrystallized salt; the calculated pH is about 4.6. Some of the solutions were also prepared from hydrochloric acid and recrystallized Tris base, and the results agreed well within the sizable experimental error that can attend the preparation of solutions from acid and base. Tertiary butylammonium chloride (*t*B·HCl) was prepared from distilled hydrochloric acid and the freshly distilled amine. The solid was recrystallized twice from methanol-acetone and dried in vacuum at 90°C. Solutions were prepared from the dried salts.

Details of the electrode preparation, cell design, and experimental procedures paralleled those already described elsewhere (*10*). The standard emf (E°) for cell A was determined from measurements on 0.01*m* HCl (*1*) and was 0.22243 *V* at 25°C.

Results and Discussion

Table I contains the emf data for cell A with the system HCl–Tris·HCl at 25°C and ionic strengths 0.1, 0.5, and 1.0 mol kg^{-1}. Similar data for the system HCl–*t*B·HCl are given in Table II. The best fit parameters and standard deviations obtained when Equation 2 was applied to the activity coefficients derived by Equation 1 are listed in Table III.

An inspection of the values of α_1 collected in Table IV shows that the systems studied here do not differ greatly from the system HCl–NH_4Cl for which data are already available (*3*, *10*). This means that the cations Tris·H$^+$, *t*B·H$^+$, and NH_4^+ have comparable effects on the activity coefficient of hydrochloric acid and presumably that the activity coefficients of the three chloride salts are not greatly different. This is not too surprising in view of the structural similarities of the ions $(CH_2OH)_3C{-}NH_3^+$ and $(CH_3)_3C{-}NH_3^+$ to the parent ammonium ion.

Considering the results at an ionic strength *I* of 0.1, one can focus on the activity coefficients of the single electrolytes by making use of the Brønsted-Guggenheim concept (*4*) of

Table I. Electromotive Force of Cell A for Hydrochloric Acid–Tris Hydrochloride Solutions at 25°C

$I = 0.1$		$I = 0.5$		$I = 1.0$	
m_{HCl}	E, V	m_{HCl}	E, V	m_{HCl}	E, V
0.01	0.41254	0.05	0.33556	0.10	0.29992
0.02	0.39466	0.10	0.31728	0.20	0.28132
0.04	0.37663	0.20	0.29861	0.40	0.26186
0.06	0.36600	0.30	0.28729	0.60	0.24982
0.08	0.35842	0.40	0.27902	0.80	0.24072
0.10	0.35248	0.50	0.27234	1.0	0.23322

Table II. Electromotive Force of Cell A for Hydrochloric Acid–*t*-Butylamine Hydrochloride Solutions at 25° C

$I = 0.1$		$I = 0.5$		$I = 1.0$	
m_{HCl}	E, V	m_{HCl}	E, V	m_{HCl}	E, V
0.01	0.41272	0.05	0.33629	0.10	0.30166
0.02	0.39479	0.10	0.31793	0.20	0.28288
0.04	0.37677	0.20	0.29909	0.40	0.26310
0.06	0.36608	0.30	0.28761	0.60	0.25065
0.08	0.35845	0.40	0.27917	0.80	0.24113
0.10	0.35248	0.50	0.37234	1.0	0.23322

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Table III. Variation of Activity Coefficient of Hydrochloric Acid with Composition of Acid–Salt Mixture. Constants of Equation 2

Ionic strength	$-\log \gamma^{\circ}_{HCl}$ [a]	α_1 [a]	β_1	$10^7 \Sigma \Delta^2$ [b]
		HCl–tris hydrochloride		
0.1	0.09917 ± 0.00008	0.0859 ± 0.0013	0	0.42
0.5	0.12102 ± 0.00014	0.0758 ± 0.0005	0	1.41
1.0	0.09175 ± 0.00035	0.0706 ± 0.0006	0	8.67
	0.09126	0.0748	−0.0045	1.45
		HCl–*t*-butylamine hydrochloride		
0.1	0.09917 ± 0.00008	0.1022 ± 0.0014	0	0.51
0.5	0.12097 ± 0.00011	0.0896 ± 0.0004	0	0.85
1.0	0.09185 ± 0.0005	0.0870 ± 0.0009	0	20.86
	0.09119	0.0938	−0.0074	0.13

[a] The assigned uncertainties are standard deviations. [b] $\Delta = \log \gamma_{exp} - \log \gamma_{calc}$.

Table IV. Harned Coefficients α_1 for Activity Coefficient of Hydrochloric Acid in HCl–MCl Solutions

	α_1 at		
M^+	$I = 0.1$	$I = 0.5$	$I = 1.0$
NH_4^+	0.090 ± 0.002 (*10*)	0.072 ± 0.002 (*10*)	0.0693 ± 0.0006 (*10*)
	0.084 ± 0.003 (*3*)	0.070 ± 0.0005 (*3*)	0.068 ± 0.0005 (*3*)
Tris·H+	0.086 ± 0.0013	0.0758 ± 0.0005	0.0706 ± 0.0006
*t*B·H+	0.102 ± 0.002	0.0896 ± 0.0004	0.0870 ± 0.001

Table V. Interaction Coefficients for Salts MCl Derived from Properties of HCl–MCl Mixtures

M^+	$B_{M,Cl}$, kg mol^{-1}	γ_{MCl}, [a] $m = 0.1$ mol kg^{-1}
NH_4^+	0.066 ± 0.006 (*10*)	0.765
	0.056 ± 0.004 (*3*)	
$(CH_2OH)_3CNH_3^+$	0.063 ± 0.003	0.765
$(CH_3)_3CHH_3^+$	0.031 ± 0.003	0.759

[a] Calculated by Equation 4.

specific interactions between ions of opposite charge. The general expression for the activity coefficient of a 1:1 electrolyte *MX* in a mixture is (*8*)

$$\log \gamma_{MX} = \frac{-AI^{1/2}}{1 + I^{1/2}} + \frac{1}{2}\sum_{X'} B_{M,X'}m_{X'} + \frac{1}{2}\sum_{M'} B_{M',X}m_{M'} \qquad (3)$$

where A is the Debye-Hückel slope (which has the value 0.5108 for aqueous solutions at 25°C), and $B_{M,X'}$ is an interaction coefficient representing the interaction between the cation M and the anion X'. For a solution of a single electrolyte *MX* of molality m mol kg^{-1}, Equation 3 reduces to

$$\log \gamma_{MX} = \frac{-AI^{1/2}}{1 + I^{1/2}} + B_{M,X}m \qquad (4)$$

When Equation 3 is applied to γ_{HCl} in HCl-MCl mixtures and compared with Equation 2, one finds

$$\alpha_1 = \tfrac{1}{2}(B_{H,Cl} - B_{M,Cl}) \qquad (5)$$

from which interaction coefficients for the single electrolytes can be calculated. Using the established value (*5*) of $B_{H,Cl}$ = 0.235 kg mol^{-1}, which is consistent with our experimental value of $\log \gamma^{\circ}_{HCl}$, we arrive at the values for $B_{M,Cl}$ given in Table V and thence (from Equation 4) at values for γ_{MCl} at an ionic strength of 0.1 mol kg^{-1}. The activity coefficient derived from isopiestic measurements of single electrolytes is 0.770 for both ammonium chloride (*11*) and Tris hydrochloride (*9*) at this molality. The agreement with the results obtained from two independent mixed electrolyte studies is satisfactory. Single electrolyte data for *t*-butylammonium chloride have not been obtained.

It is possible to estimate $B_{Tris\cdot H,Cl}$ also from an analysis of the emf measurements (*2*) for the cell

$$Pt;H_2(g, 1\ atm)\,|\,Tris{\cdot}HCl(m_1),\ Tris(m_2)\,|\,AgCl;Ag$$

at 25°C. The data can be described by Equations 1 and 3; thus,

$$\frac{E - E^{\circ}}{0.059159} + 2 \log m_1 - \log m_2 - \frac{2\,AI^{1/2}}{1 + I^{1/2}} = pK_a - 2\,B_{Tris\cdot H,Cl}m_1 + \log \gamma_{Tris} \qquad (6)$$

From Equation 6, one can calculate pK_a = 8.076 ± 0.0004, in excellent agreement with the original result (*2*) of 8.075 ± 0.0006. The value of $B_{Tris\cdot H,Cl}$ is 0.04 ± 0.004 kg mol^{-1} if γ_{Tris} is taken to be unity (*9*) at ionic strengths less than 0.1 mol kg^{-1}. The two values 0.04 and 0.06 kg mol^{-1} for $B_{Tris\cdot H,Cl}$ are in satisfactory agreement. The equivalent calculation for the *t*-butylamine–*t*-butylamine·H+ buffer solutions was not attempted because the original measurements (*7*) were made with the Ag;AgBr electrode.

The similarity between the three systems persists to the higher ionic strengths. At a total ionic strength of 0.5 mol kg^{-1}, the experimental $\log \gamma_{HCl}$ values are excellently described by Equation 2 without inclusion of the term in m_2^2. At I = 1.0 mol kg^{-1}, the situation acquires added interest. For the HCl-NH$_4$Cl system there is no suggestion of nonlinearity in the change of $\log \gamma_{HCl}$ with solution composition; that is, the term in m_2^2 does not improve the degree of fit.

The results for the HCl-Tris·HCl and HCl-*t*B·HCl systems, however, are more equivocal. Both systems might reasonably be said to obey the linear Harned expression. The maximum deviations from a straight-line treatment for the HCl-Tris·HCl system are 0.0005 in $\log \gamma_{HCl}$, equivalent to an experimental error of 0.05 mV. For the HCl–*t*B·HCl system, the deviation is 0.0008 in log γ_{HCl}. These deviations are trivial from the point of view of a calculation of activity coefficients. However, the data are fitted significantly better by the complete Equation 2, as shown by the $\Sigma\Delta^2$ figures given in Table III, which demonstrates that the deviations from linearity are systematic rather than random. We cautiously conclude, therefore, that deviations from the simple Harned relation exist at an ionic strength of 1.0 mol kg^{-1}, in contrast with the normal situation exemplified by the results for the HCl–NH_4Cl system.

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Binary Gaseous Diffusion Coefficients
IV. Sulfur Hexafluoride with *n*-Hexane, *n*-Heptane, *n*-Octane, and 2,2,4-Trimethylpentane at 1 Atm at 10–70°C

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Binary gaseous diffusion coefficients at 1-atm pressure of sulfur hexafluoride, with *n*-hexane, *n*-heptane, *n*-octane, and 2,2,4-trimethylpentane (isooctane) were measured at 10°, 25°, 40°, 55°, and 70°C by the capillary tube method of Stefan. Diffusion coefficients were calculated (a) by using Lennard-Jones (6, 12) pair potential parameters in conjunction with the Hudson-McCoubrey combining rule and (b) with a semiempirical method somewhat similar to that suggested by Chen and Othmer. Diffusion coefficients calculated via method (b) were in much better agreement with experiment than those obtained via method (a). The experimental results were used to investigate certain regularities in diffusional behavior of homologous species in mixtures with a common gas. In particular, a strikingly simple correlation (first advanced by Wakeham and Slater) was tested and found applicable, even when the common gaseous component is a pseudospherical molecule of considerable size and mass, such as SF_6. Provided that experimental data on two sufficiently spaced homologs are available, the correlation apparently offers a powerful predictive potential.

Several aspects of the diffusional behavior of polyatomic gases in mixtures with a common gas have recently been investigated in great detail (*1, 6–10, 16, 23, 28, 34, 35*). In particular, a simple and hitherto unexpected regularity within a homologous series (such as *n*-alkanes) for the binary diffusion coefficient D_{12} of members of such a series in a common gas has been reported by Elliott and Watts (*6, 7*). This heuristic correlation connected the experimental diffusion coefficients with the reduced mass $\mu = M_1M_2/(M_1 + M_2)$ of the relevant species, that is

$$D_{12} = A\mu + B \qquad (1)$$

Here, A and B are temperature dependent constants with $-B/A$ independent of temperature and approximately equal to the molar mass M_1 of the common partner gas; M_2 represents the molar mass of the homolog. However, an elementary analysis by Humphreys and Mills (*13*), with the aid of a simple rigid sphere model, revealed that linear behavior is not to be expected over extreme ranges of μ: theory predicts slightly S-shaped curves. Nevertheless, for limited ranges of μ, little deviation from linearity is predicted, and the theoretical curves meet the μ-axis at $\mu = M_1$ as indeed they must, since $\lim_{M_2 \to \infty} D_{12} = 0$. In fact, detailed analysis of the then available data indicated that deviations from linearity do exist, both in the series *n*-alkanes–air (*6*) and *n*-alkanes–nitrogen (*14*), although the experimental basis for drawing definite conclusions was rather small. Thus, to discern deviations from simple linear behavior, it was suggested that experiments be carried out either with higher members of homologous series (i.e., to cover the range $\mu/M_1 \to 1$) or with a more massive common gas (i.e., to investigate the region of small μ/M_1).

Following this suggestion, Wakeham and Slater (*29*) measured diffusion coefficients at 1 atm for the series methane through butane in argon, and combining their results with literature data for higher *n*-alkanes, were able to show conclusively that deviations from a linear plot D_{12} vs. μ exist (cf. also ref. *28*). Prior to this work we have studied the diffusional behavior of members of the *n*-alkane series with the nonpolar

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