Table I. Derivatives of 2-(*p*-Aminoaryl)-2-arylethylamines (*Continued*)

Compound	M.P., °C.[a]	Yield, %	Solvent[b]	Analysis, %[c] C	H	N	Cl
N′-Carbethoxy-2-(4′-aminophenyl)-2-(4′-methoxy-				59.39	5.98	6.93	
phenyl)ethylamine monooxalate salt	95–7	84[d]	3–7	59.11	6.22	6.71	
N′-Carbethoxy-*N*-(2′-diethylaminoethyl)-2-(4′-amino-				57.53	6.62	7.45	
phenyl)-2-phenylethylamine dioxalate salt	190–3	41[d]	5	57.18	6.87	7.34	
N′-Carbethoxy-*N*-(2′-diethylaminoethyl)-2-(4′-amino-				58.22	6.80	7.28	
3′-methylphenyl)-2-phenylethylamine dioxalate salt	177–8	57[d]	5–8	57.92	6.90	6.91	
N′-Carbethoxy-*N*-(2′-diethylaminoethyl)-2-(4′-amino-				52.62	6.21	6.82	
3′-chlorophenyl)-2-phenylethylamine dioxalate salt monohydrate	170	42[d]	5	52.45	6.23	6.53	
N′-Carbethoxy-*N*-(2′-diethylaminoethyl)-2-(4′-amino-				56.65	6.62	7.08	
3′-methoxyphenyl)-2-phenylethylamine dioxalate salt	165	83[d]	9	56.39	6.63	7.00	
N′-Carbethoxy-*N*-(2′-diethylaminoethyl)-2-(4′-amino				54.22	6.07	7.03	
phenyl)-2-(4′-chlorophenyl)ethylamine dioxalate salt	169	57[d]	9	54.18	5.94	7.22	
N′-Carbethoxy-*N*-(2′-diethylaminoethyl)-2-(4′-amino-				54.98	6.76	6.87	
phenyl)-2-(4′-methoxyphenyl)ethylamine dioxalate salt monohydrate	180–1	62[d]	5	54.87	7.05	7.08	

[a] Melting points were determined using a copper block and are uncorrected. [b] Recrystallization solvents used: 1. methanol, 2. water, 3. benzene, 4. chloroform, 5. ethanol, 6. petroleum ether (b.p. 60 to 71° C.), 7. tetrahydrofuran, 8. ethyl acetate, 9. isopropyl alcohol. Where two numbers are indicated, co-solvents were used. [c] Analyses by Midwest Microlab, Inc., Indianapolis, Ind. First series calculated, second found. [d] Yield includes the step of salt formation.

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Thermodynamic Studies of Hydrochloric Acid in Tetrahydrofuran-Water Mixtures

RABINDRA N. ROY[1] and BUDDHADEV SEN
Louisiana State University, Baton Rouge, La.

The cell, Pt, H_2(1 atm.) | HCl(m), tetrahydrofuran (X), water (Y) | Agcl, Ag, has been used to investigate the thermodynamic properties of hydrochloric acid. Activity coefficients, medium effects, relative partial molal heat contents, and heat capacities for X = 8.98, 18.21, 47.20, 73.03, and 89.00 weight % tetrahydrofuran at various temperatures have been calculated.

THE ultimate purpose of our research program is to investigate the effect of the solvent on the thermodynamics of chemical equilibria (*1, 6, 13*). Hydrochloric acid appeared to be the most natural first choice as the system to study, aimed at finding an analytical function for the so-called medium effects.

To calculate the thermodynamic properties of hydrochloric acid in aqueous-organic mixed solvents (*2-5, 8-9*), the standard potential (*12*) of the reversible cell Pt, H_2 (1 atm.) | HCl (m), THF (X), H_2O (Y)| AgCl, Ag, was evaluated by a polynomial curve-fitting program. The cell was used to determine the activity coefficients, medium effects, relative partial molal heat contents, and relative partial molal heat capacities of hydrochloric acid for five different systems and at four different temperatures. This paper also describes the means of converting the values obtained from the mixed-solvent systems to those of the standard reference aqueous state by computational technique. The primary and secondary medium effects (*10*) are calculated in tetrahydrofuran (THF)-water (*11*) and 1,2-dimethoxyethane–water (*7*) mixtures.

THEORY

The mean activity coefficients of hydrochloric acid in the mixed solvents were calculated from the following rearranged Nernst equation:

$$\ln \gamma_\pm = \frac{{}^sE^0 - [{}^sE + (2RT/F)\ln m]}{(2RT/F)} \qquad (1)$$

in which ${}^sE^0$ is the standard potential in the mixed solvent and ${}^sE$ corresponds to E_{obsd} (*4*)—i.e., the potential corrected to a hydrogen pressure of 1 atm.

The primary medium effect is considered to be due to the difference in the solution energies in two different solvents and also is a measure of the energy involved in the transfer of an ion at an infinite dilution in one solvent to an infinite dilution of another solvent. This effect (log ${}^s_w\gamma^0_\pm$ HCl) of tetrahydrofuran–water mixtures upon hydrochloric acid was calculated from the equation:

$$({}^wE^0 - {}^sE^0) = \lim_{m \to 0}\left[\frac{4.606\,RT}{F}\log {}^s_w\gamma_\pm\right] = \frac{4.606RT}{F}\log {}^s_w\gamma^0_\pm \qquad (2)$$

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[1] Present address: Drury College, Springfield, Mo.

Table I. Values of the Mean Activity Coefficients of Hydrochloric Acid in Tetrahydrofuran–Water Mixtures at Various Temperatures

X = weight % of tetrahydrofuran

m	0° C.	15° C.	25° C.	35° C.
		$X = 0$[a]		
0.1	0.8027	0.8000	0.7964	0.7918
0.05	0.8346	0.8329	0.8304	0.8265
0.02	0.8774	0.8770	0.8755	0.8731
0.01	0.9065	0.9055	0.9048	0.9025
0.005	0.9303	0.9297	0.9285	0.9268
0.002	0.9541	0.9530	0.9521	0.9513
0.001	0.9668	0.9661	0.9656	0.9647
0.0005	0.9756	0.9757	0.9752	0.9745
0.0002	0.9848	0.9844	0.9842	0.9838
0.0001	0.9890	0.9890	0.9891	0.9886
		$X = 8.98$		
0.1	0.784	0.763	0.756	0.746
0.05	0.820	0.806	0.803	0.797
0.02	0.869	0.862	0.860	0.857
0.01	0.901	0.896	0.895	0.893
0.005	0.926	0.923	0.922	0.921
0.002	0.951	0.949	0.949	0.948
0.001	0.965	0.963	0.963	0.962
0.0005	0.975	0.974	0.973	0.973
0.0002	0.984	0.983	0.983	0.983
0.0001	0.988	0.988	0.988	0.988
		$X = 18.21$		
0.1	0.766	0.758	0.745	0.739
0.05	0.809	0.804	0.797	0.793
0.02	0.863	0.861	0.857	0.854
0.01	0.897	0.896	0.893	0.891
0.005	0.923	0.923	0.921	0.920
0.002	0.950	0.949	0.948	0.948
0.001	0.964	0.964	0.963	0.962
0.0005	0.974	0.974	0.973	0.973
0.0002	0.983	0.983	0.983	0.982
0.0001	0.988	0.988	0.987	0.987
		$X = 47.20$		
0.02	0.806	0.802	0.801	0.792
0.01	0.853	0.849	0.848	0.838
0.005	0.891	0.887	0.886	0.877
0.002	0.928	0.925	0.924	0.917
0.001	0.948	0.946	0.945	0.939
0.0005	0.963	0.961	0.960	0.956
0.0002	0.976	0.975	0.974	0.971
0.0001	0.984	0.982	0.981	0.979
		$X = 73.03$		
0.1	0.327	0.296	0.276	0.240
0.05	0.349	0.341	0.312	0.287
0.02	0.448	0.444	0.416	0.397
0.01	0.543	0.535	0.511	0.496
0.005	0.636	0.626	0.607	0.594
0.002	0.742	0.733	0.719	0.709
0.001	0.806	0.798	0.788	0.781
0.0005	0.857	0.851	0.843	0.838
0.0002	0.906	0.901	0.896	0.893
0.0001	0.932	0.929	0.925	0.923
		$X = 89.00$		
0.1	0.144	0.118	0.105	0.077
0.05	0.162	0.132	0.118	0.088
0.02	0.204	0.173	0.147	0.112
0.01	0.265	0.233	0.196	0.156
0.005	0.349	0.316	0.271	0.226
0.002	0.479	0.448	0.398	0.350
0.001	0.578	0.551	0.503	0.457
0.0005	0.670	0.647	0.604	0.563
0.0002	0.770	0.753	0.719	0.687
0.0001	0.829	0.816	0.789	0.763

[a] Data corresponding to $X = 0$ taken from Harned and Owen (4).

in which ${}^{w}E^{0}$ is the standard potential of the cell in aqueous medium relative to the unit value at infinite dilution in pure water, and $\mathrm{Lt}_{m \to 0}\, {}^{S}_{w}\gamma_{\pm}$ is the mean activity coefficient of hydrochloric acid at zero molality in a mixed solvent referred to unity at infinite dilution in the aqueous state.

A secondary medium effect is defined as due to the difference in ion-ion interactions in two different solvents and is thermodynamically represented by:

$$\ln \frac{{}^{S}_{w}\gamma_{\pm}}{{}^{w}_{w}\gamma} = \mathrm{Lt}_{m \to 0}\left[\ln {}^{S}_{w}\gamma_{\pm}\right] + \ln \frac{{}^{s}_{S}\gamma_{\pm}}{{}^{w}_{w}\gamma_{\pm}} \tag{3}$$

in which superscripts w and s indicate that the measurements are being carried out in water and in mixed solvent, respectively. Subscripts w and s on the mean activity coefficients ($\gamma_{\pm}$) indicate that $\gamma_{\pm}$ is measured relative to unit value at infinite dilution in water and in mixed solvents, respectively. The term on the left-hand side represents the total medium effect and the terms on the right-hand side represent the primary and secondary medium effects, respectively.

A relative partial molal property may be defined as the difference between the partial molal property in a given solution and its value in the reference state—i.e., relative to infinite dilution of the solvent. Determination of the relative partial molal heat content, $\bar{L}_2$, from electromotive force measurements depends on the accuracy with which the temperature coefficient of the electromotive force can be determined. $\bar{L}_2$ can be computed from the equation

$$\bar{L}_2 = -F\,(a - a_o) + F\,(c - c_o)T^2 \tag{4}$$

in which T represents the absolute temperature in degrees Kelvin and the constants a, a_o, etc., can be determined from the following quadratic equations,

$$s_E = a + bT + cT^2 \tag{5}$$

and

$$s_E^0 = a_o + b_oT + c_oT^2 \tag{6}$$

The relative partial molal heat capacity, $\bar{J}_2$, of electrolytes (hydrochloric acid) in mixed solvents can be computed from the equation

$$\bar{J}_2 = 2F\,(c - c_o)T \tag{7}$$

in which coefficients c, c_0, etc., are easily determined by the method of least squares from the e.m.f. data at various temperatures.

EXPERIMENTAL

Purification of the solvent, preparation of the solution, and other experimental details have been described (*12*).

RESULTS AND DISCUSSION

The mean activity coefficients of hydrochloric acid given in Table I were calculated by computer (IBM 1620), using

Table II. Primary Medium Effect (log ${}^{s}_{w}\gamma^{\circ}_{\pm}$ HCl) of Tetrahydrofuran-Water Mixtures upon Hydrochloric Acid at Various Temperatures

X = weight % of tetrahydrofuran

X	0° C.	15° C.	25° C.	35° C.
8.98	0.0173	0.0609	0.0732	0.0517
18.21	0.1838	0.1569	0.1571	0.1420
47.20	0.3035	0.3668	0.4373	0.4083
73.03	1.0199	1.0227	1.0924	1.1641
89.00	1.8689	2.0233	2.0975	2.2289

Equation 1. The appropriate values of standard potential (${}^{s}E^{\circ}$) and observed potentials (${}^{s}E$) were obtained from the tables published earlier *(12)*. A careful examination of the data listed in Table I shows that in a given system and at a given temperature, the increase in the value of the mean activity coefficient corresponds to the decrease in molality of hydrochloric acid. The activity coefficients at any concentration decrease with increasing temperature. The general trends of our results (THF-H_2O) are in close agreement with those obtained by Harned and his coworkers in other mixed solvents *(2-5, 8-9)*. For X = 8.98 and 18.21, the error in the values of the activity coefficient was ±0.004, whereas for 47.20, 73.03, and 89.00 weight % THF the errors were estimated to be ±0.040, respectively.

Table III. Secondary Medium Effect of Tetrahydrofuran–Water Mixtures upon Hydrochloric Acid at Various Temperatures

X = weight % of tetrahydrofuran

m	0° C.	15° C.	25° C.	35° C.
		X = 8.98		
0.1	−0.010122	−0.020490	−0.022477	−0.025677
0.05	−0.007679	−0.013834	−0.014450	−0.015805
0.02	−0.004199	−0.007710	−0.007694	−0.008291
0.01	−0.002812	−0.004691	−0.004696	−0.004727
0.005	−0.001912	−0.003167	−0.002760	−0.002704
0.002	−0.001296	−0.001691	−0.001330	−0.001397
0.001	−0.000914	−0.001206	−0.000999	−0.000886
0.0005	−0.000402	−0.000862	−0.000643	−0.000532
0.0002	−0.000452	−0.000531	−0.000441	−0.000387
0.0001	−0.000243	−0.000421	−0.000461	−0.000327
		X = 18.21		
0.1	−0.020182	−0.023621	−0.029018	−0.029982
0.05	−0.013639	−0.015135	−0.018018	−0.018209
0.02	−0.007321	−0.008021	−0.009358	−0.009452
0.01	−0.004789	−0.004728	−0.005661	−0.005420
0.005	−0.003195	−0.003102	−0.003337	−0.003130
0.002	−0.002043	−0.001599	−0.001635	−0.001630
0.001	−0.001418	−0.001123	−0.001193	−0.001038
0.0005	−0.000747	−0.000794	−0.000770	−0.000633
0.0002	−0.000664	−0.000483	−0.000515	−0.000448
0.0001	−0.000390	−0.000385	−0.000512	−0.000369
		X = 47.20		
0.02	−0.036822	−0.038894	−0.038296	−0.042339
0.01	−0.026380	−0.028036	−0.028114	−0.032292
0.005	−0.018786	−0.020322	−0.020254	−0.024081
0.002	−0.012029	−0.012905	−0.012938	−0.016037
0.001	−0.008480	−0.009264	−0.009406	−0.011653
0.0005	−0.005700	−0.006625	−0.006689	−0.008358
0.0002	−0.003717	−0.004212	−0.004321	−0.005457
0.0001	−0.002476	−0.003037	−0.003226	−0.003956
		X = 73.03		
0.1	−0.390416	−0.432002	−0.460819	−0.518252
0.05	−0.378162	−0.388153	−0.424442	−0.459697
0.02	−0.291218	−0.295516	−0.323138	−0.342678
0.01	−0.221829	−0.229120	−0.247756	−0.260292
0.005	−0.165040	−0.172094	−0.184633	−0.192974
0.002	−0.108746	−0.114629	−0.121971	−0.127099
0.001	−0.078572	−0.083083	−0.088306	−0.091683
0.0005	−0.056402	−0.059521	−0.063379	−0.065691
0.0002	−0.036125	−0.038412	−0.040679	−0.042134
0.0001	−0.025756	−0.027287	−0.029114	−0.030038
		X = 89.00		
0.1	−0.746145	−0.830791	−0.881138	−0.010984
0.05	−0.711191	−0.799223	−0.846980	−0.974527
0.02	−0.633004	−0.705222	−0.776094	−0.892611
0.01	−0.533416	−0.590021	−0.663308	−0.762094
0.005	−0.425938	−0.468994	−0.534422	−0.613709
0.002	−0.299444	−0.328034	−0.378244	−0.434322
0.001	−0.223063	−0.243922	−0.282927	−0.324623
0.0005	−0.163334	−0.178653	−0.207965	−0.238553
0.0002	−0.106863	−0.116517	−0.136149	−0.156165
0.0001	−0.076706	−0.083718	−0.098086	−0.112380

Table IV. Coefficients of the Empirical Equation: $E_{obsd} = a + bT + cT^2$

m	$a \times 10^2$	$b \times 10^3$	$c \times 10^6$	Standard Error
		X = 8.98		
0.089050	10.86695	1.90426	−3.68755	0.00119
0.044490	39.46164	0.03532	−0.25967	0.00071
0.035190	43.27598	−0.18656	0.18243	0.00064
0.007790	83.11505	−2.66683	4.85265	0.00053
0.004620	90.79479	−3.10026	5.73599	0.00055
0.002310	185.29968	−9.44101	16.72599	0.00581
		X = 18.21		
0.09440	10.40319	1.80400	−3.40445	0.00248
0.045010	3.15607	2.41728	−4.23599	0.00201
0.035600	3.10113	2.45108	−4.22001	0.00192
0.013140	4.53758	2.48898	−3.97602	0.00157
0.004670	0.38614	2.92101	−4.39029	0.00134
0.002340	0.75561	2.99972	−4.30891	0.00124
		X = 47.20		
0.093390	138.05875	−6.64663	10.30573	0.00385
0.046650	82.41743	−2.75175	3.88285	0.00729
0.013620	139.54397	−6.46881	10.05421	0.00404
0.008170	180.91995	−9.25640	15.50091	0.00281
0.004840	55.79892	−0.58393	0.82117	0.00124
0.002420	161.45116	−7.71599	13.19719	0.00347
		X = 73.03		
0.096320	105.72032	−4.46721	6.23777	0.00034
0.048110	50.09249	−0.52976	−0.39505	0.00045
0.022830	−8.07969	3.56728	−7.29597	0.00039
0.014040	−40.23888	5.83925	−11.10323	0.00016
0.004990	−92.47722	9.56694	−17.28230	0.00043
0.002500	−227.93697	18.93736	−33.09884	0.00590
		X = 89.00		
0.098170	111.35684	−5.25294	7.44515	0.00032
0.049040	102.32608	−4.52393	6.35082	0.00035
0.023260	115.66118	−5.35789	7.97230	0.00119
0.014320	98.15925	−4.02875	5.64844	0.00226
0.002540	65.89399	−1.33844	0.80342	0.00293

Table V. Coefficients of the Empirical Equation

$$E_o = a_o + b_oT + c_oT^2$$

E_o = standard potential

X = weight % of tetrahydrofuran

X	$a_o \times 10^2$	$b_o \times 10^3$	$c_o \times 10^6$	Standard Error
8.98	117.9971	−5.8778	8.8506	0.000769
18.21	−0.1689	1.9829	−4.3315	0.000968
47.20	136.2621	−6.9997	10.0999	0.003896
73.03	−151.2246	12.6655	−24.4081	0.001543
89.00	−26.8913	4.3659	−11.9284	0.002415

There is no appreciable ionic association for x = 8.98 and 18.21, whereas for X = 47.20 there is a barely noticeable evidence of ionic association. Interaction appears to be considerable in 73.03 weight % THF. Hydrochloric acid behaves as a weak electrolyte at X = 89.00.

The values of the primary medium effect of THF-H_2O mixtures upon hydrochloric acid are presented in Table II. The medium has a greater effect upon the ions as the concentration of the organic solvent is gradually increased.

The values of the secondary medium effect given in Table III for five systems and at four different temperatures

Table VI. Relative Partial Molal Quantities, $\bar{L}_2$ and $\bar{J}_2$

X = weight % of tetrahydrofuran

	0° C.		15° C.		25° C.		35° C.	
m	$\bar{L}_2$	$\bar{J}_2$	$\bar{L}_2$	$\bar{J}_2$	$\bar{L}_2$	$\bar{J}_2$	$\bar{L}_2$	$\bar{J}_2$
				X = 18.21				
0.094400		11		12		13		13
0.013140		4.4		4.7		4.8		5
0.002340		0.25		0.26		0.28		0.29
				X = 47.20				
0.008170					772	74	1527	76
0.002420					526	43	958	44
				X = 73.03				
0.096320					3582	421	7867	435
0.022830					2210	236	3883	242
0.014040					1692	183	3553	189
0.004990					1069	98	2066	101
				X = 89.00				
0.04904	1656	230	5205	243	7677	251	10233	260
0.014320	1395	221	4807	233	7182	243	9639	250
0.002540	514	160	2986	169	4707	175	6488	181

were taken directly from the computer. The characteristic of this effect in the THF-H_2O media seems to be normal and conforms to a pattern similar to that in other mixed solvents (*2-5, 8, 9*).

The relative partial molal heat content, $\bar{L}_2$, and the relative partial molal heat capacity, $\bar{J}_2$ were calculated by means of Equations 4 and 7 with the appropriate coefficients given in Tables IV and V. A partial list of the values of $\bar{L}_2$ and $\bar{J}_2$ is given in Table IV. The determinations of $\bar{L}_2$ and $\bar{J}_2$ from electromotive force measurements are very sensitive to experimental errors. An error of ±32 cal. for $\bar{L}_2$ is considered satisfactory, because this error corresponds to an error of ±0.001 mv. per degree in the measurement of potential. Since the computation of $\bar{J}_2$ involves the second differential coefficient of the original electromotive force data, high accuracy cannot be expected. An error of approximately ±12 cal. for $\bar{J}_2$ is considered to be satisfactory for the highest concentration of the organic solvent (89.00%). Calorimetric values are better than those derived from electromotive force data.

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