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Activity Measurements in Aqueous Mixed Electrolyte Solutions. 4. Hydrochloric Acid–Guanidinium Chloride Mixtures of Constant Total Molality

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Activity coefficients of hydrochloric acid in aqueous mixed solutions with guanidinium chloride have been measured by using cells without liquid junction, of the type Pt,H_2(1 atm)|HX(m_A),MX(m_B)|AgCl,Ag, containing mixtures of HCl and $(NH_2)_2C{=}NH{\cdot}HCl$ in different proportions, but at constant total molality (m = 3.0, 2.0, 1.0, 0.5, 0.25, 0.1). Measurements have been carried out at four different temperatures, viz., 278.15, 288.15, 298.15, and 308.15 K. The measured activity coefficients of hydrochloric acid in the mixture have been found to obey Harned's rule. Interpretation of the results has been made in terms of Scatchard's and Pitzer's equations. It has been found that the latter gives a better fit of the experimental data but the former is reasonably adequate. Activity coefficients for guanidinium chloride in the mixtures are derived by using both the equations.

Introduction

The measurement of the activity coefficient of one electrolyte in binary mixtures with another, with or without a common ion, and the calculation of quantities like the excess free energy of mixing may lead to interesting insights into the nature of ion–ion and ion–solvent interaction. At constant total molality m ($=m_A + m_B$), the variation of the activity coefficient with composition can, in general, be expressed in terms of the equations

$$\log \gamma_A = \log {\gamma_A}^0 + Q_A y_B + R_A {y_B}^2 \quad (1)$$

$$\log \gamma_B = \log {\gamma_B}^0 + Q_B y_A + R_B {y_A}^2 \quad (2)$$

where γ_A is the activity coefficient of the component A in the mixture, ${\gamma_A}^0$ is the activity coefficient at zero concentration of the other component but at a molality equal to the total molality of the mixture, y_B is the molality fraction m_B/m of the second component, and Q_A and R_A are constants independent of the mixture composition, at a given total molality. Similar definitions apply to eq 2. Frequently, the linear form obtained by considering $R_A = 0$ in eq 1 has been found to express sufficiently accurately the measured activity coefficients of A; the electrolyte is then said to obey Harned's rule (*1*). It has been indicated by McKay (*2*) and Harned (*3*) that, even if the linear form in eq 1 holds, eq 2 with $R_B = 0$ does not follow.

In order to calculate the activity coefficient values of the second component electrolyte, after that of the first one has been determined, use can be made of either the Scatchard or the Pitzer treatments. The simplified Scatchard expression for the activity coefficient of the component A in the mixture is (*4*, *5*)

$$\log \gamma_A = \log {\gamma_A}^0 + [2({\phi_B}^0 - {\phi_A}^0) + b_{AB}^{(0,1)}m + b_{AB}^{(0,2)}m^2 + b_{AB}^{(0,3)}m^3]y_B/4.6052 \quad (3)$$

Assuming Harned's rule to be obeyed by the component A, eq 3 together with the appropriate form of eq 1 leads to

$$2({\phi_A}^0 - {\phi_B}^0) + 4.6052Q_A = b_{AB}^{(0,1)}m + b_{AB}^{(0,2)}m^2 + b_{AB}^{(0,3)}m^3 \quad (4)$$

so that the b_{AB} coefficients can be calculated from the experimental γ_A values. The equation corresponding to eq 3 for the activity coefficient of the other component in the mixtures is obtained by interchanging the A and B subscripts. ${\phi_A}^0$ and ${\phi_B}^0$ are the osmotic coefficients of pure A and B components, respectively, at the total molality of the mixture; the b_{AB}'s are interaction coefficients.

The activity coefficients of the second component in the mixtures can also be calculated alternatively by using Pitzer equations. For a mixture of two 1:1 electrolytes MX (A) and NX (B), at a total molality m, Pitzer's equation is (*6*, *7*)

$$\ln \gamma_{MX} = \ln {\gamma_{MX}}^0 + m_B[(\beta_{NX}^{(0)} - \beta_{MX}^{(0)}) + (\beta_{NX}^{(1)} - \beta_{MX}^{(1)}) \times \exp(-2m^{1/2}) + \theta_{MN} + m(C_{NX}^{\phi} - C_{MX}^{\phi}) + \tfrac{1}{2}(m + m_A)\psi_{MNX}] \quad (5)$$

where the quantities θ_{MN} and ψ_{MNX} are respectively the measures of binary and ternary interactions between the ions indicated by the subscripts. Further, the β and C terms [$\beta^{(0)}$ and $\beta^{(1)}$, corresponding to the second virial coefficient, and C^{ϕ}, corresponding to the third] are strictly pure electrolyte parameters and can be determined by least-squares fit of the following equation

$$\phi^0 - 1 + 0.39211 \frac{m^{1/2}}{1 + 1.2m^{1/2}} = \beta^{(0)}m + \beta^{(1)}e^{-2m^{1/2}}m + C^{\phi}m^2 \quad (6)$$

In equation 6, ϕ^0 is the osmotic coefficient of the pure electrolyte at the same molality as the total molality of the mixture.

Guanidinium chloride (GuCl) has been utilized extensively as an unfolding agent in protein conformation studies (*8*). The osmotic coefficient values of aqueous guanidinium chloride solutions at 25 °C over the concentration range (0.1–12.0 m) are available in the literature (*9*). This has prompted us to investigate the properties of this electrolyte in binary mixed aqueous solutions with hydrochloric acid over a modest concentration range, 0.1–3.0 m, and to see how far the Pitzer theory, or the Scatchard theory, is successful in interpreting the results. Measurements have been carried out at four different temperatures, viz., 278.15, 298.15, and 308.15 K.

Experimental Section

Hydrochloric acid of analytical reagent grade was distilled to the azeotropic composition and only the middle fraction retained. Guanidinium chloride (BDH) was recrystallized from methanol and finally dried under vacuum. No further characterization of the purity of the salt was made. Stock solutions of the electrolytes [HCl, 3.1317 m; GuCl, 3.7958 m] were prepared and their molalities determined by gravimetric chloride analysis. Triplicate analyses agreed within 0.04% for hydrochloric acid and 0.25% for guanidinium chloride. Other details of the experimental procedure, such as the preparation of the solutions, preparation of the electrodes, cell design, bath temperature control (±0.05 °C), etc., have been described elsewhere (*7*, *10*).

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Table I. Experimental EMF Data for the Cell Pt,H_2(1 atm)|HCl(m_A),GuCl(m_B)|AgCl,Ag for Various Values of m_A and m_B at Six Different Constant Total Molalities ($m = m_A + m_B$) and at Four Different Temperatures

			E(cor), V			
parameters	m_A	m_B	278.15 K	288.15 K	298.15 K	308.15 K
			m = 3.0 ± 0.0015			
	2.9975	0.0000	0.164 45	0.158 44	0.152 12	0.145 30
	2.6988	0.3008	0.170 30	0.165 30	0.158 48	0.151 63
	2.1000	0.8996	0.184 34	0.179 85	0.173 06	0.166 17
	1.4992	1.5001	0.200 43	0.195 80	0.189 25	0.182 24
	0.3040	2.6938	0.254 56	0.250 50	0.245 45	0.239 86
E°, V			0.233 77	0.229 07	0.222 64	0.215 63
$\sigma(E)$, V			0.000 15	0.000 26	0.000 15	0.000 15
			m = 2.0 ± 0.0144			
	2.0096	0.0000	0.197 43	0.192 03	0.186 24	0.179 81
	1.8002	0.2007		0.197 49	0.191 73	0.185 46
	0.9986	0.9992	0.228 32	0.223 36	0.217 92	0.212 18
	0.5999	1.3996	0.245 86	0.241 12	0.236 06	0.230 52
	0.1997	1.7696	0.276 73	0.272 65	0.268 34	0.263 58
E°, V			0.234 10	0.228 63	0.222 60	0.215 68
$\sigma(E)$, V			0.000 25	0.000 32	0.000 35	0.000 43
			m = 1.0 ± 0.0053			
	0.9988	0.0000	0.242 72	0.238 44	0.233 52	0.228 10
	0.8998	0.1003	0.246 99	0.242 68	0.237 83	0.232 50
	0.7009	0.3002	0.255 62	0.251 39	0.246 81	0.241 65
	0.4999	0.5002	0.266 14	0.262 23	0.257 77	0.252 91
	0.2999	0.6996	0.280 92	0.277 32	0.273 39	0.268 78
	0.1001	0.8870	0.310 62	0.307 78	0.304 72	0.301 08
E°, V			0.234 25	0.228 83	0.222 70	0.215 96
$\sigma(E)$, V			0.000 28	0.000 24	0.000 24	0.000 25
			m = 0.5 ± 0.0035			
	0.5000	0.0000	0.279 38	0.276 18	0.272 26	0.268 04
	0.3517	0.1507	0.290 32	0.287 06	0.283 64	0.279 47
	0.0501	0.4443	0.34154	0.340 07	0.337 96	0.335 45
E°, V			0.233 87	0.228 45	0.222 40	0.215 77
$\sigma(E)$, V			0.000 05	0.000 06	0.000 04	0.000 03
			m = 0.25 ± 0.0026			
	0.1260	0.1260	0.331 59	0.329 81	0.327 52	0.324 63
	0.0748	0.1745	0.345 02	0.343 68	0.341 66	0.339 26
	0.0250	0.2211	0.372 57	0.371 72	0.370 81	0.369 28
E°, V			0.233 44	0.228 50	0.222 24	0.215 61
$\sigma(E)$, V			0.000 08	0.000 03	0.000 05	0.000 03
			m = 0.1 ± 0.0011			
	0.0908	0.0101	0.357 37	0.356 38	0.355 26	0.352 89
	0.0491	0.0492	0.372 78	0.372 45	0.371 55	0.369 98
	0.0302	0.0704	0.384 87	0.384 38	0.385 07	0.382 73
E°, V			0.233 96	0.228 55	0.222 45	0.215 66
$\sigma(E)$, V			0.000 01	0.000 18	0.000 22	0.000 16

Calculations and Results

Table I gives the experimental results for the emf of the cell mentioned, with HCl and GuCl molalities indicated by m_A and m_B, at a number of values of the total molality, $m = m_A + m_B$. The emf values as listed in the table are those corrected to a hydrogen partial pressure of 1 atm (*11*). Data are recorded for four different temperatures in each case. Assuming that the HCl component in the mixture obeys Harned's rule, the cell emf can be written as

$$E + K\log m_A = (E^\circ - K\log m - 2K\log\gamma_A^0) - 2KQ_Ay_B \tag{7}$$

where $K = 2.3026RT/F$. Values of γ_A^0 were taken from the literature (*12*) and the least-squares method was applied for calculating E° and the standard deviations $\sigma(E)$ in E. As seen from Table I, the E° values obtained for six different total molalities at any particular temperature are very close to the literature values (*13*). In our further calculations we have used the average E° values of all different total molalities, for any particular temperature; these are 0.23390 V at 278.15 K, $\sigma(E^\circ) = \pm0.26$ mV; 0.22867 V at 288.15 K, $\sigma(E^\circ) = \pm0.22$ mV; 0.22251 V at 298.15 K, $\sigma(E^\circ) = \pm0.16$ mV; and 0.21572 V at 308.15 K, $\sigma(E^\circ) = \pm0.12$ mV.

Table II contains the molality fractions of GuCl and the experimental values of γ_{HCl}; also given are the "closeness of fit values" obtained when the values of γ_{HCl} at each total molality are fitted to eq 1 by the method of least squares, the case $R_A = 0$ being considered first. The values of Δ_1 show that Harned's rule is valid for the first component, over the temperature range studied, at least within the experimental accuracy secured. The results of such a fit (i.e., the values of Q_A, R_A) are recorded in Table III.

Analysis of the Results by the Scatchard Method

In order to be able to calculate the b_{AB} coefficients characteristic of the mixture, the values of the osmotic coefficients for the two components of the mixture (ϕ_A^0, ϕ_B^0) must be known at each constant total molality. We have used in our calculation the osmotic coefficient values for hydrochloric acid from the data of Robinson and Stokes (*14*), and for guanidinium chloride from the values listed by Bates et al. (*9*). Knowing the values of the parameters for the single electrolytes and the Harned coefficient Q_A, the left-hand side of eq 4 can be calculated at a particular molality. The values obtained for the different total molalities (m = 3.0, 2.0, 1.0, and 0.5 m) are then used for least-squares analysis of eq 4 for calculating the b_{AB}

Table II. Activity Coefficients of Hydrochloric Acid in the System HCl–GuCl–H_2O at Four Different Temperatures[a]

		5 °C			15 °C			25 °C			35 °C		
m	y_B	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	0.0000	1.421	−31	−19	1.371	33	5	1.313	1	−8	1.256	−6	−3
	0.1003	1.325	24	26	1.258	3	−1	1.222	17	15	1.175	12	12
	0.2999	1.121	12	0	1.064	−42	−15	1.043	−21	−13	1.013	−18	−20
	0.5000	0.948	4	−10	0.913	−19	14	0.901	−5	5	0.886	17	13
	0.8979	0.681	−9	3	0.674	24	−3	0.670	8	0	0.665	−5	−2
2.0	0.0000	1.065	21	−1	1.039	14	−16	1.008	14	−17	0.978	21	−16
	0.1003				0.986	15	20	0.959	16	21	0.931	15	20
	0.4996	0.795	−33	10	0.787	−47	3	0.774	−46	5	0.757	−59	3
	0.6998	0.711	−31	−15	0.710	−36	−17	0.701	−39	−21	0.691	−39	−16
	0.8848	0.652	43	6	0.657	53	9	0.653	55	11	0.647	62	9
1.0	0.0000	0.833	18	22	0.821	15	18	0.808	15	17	0.793	17	17
	0.1003	0.802	−21	−21	0.794	−13	−17	0.782	−16	−15	0.768	−15	−15
	0.3002	0.759	−17	−20	0.754	−11	−13	0.744	−16	−18	0.732	−16	−17
	0.5002	0.722	12	8	0.718	5	3	0.712	11	9	0.702	5	5
	0.6996	0.685	29	28	0.685	24	24	0.678	20	19	0.672	24	24
	0.8870	0.642	−22	−17	0.646	−17	−14	0.642	−15	−13	0.637	−15	−15
0.5	0.0000	0.774	13	0	0.767	2	0	0.759	11	0	0.746	6	0
	0.3014	0.733	−19	0	0.733	−3	0	0.724	−17	0	0.716	−9	0
	0.8886	0.672	6	0	0.673	1	0	0.671	6	0	0.666	3	0
0.25	0.5042	0.731	−4	0	0.731	3	0	0.727	−2	−1	0.721	0	0
	0.6981	0.721	8	0	0.721	−5	0	0.720	4	−1	0.715	1	−1
	0.8845	0.707	−4	0	0.715	3	−1	0.711	−2	−1	0.708	0	−1
0.1	0.1012	0.794	−13	0	0.796	−4	0	0.788	−21	0	0.788	−5	0
	0.4916	0.794	36	0	0.794	12	0	0.791	60	0	0.787	14	0
	0.7041	0.778	−23	0	0.787	−8	0	0.767	−39	0	0.781	−9	0

[a] Δ = log [experimental activity coefficient] − log [value calculated by least-squares fit to eq 1]; Δ_1 with $R_A = 0$, Δ_2 with $R_A \neq 0$.

Table III. Parameters of Eq 1 Obtained by the Method of Least Squares for the System HCl–GuCl–H_2O at Four Different Temperatures[a]

	5 °C			15 °C			25 °C			35 °C		
m	$-Q_A$	$-R_A$	$-\log \gamma_A{}^0$	$-Q_A$	$-R_A$	$-\log \gamma_A{}^0$	$-Q_A$	$-R_A$	$-\log \gamma_A{}^0$	$-Q_A$	$-R_A$	$-\log \gamma_A{}^0$
3.0	0.3585	0.0*	−0.1557	0.3424	0.0*	−0.1336	0.3260	0.0*	−0.1181	0.3081	0.0*	−0.0997
	0.3462	+0.0136	−0.1544	0.3700	−0.0305	−0.1365	0.3342	−0.0090	−0.1190	0.3055	+0.0029	−0.0994
2.0	0.2430	0.0*	−0.0253	0.2298	0.0*	−0.0154	0.2175	0.0*	−0.0020	0.2075	0.0*	+0.0116
	0.2750	−0.0379	−0.0275	0.2685	−0.0455	−0.0183	0.2571	−0.0466	−0.0051	0.2549	−0.0557	+0.0080
1.0	0.1231	0.0*	+0.0812	0.1142	0.0*	+0.0871	0.1092	0.0*	+0.0942	0.1034	0.0*	+0.1026
	0.1193	+0.0044	+0.0816	0.1118	+0.0027	+0.0873	0.1074	+0.0020	+0.0944	0.1033	+0.0001	+0.1026
0.5	0.0684	0.0*	+0.1124	0.0640	0.0*	+0.1154	0.0597	0.0*	+0.1208	0.0554	0.0*	+0.1277
	0.0839	−0.0167	+0.1111	0.0666	−0.0027	+0.1152	0.0738	−0.0152	+0.1196	0.0625	−0.0076	+0.1271
0.25	0.0383	0.0*	+0.1163	0.0259	0.0*	+0.1233	0.0242	0.0*	+0.1262	0.0223	0.0*	+0.1305
	−0.0087	+0.0339	+0.1318	0.0575	−0.0228	+0.1129	−0.0004	+0.0177	+0.1343	0.0172	+0.0036	+0.1322
0.10	0.0135	0.0*	+0.0973	0.0076	0.0*	+0.0976	0.0170	0.0*	+0.0996	0.0061	0.0*	+0.1021
	−0.0389	+0.0673	+0.1032	−0.0102	+0.0228	+0.0996	−0.0707	+0.1125	+0.1094	−0.0138	+0.0256	+0.1044

[a] * indicates set equal to zero.

Table IV. Scatchard's Mixed Electrolyte Parameters for the System HCl–GuCl at 25 °C

parameters	values	parameters	values
$b_{AB}^{(0,1)}$	−0.01701	$b_{AB}^{(1,2)}$	0.0[a]
$b_{AB}^{(0,2)}$	−0.02272	$b_{AB}^{(1,3)}$	0.0[a]
$b_{AB}^{(0,3)}$	0.00141		

[a] Set equal to zero.

parameters, which are listed in Table IV. The reason for not considering the total molality sets where $m < 0.5$ m has been discussed earlier (*7*, *10*).

The magnitudes of the $\Delta_3^{(S)}$ values listed in Table VI show the success with which eq 4 can be applied for reproducing the experimental activity coefficient values of hydrochloric acid. The activity coefficient values of guanidinium chloride in the mixture can be obtained from the analogue of eq 3 by using the same b_{AB} values, which are also listed in Table VI.

Analysis of the Results by the Pitzer Method

For the analysis of our results according to the Pitzer formalism, we make use of eq 5. The Pitzer pure electrolyte parameters for the hydrochloric acid component are already available in literature (*15*), but for obtaining the values of the other component (i.e., GuCl) the osmotic coefficient data of Bates et al. (*9*) have been fitted (least squares) to eq 6. The values so obtained are listed in Table V, together with the standard deviation of fit in ϕ, and the range over which m was fitted.

Table V. Best-Fitting Pitzer Parameters of Eq 6 for HCl and GuCl at 25 °C

parameters	HCl	GuCl
β^0	0.1775	−0.0463
β^1	0.2945	0.1572
C^ϕ	0.0008	0.0059
range of m fitted	0.1–6.0[a]	0.1–3.0
(s.d. in ϕ) × 10^3		0.3

[a] Reference *14*.

Knowing the Pitzer pure electrolyte parameters, eq 5 can be used to find out the two unknown quantities θ_{MN} and ψ_{MNX}. These may be calculated by using a graphical method. The method defines a quantity $\Delta \ln \gamma_{HCl}$ as the difference between the experimental value of $\ln \gamma_{HCl}$, listed in Table II in the form of γ_{HCl}, and that calculated from eq 5 with θ_{MN} and ψ_{MNX} set equal to zero. This yields

$$(\Delta \ln \gamma_{MX})/m_B = \theta_{MN} + \tfrac{1}{2}(m + m_A)\psi_{MNX} \qquad (8)$$

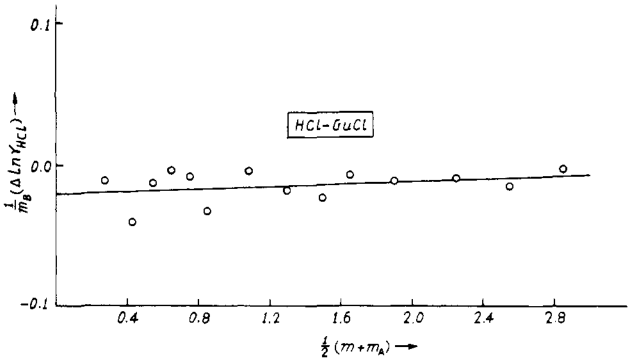

Figure 1. Plot of $(1/m_B)(\Delta \ln \gamma_{HCl})$ vs $^1/_2(m + m_A)$ for the system HCl-GuCl at 25 °C.

so that a plot of $(\Delta \ln \gamma_{MX})/m_B$ vs $^1/_2(m + m_A)$ (Figure 1) gives a straight line with intercept θ_{MN} and slope ψ_{MNX}. These values together with the standard deviation of fit σ, and the range of m over which it was fitted, are $\theta_{MN} = -0.0203$, $\psi_{MNX} = 0.0045$, $\sigma = 0.01$, and $m = 0.5$–3.0 m.

The magnitudes of the $\Delta_4^{(P)}$ values listed in Table VI show the success of the Pitzer eq 5 for reproducing the activity coefficients of hydrochloric acid. Also given in the same table are the activity coefficients of guanidinium chloride, calculated by using the Pitzer equation (an equation analogous to eq 5) using the same θ_{MN} and ψ_{MNX} values. The values of $\sigma^{(S)}$ and $\sigma^{(P)}$, which give respectively the standard deviation of the fits of the log γ_{HCl} values in Scatchard's and Pitzer's analysis, are also included in Table VI.

Discussion

As mentioned already, measurements were carried out at four different temperatures in anticipation of the possibility of the subsequent utilization of the results for the calculation of thermochemical quantities of interest, when the necessary background information is available. For the present, the osmotic data being available at 25 °C, the application fo Scathard and Pitzer analyses have been restricted to this temperature only.

The Scatchard and Pitzer equations are written in terms of some pure electrolyte parameters and a minimum number of mixed electrolyte parameters, so as to reproduce the observed thermodynamic properties with the least possible deviation. Scatchard's simplified eq 3 contains three interaction parameters ($b_{AB}^{(0,1)}$, $b_{AB}^{(0,2)}$, $b_{AB}^{(0,3)}$) whose physical meaning is vague. On the other hand, Pitzer's eq 5 has effectively only two parameters (θ_{MN}, ψ_{MNX}) which characterize specific types of ionic interactions in the mixture. The present results (Table VI) show that $\sigma^{(P)}$ is less than $\sigma^{(S)}$ for all the total molality mixtures studied (except at $m = 1.0$ m, where $\sigma^{(S)} = \sigma^{(P)}$, so that apparently the Pitzer two-parameter equation is more successful than the Scatchard three-parameter one. Our earlier work (*7*) on activity measurements in HCl-quaternary ammonium chloride mixed electrolyte systems at 25 °C showed that $\sigma^{(P)}$ was less than $\sigma^{(S)}$ for the total molalities $m = 3$, 2, 0.2, and 0.1 m, while for the other two total molalities ($m = 1$, 0.5 m) the reverse was true.

Further refinement of the analysis of the experimental results by the Pitzer method would be to postulate a concentration dependence of θ and ψ. Pitzer has split θ into an electronic interaction dependent part $E_{\theta_{ij}}$ and a short-range interaction dependent part $S_{\theta_{ij}}$: $\theta_{ij} = E_{\theta_{ij}} + S_{\theta_{ij}}$, with the assumption that only the first part is ionic strength dependent. The part $E_{\theta_{ij}}$ has been expressed in terms of certain J functions such that for symmetrical electrolytes $E_{\theta_{ij}}$ vanishes. Hence effectively for the present system (and for symmetrical mixtures in general) θ is concentration independent. [However, Friedman (*16*) has shown that there is a limiting law for the ionic strength dependence of θ, applicable for symmetrical mixtures. This law when expressed in terms of Pitzer parameters leads to certain equations derived by Pitzer (*17*), and applied to the systems HCl–KCl and HCl–CsCl; it was found that the improvement over constant θ results was not significant so that this complexity is unjustified.]

Table VI. Activity Coefficient of Guanidinium 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_A	$-\log \gamma_B^{(S)}$	$-\log \gamma_B^{(P)}$	$10^4\Delta_3^{(S)}$	$10^4\Delta_4^{(P)}$	$\sigma^{(S)}$	$\sigma^{(P)}$
3.0	0.9992	0.217	0.166	−12	−12		
	0.8996	0.244	0.197	2	5		
	0.7000	0.295	0.258	−48	−26	0.0070	0.0031
	0.4997	0.345	0.318	−58	4		
	0.1013	0.442	0.436	−138	65		
2.0	1.0048	0.224	0.203	−1	−1		
	0.9001	0.243	0.224	0	4		
	0.4993	0.315	0.303	−85	−38	0.0059	0.0046
	0.2999	0.350	0.342	−99	−17		
	0.0999	0.384	0.381	−30	94		
1.0	0.9988	0.211	0.208	−6	−6		
	0.8998	0.221	0.218	−35	−32		
	0.7009	0.240	0.238	−33	−21		
	0.4999	0.260	0.258	−5	19	0.0024	0.0024
	0.2999	0.279	0.278	2	40		
	0.1001	0.298	0.298	−35	18		
0.5	1.0000	0.183	0.183	11	11		
	0.7035	0.199	0.198	−25	−15	0.0018	0.0013
	0.1003	0.230	0.230	−18	14		
0.25	0.5038	0.166	0.166	−42	−33		
	0.2992	0.172	0.172	−25	−11	0.0030	0.0019
	0.0998	0.177	0.177	−21	−3		
0.10	0.9082	0.114	0.115	−31	−30		
	0.4912	0.119	0.120	35	39	0.0049	0.0048
	0.3018	0.122	0.122	−72	−68		

[a] Δ_3 = log [experimental activity coefficient] − log [value calculated by least-squares fit to eq 3]. Δ_4 = log [experimental activity coefficient] − log [value calculated by least-squares fit to eq 5].

Registry No. GuCl, 50-01-1; HCl, 7647-01-0.

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