



Figure 1. Equivalent conductance of LiBF_4 -THF solutions at 25 °C: O, dried solutions; X, undried solutions.

procedure was then successively repeated adding increments of salt to cover the concentration range.

Results and discussion

In arriving at the volume concentrations, C , listed in Table I, use was made of the fact that the ratio m/C changes quite slowly and linearly with concentration. Thus we measured solution densities of 1.138, 1.147, and 1.240 g cm^{-3} at 25 °C and $m = 0, 0.344$, and 3.218, respectively, enabling us to calculate C and m/C at these three values. Then from the linear plot of m vs. m/C the other m/C and hence C values were interpolated. We estimate a maximum error of $\pm 1\%$ in C due to this interpolation. The total uncertainties in m , c , κ , and λ are estimated as $\pm 1, 2, 2$, and 4%, respectively. Sharply rising dissolution times at the higher concentrations indicated that the solubility of LiBF_4 in THF is within a few tenths molar of 2.6 mol dm^{-3} . The resistivity of the pure solvent THF (both dried and

undried) was too great to be measured with our bridge which means that its conductivity was below $9 \times 10^{-9} \Omega^{-1} \text{cm}^{-1}$. Other workers (1) have reported a value of 0.4×10^{-9} for pure THF.

In Figure 1 the smooth merging of the curves for dried and undried solutions shows that, within experimental error, water traces do not affect conductivity. This is true even in the most dilute solution where the undried THF's nominal water content of 0.01% or 0.006 mol dm^{-3} is four times that of the salt. Thus there is no large, specific effect of water on the conductance (as opposed to a small, general effect operating via changes in solution fluidity). This accords with data on alkali metal salts in a variety of solvents reviewed by Fernandez-Prini (2). The low values of λ , 0.2–2.0, reported here point to extensive ion association. Minima in λ at low concentration such as appears in Figure 1 have commonly been observed (2) in solvents of dielectric constant below 10–15 (THF, 7.39 at 25 °C) and attributed to the conversion of nonconducting ion pairs to conductive ion triplets (3). The maximum in λ at high concentrations may be associated with the sharply increasing solution viscosity that we qualitatively observed in this region. Such maxima are frequently observed in aprotic solvents and have also been described as due to "activity effects" (4). The highest conductance, $4 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$, in our data at about 2.2 mol dm^{-3} is quite respectable and must qualify a statement (5) to the effect that polarography in THF is difficult due to poorly conducting solutions. In fact, conductivity as high as $11 \times 10^{-3} \Omega^{-1} \text{cm}^{-1}$ has been attained in THF-propylene carbonate mixtures used as battery electrolytes (6).

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Received for review February 7, 1978. Accepted June 5, 1978. This work was supported by the Independent Research Program of the U.S. Naval Surface Weapons Center, White Oak, Md.

Activity Coefficients of Hydrochloric Acid in HCl-KCl-H₂O Mixtures at Ionic Strengths up to 1.5 mol kg⁻¹ and Temperatures from 5 to 45 °C

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Electromotive-force measurements of the cell $\text{Pt}; \text{H}_2(\text{g}, 1 \text{ atm}) | \text{HCl}(m_A), \text{KCl}(m_B) | \text{AgCl}; \text{Ag}$ have been made at five ionic strengths from 0.1 to 1.5 mol kg^{-1} and over the temperature range 5–45 °C. The results are interpreted in terms of Harned's rule for the activity coefficient of hydrochloric acid. Up to 1.5 mol kg^{-1} , $\log \gamma_{\text{HCl}}$ varies linearly with solution composition at constant ionic strength. It is also demonstrated that the partial molal enthalpy of HCl-KCl-H₂O solutions follows an expression analogous to Harned's rule up to ionic strengths at least as high as 1.5 mol kg^{-1} .

Introduction

We have recently reported (10) measurements of the activity coefficient of hydrochloric acid in HCl/NaCl mixtures at several ionic strengths from 0.1000 to 0.8720 mol kg^{-1} and over the temperature range 5–45 °C. These measurements focused on our interest in developing a scale of pH for seawater systems (3), and the temperature range and choice of ionic strengths reflected this interest. In a similar manner we now report measurements of γ_{HCl} in HCl/KCl mixtures over the same temperature range for values of the ionic strength from 0.1 to 1.5 mol kg^{-1} . The present work is a more comprehensive study

Table I. Electromotive Force of Cells of Type A Containing HCl/KCl Mixtures from 5 to 45 °C, in Volts

y_B	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C
Ionic Strength = 0.1000 mol kg ⁻¹									
0	0.354 98	0.354 58	0.354 02	0.353 31	0.352 47	0.351 49	0.350 38	0.349 14	0.347 79
0.1	0.357 65	0.357 26	0.356 74	0.356 08	0.355 28	0.354 37	0.353 32	0.352 14	0.350 83
0.3	0.363 87	0.363 60	0.363 20	0.362 64	0.361 92	0.361 13	0.360 18	0.359 11	0.357 89
0.5	0.372 13	0.371 98	0.371 70	0.371 28	0.370 73	0.370 05	0.369 24	0.368 29	0.367 22
0.7	0.384 59	0.384 67	0.384 60	0.384 39	0.384 07	0.383 60	0.383 00	0.382 28	0.381 42
0.9	0.411 12	0.411 66	0.412 07	0.412 34	0.412 48	0.412 42	0.412 30	0.412 07	0.411 68
Ionic Strength = 0.3809 mol kg ⁻¹									
0	0.292 96	0.291 56	0.290 00	0.288 30	0.286 45	0.284 52	0.282 45	0.280 25	0.277 93
0.1	0.295 79	0.294 43	0.292 90	0.291 24	0.289 43	0.287 55	0.285 51	0.283 36	0.281 08
0.3	0.302 50	0.301 22	0.299 78	0.298 21	0.296 50	0.294 71	0.292 77	0.290 71	0.288 53
0.5	0.311 21	0.310 06	0.308 76	0.307 32	0.305 71	0.304 09	0.302 28	0.300 34	0.298 28
0.7	0.324 14	0.323 19	0.322 09	0.320 86	0.319 48	0.318 09	0.316 44	0.314 72	0.312 88
0.9	0.351 14	0.350 63	0.349 99	0.349 22	0.348 31	0.347 31	0.346 17	0.344 92	0.343 53
Ionic Strength = 0.6729 mol kg ⁻¹									
0	0.264 30	0.262 45	0.260 49	0.258 34	0.256 18	0.253 74	0.251 25	0.248 67	0.245 91
0.1	0.267 39	0.265 57	0.263 64	0.261 53	0.259 39	0.257 00	0.254 54	0.252 01	0.249 27
0.3	0.274 53	0.272 79	0.270 95	0.268 91	0.266 87	0.264 57	0.262 20	0.259 76	0.257 09
0.5	0.283 70	0.282 07	0.280 36	0.278 44	0.276 53	0.274 34	0.272 09	0.269 78	0.267 25
0.7	0.297 00	0.295 57	0.294 06	0.292 34	0.290 63	0.288 64	0.286 60	0.284 49	0.282 18
0.9	0.324 59	0.323 51	0.322 41	0.321 13	0.319 87	0.318 25	0.316 64	0.315 20	0.313 34
Ionic Strength = 0.8720 mol kg ⁻¹									
0	0.250 37	0.248 35	0.246 17	0.243 86	0.241 42	0.238 87	0.236 21	0.233 43	0.230 55
0.1	0.253 67	0.251 67	0.249 52	0.247 24	0.244 84	0.242 36	0.239 64	0.236 88	0.234 04
0.3	0.261 07	0.259 14	0.257 06	0.254 87	0.252 55	0.250 14	0.247 53	0.244 86	0.242 09
0.5	0.270 56	0.268 74	0.266 76	0.264 69	0.262 48	0.260 21	0.257 69	0.255 12	0.252 48
0.7	0.284 23	0.282 57	0.280 78	0.278 90	0.276 89	0.274 81	0.272 48	0.270 12	0.267 68
0.9	0.311 92	0.310 72	0.309 39	0.307 95	0.306 39	0.304 75	0.302 87	0.300 94	0.298 94
Ionic Strength = 1.5000 mol kg ⁻¹									
0	0.217 80	0.215 34	0.212 72	0.210 00	0.207 21	0.204 26	0.201 22	0.198 07	0.194 84
0.1	0.221 51	0.219 10	0.216 50	0.213 82	0.211 04	0.208 08	0.205 08	0.201 95	0.198 76
0.3	0.230 00	0.227 62	0.225 08	0.222 44	0.219 72	0.216 86	0.213 89	0.210 85	0.207 70
0.5	0.240 42	0.238 18	0.235 72	0.233 18	0.230 55	0.227 80	0.224 95	0.221 99	0.218 97
0.7	0.255 03	0.252 97	0.250 69	0.248 32	0.245 85	0.243 24	0.240 56	0.237 78	0.234 92
0.9	0.283 75	0.282 04	0.280 19	0.278 24	0.276 21	0.274 05	0.271 81	0.269 44	0.266 92

Table II. Harned Coefficients (Eq 2) for HCl-KCl-H₂O Solutions from $I = 0.1$ to $I = 1.5$ mol kg⁻¹ and at Temperatures from 5 to 45 °C

	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C
Ionic Strength = 0.1000 mol kg ⁻¹ ; $d\alpha_{12}/dT = -0.000 74$									
α_{12}	0.0940	0.0886	0.0842	0.0810	0.0796	0.0715	0.0692	0.0683	0.0645
$\sigma(\alpha_{12})$	0.0018	0.0014	0.0020	0.0020	0.0013	0.0032	0.0034	0.0039	0.0034
$\sigma(\log \gamma_{HCl})$	0.00014	0.00011	0.00015	0.00016	0.00010	0.00025	0.00026	0.00030	0.00027
Ionic Strength = 0.3809 mol kg ⁻¹ ; $d\alpha_{12}/dT = -0.00055$									
α_{12}	0.0793	0.0753	0.0723	0.0695	0.0668	0.0643	0.0619	0.0598	0.0574
$\sigma(\alpha_{12})$	0.0004	0.0003	0.0004	0.0004	0.0006	0.0002	0.0003	0.0003	0.0004
$\sigma(\log \gamma_{HCl})$	0.00012	0.00010	0.00011	0.00011	0.00018	0.00006	0.00010	0.00010	0.00013
Ionic Strength = 0.6729 mol kg ⁻¹ ; $d\alpha_{12}/dT = -0.00049$									
α_{12}	0.0755	0.0713	0.0684	0.0655	0.0632	0.0600	0.0576	0.0578	0.0558
$\sigma(\alpha_{12})$	0.0009	0.0004	0.0003	0.0002	0.0002	0.0005	0.0006	0.0006	0.0005
$\sigma(\log \gamma_{HCl})$	0.00045	0.00020	0.00014	0.00011	0.00011	0.00029	0.00032	0.00029	0.00028
Ionic Strength = 0.8720 mol kg ⁻¹ ; $d\alpha_{12}/dT = -0.000 50$									
α_{12}	0.0733	0.0700	0.0671	0.0647	0.0623	0.0603	0.0574	0.0551	0.0532
$\sigma(\alpha_{12})$	0.0004	0.0003	0.0003	0.0003	0.0003	0.0005	0.0001	0.0001	0.00015
$\sigma(\log \gamma_{HCl})$	0.00029	0.00023	0.00020	0.00020	0.00021	0.00033	0.00006	0.00008	0.00010
Ionic Strength = 1.5000 mol kg ⁻¹ ; $d\alpha_{12}/dT = -0.000 49$									
α_{12}	0.0722	0.0695	0.0668	0.0642	0.0616	0.0594	0.0573	0.0551	0.0527
$\sigma(\alpha_{12})$	0.0002	0.0003	0.0003	0.0003	0.0002	0.0003	0.0002	0.0003	0.0005
$\sigma(\log \gamma_{HCl})$	0.00028	0.00038	0.00034	0.00034	0.00029	0.00034	0.00028	0.00034	0.00055

of dilute HCl/KCl solutions than hitherto undertaken (5–7), and we have attempted to relate our measurements to our interest in seawater while recognizing that potassium chloride is only a minor constituent of natural seawater. In addition, we have extended our measurements to an ionic strength of 1.5 mol kg⁻¹ in an attempt to determine whether our earlier finding that the partial molal enthalpy of electrolyte mixtures is a linear function

of composition applies at higher ionic strengths.

Experimental Section

Hydrochloric acid was distilled twice and the concentrated stock solution standardized by gravimetric analysis for chloride. Potassium chloride of reagent grade was recrystallized twice

from water and dried at 300 °C. Stock solutions were prepared from the dried salt. A sensitive spot test (14) showed the bromide content of the KCl to be less than 0.002 mol %. Solutions were prepared to have an ionic strength and solution composition within 0.01% of the nominal values. Other details of electrode preparation, cell design, and relevant experimental procedures have been given elsewhere (10, 12). The standard potential of the Ag|AgCl electrode at 25 °C was 0.222 43 V, as determined from measurements on 0.01 *m* HCl (2). As before (10), values for the standard potential at temperatures other than 25 °C were based on those given by Bates and Bower (1) and the measured difference in the values at 25 °C (0.09 mV) from the two studies. This approach is supported by the results of a number of measurements on 0.01 *m* HCl solutions over the temperature range 5–55 °C.

Results

Table I contains values for the electromotive force of the cell Pt;H₂(g, 1 atm)|HCl(*m*_A),KCl(*m*_B)|AgCl;Ag (A) from 5 to 45 °C for five values of the ionic strength between 0.1 and 1.5 mol kg⁻¹. The solution compositions are expressed in terms of the ionic strength (*I*) and the ionic strength fraction (*y*_B) of potassium chloride; thus *m*_B = *y*_B*I*.

The mean ionic activity coefficient of hydrochloric acid is related to the emf of cell (A) by the Nernst equation

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

and activity coefficients so derived are fitted to the Harned equation (8) which states that at constant temperature and ionic strength

$$\log \gamma_{\text{HCl}} = \log \gamma_{\text{HCl}}^\circ - \alpha_{12}m_{\text{B}} \quad (2)$$

In eq 2, $\gamma_{\text{HCl}}^\circ$ is the activity coefficient of hydrochloric acid in a solution containing only HCl but having the same ionic strength as the mixture, and α_{12} is the Harned coefficient, which for a particular electrolyte mixture depends on both temperature and ionic strength. In Table II, values of α_{12} for the system HCl/KCl over the ranges of temperature and ionic strength studied here are listed. Also given are values of $\sigma(\log \gamma_{\text{HCl}})$, the standard deviation of the experimental $\log \gamma_{\text{HCl}}$ values from the best-fit values given by eq 2. Our estimated experimental precision is ± 0.05 mV, and the $\sigma(\log \gamma_{\text{HCl}})$ values are, with one exception (*I* = 0.6729, *t* = 5 °C), consistent with this estimate. The results at *I* = 1.5 mol kg⁻¹ are better fitted by the full Harned expression (8) which includes the term $-\beta_{12}m_{\text{B}}^2$, but the data are still represented by eq 2 to within ± 0.0005 in $\log \gamma_{\text{HCl}}$, equivalent to our anticipated error of ± 0.05 mV in *E*.

Also given in Table II are values for the derivative $d\alpha_{12}/dT$ at each ionic strength. We have observed earlier (10) in studies of the system HCl–NaCl–H₂O that this parameter is essentially independent of ionic strength. This regularity would suggest that the relative partial molal enthalpy of the solutions is a linear function of solution composition for a given temperature and ionic strength. The same behavior is exhibited by HCl/KCl solutions up to 1.5 mol kg⁻¹, since the values of $d\alpha_{12}/dT$ can be regarded as constant, provided suitable account is taken of the uncertainty in α_{12} values at *I* = 0.1 mol kg⁻¹.

Where our results can be compared with previous work, the agreement is not always satisfactory. This comparison is most readily made with the molality dependence of the Harned coefficient α_{12} at 25 °C. At 0.1 mol kg⁻¹, our value of 0.079 kg mol⁻¹ is in excellent agreement with the value 0.077 obtained from the results of Güntelberg (4). Above an ionic strength of 0.5 mol kg⁻¹, however, our values of α_{12} are significantly higher than those obtained by Harned and Hamer (7) and Harned and Gancy (6), the difference being as much as 0.007 in α_{12} at *I* = 1.5 mol kg⁻¹. The reason for this discrepancy is not obvious, but to resolve the problem we have made numerous measurements on HCl–KCl–H₂O solutions at *I* = 1.5 mol kg⁻¹, all of which support our value of $\alpha_{12} = 0.062$ kg mol⁻¹. This disagreement is discussed more fully elsewhere (9), where results for this system at 25 °C up to an ionic strength of 3 mol kg⁻¹ are presented. These data permit a realistic interpretation in terms of mixed-electrolyte treatments (11, 13), which concentrate on the ion–ion interactions most likely to control the behavior of this system.

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Received for review February, 9, 1978. Accepted June 8, 1978. This work was supported in part by the National Science Foundation under Grants CHE76 24556 and OCE76 24384.