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Activity Coefficients of (Hydrogen Chloride + Europium Chloride) (aq) Using Harned's Rule and the Pitzer Formalism

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Activity coefficients of HCl in (hydrogen chloride + europium chloride) have been determined at temperatures ranging from 278.15 K to 328.15 K at 5 K intervals and at eight constant total ionic strengths of (0.025, 0.05, 0.1, 0.25, 0.5, 1.0, 1.5, and 2.0) mol kg^{-1}. Experimental cell potentials were obtained using a cell without liquid junction of the type Pt|H_2(g, p = 101.325 kPa)|HCl (m_A), $EuCl_3$ (m_B)|AgCl(s)|Ag(s). The treatment of Harned has been used to describe the mean molal activity coefficient of hydrochloric acid as a function of ionic strength in acid salt mixtures. Results indicate that the quadratic form is sufficient for the full range of Y_B (the ionic strength fraction of the salt) to 0.9 at all the experimental ionic strengths. The ion-interaction model of Pitzer has also been used to calculate Pitzer's mixing parameters $\Theta_{H,Eu}$ and $\Psi_{H,Cl,Eu}$ for the system $H^+ + Eu^{3+} + Cl^- + H_2O$. The values found, $\Theta_{H,Eu} = 0.2 \pm 0.03$ and $\Psi_{H,Cl,Eu} = 0$, were similar to those for other trivalent ions studied previously. The parameters used in this study reproduce the activity coefficients of HCl in the mixtures to within 0.016 over the entire range of ionic strengths and within 0.009 for $I > 0.05$ mol kg^{-1} over the entire temperature range.

1. Introduction

Our laboratory has been involved in the investigation of the thermodynamic properties of aqueous solutions of mixed electrolytes, particularly the nature and extent of ion−solvent and ion−ion interactions for 1−1, 2−1, 3−1, and 4−1mixing such as HCl + NaCl + H_2O,[1] HCl + NH_4-Cl + H_2O,[2] HCl + $MgCl_2$ + H_2O,[3] HCl + $NiCl_2$ + H_2O,[4] HCl + $CaCl_2$ + H_2O,[5] HCl + $BaCl_2$ + H_2O,[6] HCl + $LaCl_3$ + H_2O,[7] HCl + $InCl_3$ + H_2O,[8,9] HCl + $AlCl_3$ + H_2O,[10] and HCl + $ThCl_4$ + H_2O,[11] respectively. The higher electrostatic term is zero for 1−1 mixing, small for 2−1 mixing, but substantial for 3−1 and 4−1 mixing. The investigation of the heavy metals such as the lanthanide elements is important in the natural environment due to contamination from petroleum cracking catalysts released as refinery waste products. The thermodynamic properties (activity coefficients) of pure aqueous rare-earth chlorides have been investigated at 298.15 K by Spedding et al.,[12] Fukushi et al.,[13] and Iwamoto et al.[14] As a continuation of previous studies for HCl + $GaCl_3$ + H_2O,[15,16] HCl + $GdCl_3$ + H_2O,[17] and HCl + $SmCl_3$ + H_2O,[18] we have attempted to study the thermodynamics of the $H^+ + Eu^{3+} + Cl^- + H_2O$ system, which is both challenging and interesting.

It has been reported by Kim and Frederick[19] that the accurate values of the activity coefficient are very important in the calculation of the solubilities of inorganic species in multicomponent aqueous ionic solutions of high ionic strength. This assertion has some validity even when trace amounts of only a few chemical species are present. Because of lack of suitable reversible electrodes, most of our knowledge about the investigation of multivalent electrolyte solutions comes from isopiestic and freezing point measurements. One of the main objectives of this paper is to provide accurate activity coefficients of HCl and $EuCl_3$ in their mixtures from emf measurements in the temperature range from 278.15 to 328.15 K at 5 K intervals, and over a wide range of constant total ionic strength ((I = 0.025, 0.05, 0.1, 0.25, 0.5, 1.0, 1.5, and 2.0) mol kg^{-1}).

As a common practice in our laboratory for research of this type (mixed electrolyte system with a common anion), the electromotive force method was employed to determine the activity coefficients of HCl in mixtures of HCl + $EuCl_3$. The cell without liquid junction is given below:

$$\mathrm{Pt}|\mathrm{H_2}(\mathrm{g},\ p = 101.325\ \mathrm{kPa})|\mathrm{HCl}\ (m_A),\ \mathrm{EuCl_3}(m_B)|\mathrm{AgCl(s)}|\mathrm{Ag(s)} \quad \text{(A)}$$

where m_A and m_B represent molalities of the salt, respectively; hydrogen and silver + silver chloride electrodes are reversible with respect to H^+ and Cl^- present in the cell solutions. The emf from the familiar Nernst equation for the cell (A) is given by

$$E = E° - k \log a_{HCl} \quad (1)$$

and

$$\log \gamma_{HCl} = -\{(E - E°)/2k + (1/2) \log[m_A(m_A + 3m_B)]\} \quad (2)$$

in which $k = RT \ln 10/F$, $E°$ is the standard potential of the silver + silver chloride electrode, and a_{HCl} is the activity of HCl.

This paper contains experimental emf data for the HCl + $EuCl_3$ + H_2O system. The mean molal activity coef-

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Table 1. Electromotive Force (*E*) for the HCl + $EuCl_3$ System As a Function of Temperature and Ionic Strength

			E/mV										
I/(mol kg^{-1})	m_A/(mol kg^{-1})	m_B/(mol kg^{-1})	5 °C	10 °C	15 °C	20 °C	25 °C	30 °C	35 °C	40 °C	45 °C	50 °C	55 °C
0.025	0.025 00	0.000 00	417.92	418.49	418.98	419.30	419.54	419.60	419.57	419.37	419.02	418.66	417.88
	0.022 32	0.000 45	421.77	422.45	423.04	423.42	423.73	423.87	423.88	423.77	423.46	423.14	422.52
	0.017 39	0.001 27	429.93	430.82	431.55	432.11	432.56	432.87	433.01	433.06	432.90	432.64	432.25
	0.015 02	0.001 66	434.57	435.54	436.38	436.97	437.55	437.95	438.20	438.34	438.29	438.12	437.87
	0.012 39	0.002 10	440.60	441.69	442.67	443.31	444.02	444.55	444.85	445.21	445.20	445.03	444.91
	0.010 01	0.002 50	446.85	448.08	449.18	449.88	450.74	451.38	451.89	452.23	452.44	452.36	452.33
	0.007 45	0.002 93	455.47	456.83	458.12	458.88	459.93	460.76	461.38	461.90	462.23	462.33	462.43
	0.002 50	0.003 75	484.64	486.48	488.40	489.43	491.21	492.56	493.78	494.81	495.69	496.33	496.91
0.05	0.050 00	0.000 00	386.62	386.69	386.67	386.44	386.10	385.65	385.11	384.37	383.46	382.57	381.28
	0.045 08	0.000 82	389.99	390.09	390.16	390.07	389.70	389.30	388.77	388.10	387.39	386.62	385.37
	0.034 90	0.002 52	398.33	398.72	398.96	398.98	398.97	398.40	398.08	397.61	397.02	396.46	395.35
	0.030 16	0.003 31	403.10	403.57	403.86	404.00	403.99	403.63	403.32	402.87	402.34	401.75	400.87
	0.025 27	0.004 12	408.48	409.03	409.49	409.90	409.99	409.57	409.37	408.99	408.55	408.23	407.45
	0.019 75	0.005 04	415.91	416.58	417.24	417.80	418.20	417.60	417.55	417.39	417.12	416.77	416.30
	0.015 03	0.005 83	424.06	424.87	425.61	426.26	426.80	426.49	426.56	426.46	426.25	425.86	425.59
	0.005 00	0.007 50	453.96	455.42	456.70	457.87	458.97	459.21	459.80	460.08	460.20	460.04	460.67
0.1	0.100 00	0.000 00	355.23	354.77	354.20	353.46	352.62	351.61	350.54	349.32	347.91	346.47	344.65
	0.089 75	0.001 71	359.00	358.60	358.11	357.45	356.66	355.70	354.66	353.42	352.18	350.76	349.10
	0.069 78	0.005 04	367.61	367.43	367.09	366.55	365.92	365.11	364.23	363.15	362.01	360.73	359.33
	0.059 92	0.006 68	372.49	372.41	372.18	371.75	371.19	370.50	369.69	368.72	367.67	366.45	365.19
	0.048 96	0.008 51	379.03	379.05	378.95	378.65	378.19	377.63	376.93	376.10	375.18	374.09	373.09
	0.039 04	0.010 16	386.01	386.21	386.23	386.04	385.75	385.32	384.77	384.09	383.29	382.35	381.34
	0.029 95	0.011 68	394.02	394.36	394.51	394.45	394.32	394.05	393.65	393.15	392.52	391.77	390.87
	0.010 17	0.014 97	423.77	424.72	425.43	425.92	426.39	426.66	426.86	427.02	426.89	426.75	426.32
0.25	0.250 00	0.000 00	313.23	312.13	310.88	309.50	308.03	306.38	304.56	302.64	300.62	298.43	296.24
	0.224 95	0.004 17	317.12	316.07	314.88	313.48	312.17	310.58	308.83	306.95	305.01	302.98	300.86
	0.175 12	0.012 48	326.01	325.18	324.14	322.97	321.68	320.27	318.71	317.04	315.30	313.47	311.56
	0.150 10	0.016 65	331.43	330.64	329.73	328.67	327.44	326.09	324.61	322.97	321.27	319.39	317.50
	0.125 08	0.020 82	337.58	336.90	336.09	335.12	334.04	332.82	331.46	329.98	328.41	326.71	324.88
	0.099 16	0.025 14	345.17	344.67	343.97	343.16	342.10	341.00	339.79	338.43	336.96	335.37	333.70
	0.074 57	0.029 24	353.84	353.47	352.96	352.27	351.38	350.43	349.36	348.17	346.92	345.52	344.05
	0.025 08	0.037 49	384.67	384.87	384.88	384.81	384.34	383.92	383.37	382.68	381.92	381.06	380.19
0.5	0.500 00	0.000 00	279.90	278.25	276.47	274.54	272.48	270.32	268.10	265.66	263.11	260.51	257.63
	0.451 41	0.008 10	283.99	282.44	280.72	278.91	276.89	274.80	272.57	270.22	267.75	265.15	262.32
	0.351 00	0.024 83	293.62	292.21	290.66	288.94	287.06	285.20	283.11	280.84	278.59	276.15	273.67
	0.300 01	0.033 33	299.21	297.85	296.44	294.68	292.92	291.00	289.14	287.00	284.84	282.52	280.13
	0.251 28	0.041 45	305.20	304.00	302.66	301.18	299.56	297.79	295.88	293.85	291.83	289.57	287.22
	0.200 40	0.049 93	312.72	311.65	310.45	309.13	307.65	305.97	304.21	302.29	300.44	298.42	296.20
	0.152 86	0.057 86	321.13	320.21	319.11	317.93	316.56	315.15	313.53	311.82	309.98	308.06	306.00
	0.048 62	0.075 23	353.45	353.16	352.68	352.01	351.12	350.40	349.39	348.25	346.93	345.53	344.18
1	1.000 00	0.000 00	242.88	240.75	238.48	236.04	233.49	230.85	228.16	226.01	222.33	219.34	216.11
	0.898 86	0.016 86	247.55	245.40	243.16	240.78	238.36	235.87	233.17	231.10	227.46	224.49	221.34
	0.700 14	0.049 98	257.91	255.94	253.86	251.69	249.40	246.96	244.44	242.46	238.92	236.12	233.10
	0.603 16	0.066 14	263.72	261.82	259.86	257.75	255.62	253.16	250.73	248.88	245.48	242.75	239.87
	0.502 32	0.082 95	270.51	268.68	266.82	264.71	262.67	260.44	258.11	256.32	252.99	250.35	247.55
	0.396 24	0.100 63	279.04	277.34	275.61	273.62	271.68	269.66	267.43	265.78	262.58	260.05	257.36
	0.301 83	0.116 36	287.83	286.27	284.67	282.93	281.15	279.20	277.11	275.57	272.51	270.14	267.65
	0.101 69	0.149 72	319.63	318.73	317.69	316.53	315.27	313.75	312.18	311.18	308.66	306.78	304.63
1.5	1.500 00	0.000 00	218.00	215.55	213.02	210.24	207.39	204.50	201.47	198.49	195.12	191.88	188.41
	1.350 78	0.024 87	223.29	220.90	218.41	215.62	212.74	210.09	207.10	203.65	200.11	196.82	193.15
	1.054 70	0.074 22	234.36	232.09	229.72	227.23	224.63	221.89	219.03	215.47	211.88	208.37	204.81
	0.902 54	0.099 58	240.74	238.55	236.23	233.80	231.32	228.72	225.96	222.52	218.95	215.33	211.72
	0.75310	0.124 48	247.69	245.55	243.32	241.04	238.60	236.12	233.49	230.16	226.72	223.21	219.35
	0.611 84	0.148 03	255.05	253.17	251.07	248.74	246.60	244.23	241.70	238.51	235.19	231.82	228.09
	0.448 92	0.175 18	265.63	263.91	262.04	259.92	257.92	255.68	253.34	250.23	247.05	243.87	240.32
	0.151 40	0.224 77	297.34	296.17	294.84	293.20	291.78	290.14	288.34	285.91	283.35	280.74	277.77
2	2.000 00	0.000 00	198.09	195.42	192.62	189.72	186.51	183.41	180.39	177.02	173.45	170.00	166.18
	1.800 75	0.033 21	203.59	200.94	198.16	195.28	192.21	189.17	185.99	182.68	179.30	175.74	172.06
	1.404 78	0.099 20	215.41	212.85	210.23	207.54	204.68	201.68	198.69	195.56	192.33	188.85	185.21
	1.205 30	0.132 45	222.18	219.84	217.30	214.69	211.92	209.08	206.16	203.12	199.94	196.61	193.11
	1.007 37	0.165 44	229.63	227.41	224.98	222.57	219.80	217.03	214.19	211.27	208.14	204.95	201.36
	0.805 94	0.199 01	238.24	236.11	233.82	231.52	228.95	226.36	223.63	220.90	218.01	215.00	211.68
	0.605 26	0.232 46	248.65	246.69	244.61	242.44	240.04	237.50	234.94	232.28	229.46	226.58	223.46
	0.206 65	0.298 89	282.15	280.73	279.19	277.56	275.69	273.73	271.68	269.59	267.27	264.83	262.41

ficients of HCl in HCl + $EuCl_3$ + H_2O have been calculated in terms of Harned's rule and Pitzer's ion-interaction theory.

2. Experimental Section

Reagent grade hydrochloric acid was distilled twice. Three different hydrochloric acid stock solutions ($m \approx 0.1$, 1, and 4.0 mol kg^{-1}) were prepared by dilution of the middle fraction of twice-distilled constant-boiling acid. The molalities of the stock solutions were determined gravimetrically as silver chloride with an accuracy better than ±0.02%. Stock solutions of europium chloride were prepared by dissolving solid $EuCl_3{\cdot}6H_2O$ (GFS, 99.9% purity). It was assayed as AgCl and was known to within ±0.02%. Experimental cell solutions for all runs were made by mass dilution of the appropriate stock solutions. Proper care was

Table 2. Constants for Eq 3

I^a	$10^4(\log \gamma_{\text{Aexp}})$	$10^4(\log \gamma_{\text{Å}} \pm \sigma)$	$10^4(\alpha_{\text{AB}} \pm \sigma)$	$10^4(\beta_{\text{AB}} \pm \sigma)$	10^4(rmsd)	I^a	$10^4(\log \gamma_{\text{Aexp}})$	$10^4(\log \gamma_{\text{Å}} \pm \sigma)$	$10^4(\alpha_{\text{AB}} \pm \sigma)$	$10^4(\beta_{\text{AB}} \pm \sigma)$	10^4(rmsd)
5 °C											
0.025	−614	−612 ± 11	−275 ± 11	0	17	0.5	−1120	−1133 ± 7	328 ± 13	0	11
		−612 ± 4	−115 ± 21	−183 ± 23	5			−1122 ± 5	415 ± 24	−100 ± 26	6
0.05	−788	−783 ± 4	−216 ± 8	0	6	1	−776	−778 ± 4	777 ± 8	0	7
		−787 ± 5	−246 ± 25	34 ± 27	6			−775 ± 5	802 ± 3	−29 ± 30	7
0.1	−955	−953 ± 3	−58 ± 6	0	5	1.5	−283	−327 ± 20	1012 ± 39	0	3
		−956 ± 4	−88 ± 18	34 ± 20	4			−291 ± 7	1296 ± 34	−326 ± 38	8
0.25	−1130	−1116 ± 8	196 ± 15	0	12	2	271	275 ± 9	1533 ± 18	0	14
		−1129 ± 5	90 ± 25	122 ± 27	6			262 ± 8	1428 ± 41	121 ± 45	10
10 °C											
0.025	−610	−632 ± 13	−266 ± 26	0	21	0.5	−1140	−1152 ± 6	329 ± 11	0	9
		−608 ± 4	−74 ± 19	−220 ± 21	5			−1143 ± 5	396 ± 24	−78 ± 26	6
0.05	−790	−785 ± 5	−201 ± 13	0	8	1	−813	−809 ± 4	760 ± 8	0	7
		−788 ± 68	−228 ± 34	31 ± 37	8			−810 ± 6	749 ± 29	13 ± 32	7
0.1	−960	−956 ± 4	−40 ± 7	0	6	1.5	−330	−370 ± 18	999 ± 34	0	3
		−961 ± 4	−79 ± 19	45 ± 21	5			−338 ± 6	1251 ± 33	−290 ± 36	8
0.25	−1145	−1131 ± 8	198 ± 16	0	12	2	211	219 ± 9	1512 ± 18	0	14
		−1144 ± 5	91 ± 25	122 ± 27	6			205 ± 7	1403 ± 38	125 ± 41	9
15 °C											
0.025	−613	−633 ± 12	−2461 ± 23	0	18	0.5	−1160	−1173 ± 6	326 ± 12	0	10
		−612 ± 4	−78 ± 21	−193 ± 23	5			−1164 ± 6	396 ± 28	−81 ± 3003	7
0.05	−798	−793 ± 3	−190 ± 4	0	5	1	−849	−843 ± 5	747 ± 9	0	7
		−795 ± 4	−208 ± 22	20 ± 25	5			−845 ± 6	734 ± 32	15 ± 35	8
0.1	−968	−965 ± 3	−36 ± 6	0	5	1.5	−382	−418 ± 16	977 ± 31	0	2
		−962 ± 3	−72 ± 16	42 ± 17	4			−390 ± 7	1195 ± 37	−251 ± 40	9
0.25	−1160	−1146 ± 8	197 ± 15	0	12	2	152	163 ± 10	1490 ± 19	0	15
		−1159 ± 4	94 ± 22	118 ± 24	5			147 ± 6	1361 ± 33	149 ± 36	8
20 °C											
0.025	−616	−644 ± 17	−289 ± 32	0	26	0.5	−1182	−1194 ± 6	321 ± 11	0	9
		−613 ± 4	−47 ± 21	−278 ± 23	5			−1187 ± 6	380 ± 28	−67 ± 30	7
0.05	−801	−798 ± 2	−169 ± 4	0	3	1	−883	−877 ± 5	732 ± 10	0	8
		−798 ± 3	−164 ± 14	−6 ± 15	3			−881 ± 6	701 ± 32	36 ± 35	8
0.1	−977	−973 ± 3	−38 ± 6	0	5	1.5	−426	−463 ± 18	952 ± 35	0	3
		−978 ± 3	−76 ± 14	44 ± 15	3			−431 ± 8	1201 ± 40	−287 ± 43	10
0.25	−1177	−1160 ± 9	201 ± 17	0	13	2	89	100 ± 9	1491 ± 17	0	14
		−1173 ± 6	91 ± 29	127 ± 32	7			86 ± 6	1355 ± 30	133 ± 33	7
25 °C											
0.025	−625	−648 ± 14	−261 ± 26	0	21	0.5	−1207	−1218 ± 7	313 ± 13	0	10
		−624 ± 3	−65 ± 17	−224 ± 19	4			−1209 ± 6	389 ± 28	−88 ± 30	7
0.05	−810	−803 ± 4	−142 ± 7	0	6	1	−921	−919 ± 4	724 ± 8	0	6
		−803 ± 5	−143 ± 27	1 ± 29	7			−921 ± 6	712 ± 28	13 ± 30	7
0.1	−990	−984 ± 5	−32 ± 5	0	8	1.5	−477	−507 ± 17	960 ± 33	0	3
		−992 ± 3	−95 ± 17	72 ± 19	4			−473 ± 7	1196 ± 36	−272 ± 98	9
0.25	−1201	−1189 ± 7	172 ± 14	0	11	2	39	48 ± 8	1454 ± 16	0	13
		−1200 ± 5	80 ± 23	106 ± 25	6			35 ± 6	1347 ± 29	123 ± 32	7
30 °C											
0.025	−631	−654 ± 14	252 ± 26	0	21	0.5	−1233	−1244 ± 5	317 ± 10	0	8
		−629 ± 4	−57 ± 18	−224 ± 20	5			−1237 ± 5	371 ± 23	−62 ± 25	6
0.05	−819	−811 ± 5	−203 ± −10	0	8	1	−962	−962 ± 4	703 ± 8	0	6
		−817 ± 6	−252 ± 28	56 ± 31	7			−963 ± 5	697 ± 27	6 ± 30	7
0.1	−1000	−992 ± 5	−26 ± 10	0	8	1.5	−532	−566 ± 15	936 ± 29	0	3
		−1001 ± 3	−94 ± 14	78 ± 15	3			−539 ± 6	1149 ± 32	−245 ± 35	8
0.25	−1220	−1208 ± 7	168 ± 13	0	10	2	−29	−18 ± 9	1420 ± 18	0	14
		−1219 ± 4	81 ± 22	99 ± 24	5			−33 ± 6	1302 ± 30	139 ± 33	7
35 °C											
0.025	−637	−657 ± 14	−248 ± 23	0	18	0.5	−1261	−1266 ± 4	309 ± 7	0	6
		−635 ± 3	−74 ± 13	−199 ± 14	3			−1264 ± 5	331 ± 24	−26 ± 26	6
0.05	−830	−820 ± 5	−209 ± 9	0	7	1	−1005	−1003 ± 4	683 ± 7	0	6
		−826 ± 5	−255 ± 25	53 ± 28	6			−1003 ± 5	681 ± 25	3 ± 27	6
0.1	−1013	−1002 ± 7	−25 ± 13	0	10	1.5	−583	−614 ± 14	921 ± 27	0	2
		−1014 ± 3	−116 ± 15	105 ± 17	4			−590 ± 6	1118 ± 30	−227 ± 33	7
0.25	−1232	−1221 ± 6	168 ± 12	0	9	2	−109	−89 ± 10	1381 ± 20	0	16
		−1231 ± 5	94 ± 23	86 ± 25	6			−107 ± 5	1238 ± 27	164 ± 30	7
40 °C											
0.025	−646	−667 ± 14	−245 ± 26	0	21	0.5	−1287	−1291 ± 3	306 ± 5	0	4
		−643 ± 5	−53 ± 23	−220 ± 25	6			−1291 ± 4	311 ± 18	−6 ± 20	5
0.05	−840	−835 ± 3	−221 ± 5	0	4	1	−1047	−1047 ± 4	663 ± 7	0	6
		−835 ± 4	−227 ± 19	6 ± 21	5			−1047 ± 5	660 ± 26	4 ± 29	6
0.1	−1030	−1012 ± 9	−11 ± 18	0	14	1.5	−653	−653 ± 5	856 ± 9	0	7
		−282 ± 3	−143 ± 17	152 ± 18	4			−647 ± 5	906 ± 23	−57 ± 26	6
0.25	−1253	−1422 ± 6	167 ± 11	0	9	2	−174	−155 ± 10	136 ± 19	0	15
		−1250 ± 5	99 ± 23	78 ± 26	6			−172 ± 6	1229 ± 28	155 ± 31	7
45 °C											
0.025	−652	−671 ± 13	−242 ± 24	0	19	0.5	−1313	−1321 ± 5	302 ± 9	0	7
		−648 ± 4	−62 ± 18	−206 ± 20	4			−1315 ± 4	349 ± 22	−54 ± 24	5
0.05	−846	−850 ± 4	−236 ± −8	0	7	1	−1093	−1090 ± 4	646 ± 8	0	6
		−844 ± 3	−182 ± 14	−63 ± 15	3			−1092 ± 5	633 ± 27	14 ± 30	7
0.1	−1040	−1026 ± 9	−10 ± 16	0	13	1.5	−699	−683 ± 6	808 ± 11	0	9
		−1041 ± 3	−133 ± 14	141 ± 15	3			−689 ± 7	762 ± 34	52 ± 37	8
0.25	−1274	−1264 ± 5	165 ± 10	0	8	2	−232	−219 ± 9	134 ± 17	0	13
		−1292 ± 4	105 ± 20	70 ± 22	5			−233 ± 6	1229 ± 28	128 ± 31	7

Table 2 (Continued)

I^a	$10^4(\log \gamma_{\text{Aexp}})$	$10^4(\log \gamma_{\text{Å}} \pm \sigma)$	$10^4(\alpha_{\text{AB}} \pm \sigma)$	$10^4(\beta_{\text{AB}} \pm \sigma)$	10^4(rmsd)	I^a	$10^4(\log \gamma_{\text{Aexp}})$	$10^4(\log \gamma_{\text{Å}} \pm \sigma)$	$10^4(\alpha_{\text{AB}} \pm \sigma)$	$10^4(\beta_{\text{AB}} \pm \sigma)$	10^4(rmsd)
					50 °C						
0.025	−661	−679 ± 11	−263 ± 21	0	16	0.5	−1339	−1344 ± 5	297 ± 10	0	8
		−659 ± 3	−109 ± 13	−177 ± 14	3			−1339 ± 6	342 ± 28	−52 ± 31	7
0.05	−857	−875 ± 12	−272 ± 23	0	18	1	−1138	−1135 ± 4	626 ± 7	0	6
		−854 ± 4	−104 ± 20	−192 ± 22	5			−1136 ± 5	619 ± 25	9 ± 28	6
0.1	−1052	−1033 ± 11	−5 ± 21	0	17	1.5	−758	−730 ± 13	737 ± 25	0	20
		−1053 ± 3	−162 ± 17	181 ± 18	4			−751 ± 7	569 ± 37	194 ± 41	9
0.25	−1285	−1380 ± 6	165 ± 11	0	9	2	−301	−280 ± 10	1313 ± 19	0	15
		−1287 ± 6	109 ± 30	65 ± 32	7			−296 ± 7	1188 ± 33	144 ± 36	8
					55 °C						
0.025	−666	−690 ± 14	−250 ± 27	0	22	0.5	−1370	−1376 ± 6	311 ± 12	0	9
		−664 ± 3	−46 ± 16	−233 ± 17	4			−1370 ± 7	362 ± 33	−58 ± 36	8
0.05	−865	−872 ± 6	−213 ± 12	0	10	1	−1192	−1191 ± 4	608 ± 8	0	6
		−862 ± 4	−130 ± 19	−95 ± 21	5			−1188 ± 5	632 ± 26	−27 ± 28	6
0.1	−1063	−1052 ± 7	10 ± 12	0	10	1.5	−826	−788 ± 17	657 ± 33	0	27
		−1062 ± 7	−78 ± 19	101 ± 20	5			−818 ± 8	418 ± 39	275 ± 42	9
0.25	−1325	−1319 ± 7	165 ± 14	0	11	2	−368	−345 ± 14	1297 ± 27	0	21
		−133 ± 7	91 ± 34	85 ± 37	8			−367 ± 8	1114 ± 37	212 ± 34	10

[a] mol kg^{-1}.

taken to avoid loss of water to evaporation, and vacuum corrections were applied to all weighings.

The emf voltages were measured using a Keithley (model 191) digital voltmeter. The emf cells were placed in a thermostatic bath, regulated to within ±0.005 K. The temperature of the bath was monitored with a digital platinum resistance thermometer (Guildline model 9540). Since an uncertainty of 0.1 K corresponds to an uncertainty of approximately 0.05 mV in emf, the temperature variations between each cell were considered negligible. The cells were of the all-glass type, providing a triple saturator for the hydrogen gas, as described by Bates.[20] The hydrogen electrodes were prepared in the usual manner[17] and platinized according to the recommendation of Feltham and Spiro.[21] The (Ag + AgCl) electrodes were of the thermal electrolytic type[20] with a bias potential within 0.05 mV. The first emf measurement was made at 298.15 K; the temperature was then lowered to 278.15 K in increments of 5 K. The emf was measured again at 298.15 K and finally at temperatures incremented by 5 K up to 328.15 K. Typically, the average deviation between the emf readings taken at the start of the run and in the middle at 298.15 K was well within 0.06 mV, which corresponds to an uncertainty of 5×10^{-4} in $\log \gamma_{\text{HCl}}$ at that temperature. The uncertainty in the experimental potentials is primarily related to (i) irreversible behavior of the electrodes, especially at high ionic strengths, (ii) errors made in the preparation of stock solutions as well as cell solutions, (iii) consistency of temperature measurement and control, and (iv) purity (oxygen free) of the hydrogen gas. The emf method has been found to produce excellent data for mixtures of HCl and metal chloride salts with multiple electric charges.[1,5,7,11,22] All the emf measurements corrected to a standard atmospheric pressure of 101.325 kPa are listed in Table 1. The values of the standard electrode potentials, $E°$, at the experimental temperatures were taken from ref 17.

3. Calculations and Results

3.1. Harned's Equations. It has been shown by Harned[23] that, for many mixed electrolyte solutions (acid salt mixtures) with a common ion at constant total ionic strength, the activity coefficients can be expressed using the Harned equation:

$$\log \gamma_{\text{A}} = \log \gamma°_{\text{A}} - \alpha_{\text{AB}} Y_{\text{B}} - \beta_{\text{AB}} {Y_{\text{B}}}^2 \tag{3}$$

in which $Y_{\text{B}} = 6m_{\text{B}}/(m_{\text{A}} + 6m_{\text{B}})$ is the ionic strength fraction of EuCl_3 (B), α_{AB} and β_{AB} are interaction coefficients, and γ_{A} and $\gamma°_{\text{A}}$ are the activity coefficients of HCl in the mixture and in pure HCl at an ionic strength equal to the total ionic strength of the mixture, respectively. When $\beta_{\text{AB}} = 0$ in eq 3, Harned's rule is obeyed. The values of $\log \gamma°_{\text{A}}$, α_{AB}, and β_{AB} along with the standard deviation of the fit of $\log \gamma_{\text{A}}$ versus Y_{B} are given in Table 2.

3.2. Pitzer's Equations for Mixed Electrolytes. The present paper reports an analysis of the results (activity coefficients, Pitzer's mixing parameters $\Theta_{\text{H,Eu}}$ and $\Psi_{\text{H,Cl,Eu}}$, etc.) in terms of the comprehensive ion-interaction treatment of Pitzer.[15,24−27] The behavior is fairly simple for salts with singly charged cations, with only minor differences between the H−M interactions of unlike ions and the average for H−H and M−M interactions.[28] These differences are substantial for 3−1 mixing. The mean molal activity coefficient of HCl and the ion-interaction equation for $\ln \gamma_{\text{HCl}}$[26] in a mixed solution of HCl + EuCl_3 are given by

$$\begin{aligned} \ln \gamma_{\text{HCl}} = {} & f^{\gamma} + (m_{\text{H}} + m_{\text{Cl}})(B_{\text{HCl}} + m_{\text{Cl}} C_{\text{HCl}}) + \\ & m_{\text{Eu}}(B_{\text{EuCl}_3} + m_{\text{Cl}} C_{\text{EuCl}_3} + {}^{\text{E}}\Theta_{\text{H,Eu}} + \Theta_{\text{H,Eu}}) + \\ & m_{\text{H}} m_{\text{Cl}}(B'_{\text{HCl}} + C_{\text{HCl}}) + m_{\text{Eu}} m_{\text{Cl}}(B'_{\text{EuCl}_3} + C_{\text{EuCl}_3} + \\ & {}^{1}/_{2}\Psi_{\text{H,Eu,Cl}}) + m_{\text{H}} m_{\text{Eu}}({}^{\text{E}}\Theta'_{\text{H,Eu}} + {}^{1}/_{2}\Psi_{\text{H,Eu,Cl}}) \end{aligned} \tag{4}$$

where

$$f^{\gamma} = -A_{\phi}[I^{1/2}/(1 + 1.2I^{1/2}) + (2/1.2)\ln(1 + 1.2I^{1/2})] \tag{5}$$

$$B_{\text{MX}} = \beta^{(0)}{}_{\text{MX}} + (2\beta^{(1)}{}_{\text{MX}}/4I)[1 - (1 + 2I^{1/2})\exp(-2I^{1/2})] \tag{6}$$

$$B'_{\text{MX}} = (\beta^{(1)}{}_{\text{MX}}/2I^2)[-1 + (1 + 2I^{1/2} + 2I)\exp(-2I^{1/2})] \tag{7}$$

$$C_{\text{MX}} = C^{\phi}{}_{\text{MX}}/(2|Z_{\text{M}} Z_{\text{X}}|^{1/2}) \tag{8}$$

The Debye−Hückel limiting law is determined from[29]

$$A_{\phi} = (1/3)(2\pi N\rho_{\text{w}}/1000)^{1/2}[e^2/(DkT)]^{3/2} \tag{9}$$

where T is the temperature in Kelvin, N = Avogadro number = $6.022\,045 \times 10^{23}$, ρ_{w} = density of water, e = charge of electron = $1.602\,177 \times 10^{-19}$ C, D = relative

Table 3. Pitzer Parameters for HCl and $EuCl_3$ and Their Mixtures at 25 °C[a]

electrolyte	$\beta^{(0)}$	$\beta^{(1)}$	$10^{-2}C^{\phi}$	ref
HCl	0.175 57	0.2978	0.1369	32
$EuCl_3$	0.607 67	5.6	−2.105	31

electrolyte	$10^{-5}\partial\beta^{(0)}/\partial T$	$10^{-2}\partial\beta^{(1)}/\partial T$	$10^{-4}\partial C^{\phi}/\partial T$	ref
$EuCl_3$	1.58	0.852	−3.21	31

electrolyte	$10^{-5}\beta^{(0)J}$	$10^{-5}\beta^{(1)J}$	$10^{-7}C^{J}$	ref
$EuCl_3$	−1.3559	16.1856	0	33

electrolyte	$\Theta_{H,Eu}$	$\Psi_{H,Eu,Cl}$	ref
HCl + $EuCl_3$	0.2 ± 0.03	0	this study

[a] The equations relating these parameters are given in ref 34.

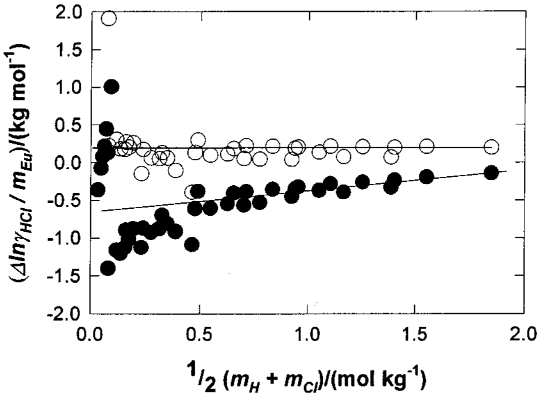

Figure 1. Values of $\Delta \ln \gamma_{HCl}/m_{Eu}$ = [$\ln \gamma_{HCl}$(meas) − $\ln \gamma_{HCl}$(calc)]/m_{Eu} as a function of $^1/_2(m_H + m_{Cl})$ at 25 °C. The open circles are calculated with unsymmetrical mixing terms, and the closed circles, without. The intercept of the line going through the empty circles gives $\Theta_{H,Eu} = 0.2 \pm 0.03$, and its slope gives $\Psi_{H,Eu,Cl} = 0$.

permittivity of water, and k = Boltzmann constant = $1.380\ 66 \times 10^{-23}$ J K^{-1}. The relative permittivity of water (D) was calculated from the equations of Bradley and Pitzer[30] and was described elsewhere.[18]

The values of $\beta^{(0)}$, $\beta^{(1)}$, and C^{ϕ} for $EuCl_3$ are only available[31] at 25 °C and are given in Table 3, along with the values for HCl which were taken from Campbell et al.[32] The higher order mixing terms $\Theta_{H,Eu}$ and $\Psi_{H,Eu,Cl}$ can be estimated from

$$\Delta \ln \gamma_{HCl} = \ln \gamma_{HCl}(\text{meas}) - \ln \gamma_{HCl}(\text{calc}) = m_{Eu}[\Theta_{H,Eu} + {}^1/_2(m_H + m_{Cl})\Psi_{H,Eu,Cl}] \qquad (10)$$

where $\ln \gamma_{HCl}$(meas) is the measured value and $\ln \gamma_{HCl}$(calc) is the calculated value using all the known parameters including the higher order electrical contributions,[25] $^E\Theta_{H,Eu}$ and $^E\Theta'_{H,Eu}$. A plot of $\Delta \ln \gamma_{HCl}/m_{Eu}$ as a function of $^1/_2(m_H + m_{Cl})$ at 25 °C is shown in Figure 1. For clarity purposes, the scale on the y axis has been set from −2 to 2 but the actual deviations go up to 14 with unsymmetrical mixing terms (18 without) at low values of $^1/_2(m_H + m_{Cl})$. The closed circles are the values calculated without the unsymmetrical mixing terms $^E\Theta_{H,Eu}$ and $^E\Theta'_{H,Eu}$ while the open circles are calculated with them. The least-squares fit of the open circles, weighed by the molality of europium, gives a value of $\Theta_{H,Eu} = 0.2 \pm 0.03$. An F-test showed that adding the $\Psi_{H,Eu,Cl}$ term did not improve the fit significantly at 25 °C. A comparison of the values of γ_{HCl} at 25 °C calculated with and without $\Theta_{H,Eu}$ is shown in Figure 2. The standard errors in γ_{HCl} are 0.016 with and 0.021 without the higher order electrical terms. These standard errors come down to 0.008 and 0.018, respectively, for ionic strengths above 0.05 mol kg^{-1}.

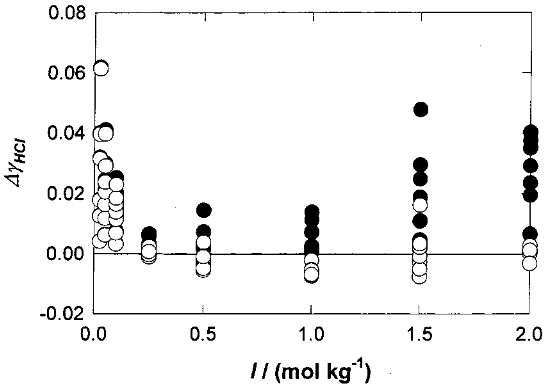

Figure 2. Values of $\Delta \ln \gamma_{HCl}$ = [$\ln \gamma_{HCl}$(meas) − $\ln \gamma_{HCl}$(calc)] at 25 °C. The activity coefficients are calculated with (open circles) and without (closed circles) the higher order electrical terms ($\Theta_{H,Eu}$ = 0.2 and $\Psi_{H,Eu,Cl}$ = 0).

Enthalpy[31] and heat capacity[33] data are available for $EuCl_3$ and are given in Table 3. These thermodynamic data have been used to estimate the effect of temperature on the Pitzer parameters for $EuCl_3$. The resulting temperature dependence of the $EuCl_3$ parameters can be expressed by

$$\beta^{(0)}{}_{EuCl_3} = 0.607\ 67 + [(-1.3559 \times 10^{-5})/3T_R - (1.58 \times 10^{-5})]T_R^{\,2}(1/T - 1/T_R) + (-1.3559 \times 10^{-5})/6(T^2 - T_R^{\,2}) \qquad (11)$$

$$\beta^{(1)}{}_{EuCl_3} = 5.6 + [(1.61856 \times 10^{-4})/3T_R - (0.852 \times 10^{-2})]T_R^{\,2}(1/T - 1/T_R) + (1.61856 \times 10^{-4})/6(T^2 - T_R^{\,2}) \qquad (12)$$

$$C^{\phi}{}_{EuCl_3} = -2.105 \times 10^{-2} + (3.21 \times 10^{-4})T_R^{\,2}(1/T - 1/T_R) \qquad (13)$$

where T is the temperature in Kelvin and T_R = 298.15 K.

Using these parameters (eqs 11 to 13) and the value of $\Theta_{H,Eu}$ previously determined, we calculated the mean activity coefficients of HCl. A comparison of these results with the experimental values is shown as a function of temperature and ionic strength in Figure 3 (the bottom graph only shows ionic strengths higher than 0.05 mol kg^{-1}). The effect of temperature on $\Theta_{H,Eu}$ was not needed to reproduce the experimental data. For $I > 0.05$ mol kg^{-1}, the average deviation in γ_{HCl} is 0.002 ± 0.009. The standard error on γ_{HCl} over the entire range of temperatures and ionic strengths is $\sigma = 0.017$ and decreases to $\sigma = 0.009$ for $I > 0.05$ mol kg^{-1}, which is slightly higher than the experimental error due to some scatter in the data. The value of $\Theta_{H,Eu}$ (0.2 ± 0.03) for the interactions of H−Eu is comparable to the values determined for other trivalent ions such as La(III)[7] (0.278 ± 0.009) and Sm(III)[18] (0.2 ± 0.01). These results indicate that most rare earth ions have similar values of $\Theta_{H,Ln}$. The lower value of Θ for Gd[17] (0.07) is partly due to the need for a Ψ term. The value determined in this study can be used to make reasonable estimates of activity coefficients in similar systems which have not been studied yet. For ions which hydrolyze, like In(III)[8,9] or Ga(III),[15,16] the determination of this parameter

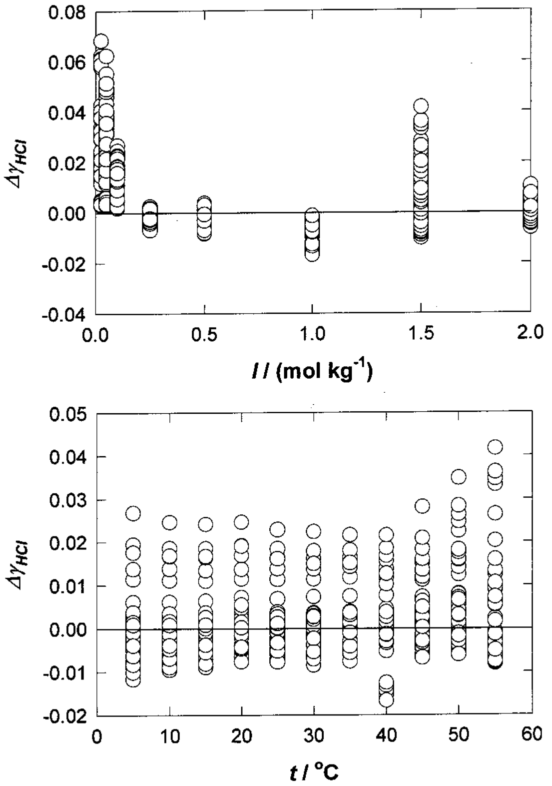

Figure 3. Values of $\Delta \ln \gamma_{HCl} = [\ln \gamma_{HCl}(\text{meas}) - \ln \gamma_{HCl}(\text{calc})]$ at all temperatures and ionic strengths (the bottom graph only shows ionic strengths higher than 0.05 mol kg^{-1}). The values were calculated using $\Theta_{H,Eu} = 0.2$ and $\Psi_{H,Eu,Cl} = 0$ with unsymmetrical mixing terms over the entire temperature range.

is more complicated, as the hydrolyzed product has to be taken into account and the value of Θ cannot be separated from the hydrolysis constant.

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