Activity Coefficients in Mixed Aqueous Solutions from Electromotive Force Measurements. Mixtures of Hydrochloric Acid with Trichloroacetic, Trifluoroacetic, and Iodic Acids

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Osmotic and activity coefficients are reported for trichloroacetic acid solutions in the concentration range 0–2.0 *m*. Activity coefficients calculated from electromotive force measurements are reported for mixtures of hydrochloric acid with trichloroacetic, trifluoroacetic, and iodic acids over the approximate range 0–1.0 *m* at 298.15 K.

We have been interested for some time in the behavior of "almost strong" acids. This is a relatively small group which is comprised of acids having an ionization constant in the range 10^{-1}–10. Studies of some of these acids such as iodic acid and sulfamic acid have yielded no unexpected results. Trichloroacetic (HTCA) and trifluoroacetic (HFTA) acids have been, however, quite interesting subjects of investigation since their ionization processes are more difficult to define.

Our first difficulties arose with HTCA when we observed (*1*) that an extrapolation of the concentration equilibrium quotient to infinite dilution was not possible using the Debye–Hückel relationship. This was, of course, due to the fact that acid activity coefficients did not follow the D–H limiting law in dilute solutions. Covington and co-workers subsequently observed (*2*) that the ionization constant of HTCA as measured from Raman spectra of the carboxyl stretching frequency was an order of magnitude larger than had been reported earlier from dilute solution measurements of the hydrogen ion concentration. We proposed (*3*) that this unusual behavior was caused by a competition for free protons between the carboxyl group which forms a covalent bond and the trichloro end of the acid which is available to form a very stable hydrogen-bonded ion pair. Nuclear magnetic resonance measurements (*4*) of chlorine line broadening and chemical shifts furnished experimental evidence for hydrogen bonding to the trichloro group of HTCA. The emf data of this paper are presented as further evidence of the somewhat surprising conclusions which were required by the earlier work on trichloro- and trifluoroacetic acids.

Method

We have been unable to measure osmotic and activity coefficients of the trihaloacetic acids by the isopiestic technique because of their volatility in aqueous solutions. A somewhat less accurate technique, vapor pressure osmometry, permits the estimation of osmotic activity coefficients in dilute solutions (*5*, *6*) to somewhat better than ±1% uncertainty even when the solute is slightly volatile. We have used this method to measure the reported coefficients for HTCA. The greater volatility of HTFA caused too large an uncertainty to justify the publication of the data. The measurements were performed in the manner described previously (*5*) with each solution of HTCA being bracketed by two solutions of NaCl of known water activity. Activity coefficients were calculated from the Gibbs–Duhem relationship.

The electromotive force measurements were made using a low-resistance glass electrode rather than a platinum electrode with bubbling hydrogen because of unwanted secondary electrode reactions which will be discussed later. A description of the electrode has been given previously (*7*) and the experimental techniques and potentiometer for high-resistance systems have also been described (*8*).

Results and Discussion

Osmotic and activity coefficients of trichloroacetic acid are given in Table I. A comparison of the values of these coefficients with those of other 1,1 electrolytes suggest that HTCA cannot be a very weak acid. This type of data can be deceptive, however, because of solvation or solvent structure altering effects on activity and osmotic coefficients. The ratio of the osmotic coefficients of the acid to one of its salts is a better guide to acid strengths and this ratio for acid to lithium salt for I^-, NO_3^-, TCA^- and IO_3^- are shown in Figure 1. From this comparison HTCA again appears to be a stronger acid than HIO_3 (*2*).

It was our original intention to study the HCl–trihaloacetic acid systems using the cell Pt, H_2, HCl (m_1),HTXA (m_2),AgCl,Ag but the platinized platinum electrode catalyzed secondary electrode reactions leading to unstable voltages. It is believed that one such reaction is removal of the halogen atom by a proton since tribromoacetic acid is observed to become colored rather rapidly when placed in platinum isopiestic dishes. It was, therefore, necessary to use a glass electrode to measure hydrogen ion activity in the manner described in the experimental portion. Experimental data for the HCl–HTCA and HCl–HTFA systems are given in Tables II and III. The HCl activity coefficients are calculated from the relationship

$$\epsilon = \epsilon^\circ - 0.1183 \log (m \pm \gamma_\pm)_{HCl}$$

The value of ϵ° is, of course, dependent upon the concentration of internal HCl. The method of calibration of the electrode is the same as was previously reported (*7*). A comparison of these data with the activity coefficients of HCl in HCl–HIO_3 solutions is very desirable since reported measurements of K_a for HIO_3 and HTCA by conductance or indicator techniques yield very similar ionization constants (*2*). Another difficulty arose here when it was observed that voltages of solutions more concentrated than 0.1 *m* in HIO_3 were unstable. This is caused by a secondary electrode reaction with the AgCl electrode which can be represented by the equation

$$HIO_3 + 5HCl + AgCl = 3Cl_2 + AgI + 3H_2O \quad \epsilon^\circ = +0.751 \text{ V}$$

This reaction occurs very slowly relative to the primary electrode reaction in dilute solutions, and the data for solutions less concentrated in HIO_3 than 0.1 *m* are believed to be very nearly correct. The HCl–HIO_3 system is included with the HCl–trihaloacetic acid systems in Figure 2 and to furnish a comparison the HCl-*p*-toluenesulfonic acid system (*9*) is also included. The data of Figure 2 indicate again that the trihaloacetic acids are appreciably stronger acids than iodic acid (with HTFA lowering the activity coeficient of HCl more than HTCA in solutions more dilute than μ = 1.0 *m*) and are in agreement with previous results obtained by Raman measurements (*2*) and ion exchange (*1*, *3*). It appears than that one may obtain a value of K_a for HTCA of greater than unity by several experimental methods

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Table I. Osmotic and Activity Coefficients of Trichloroacetic Acid at 298.15 K

molality	Φ	γ	molality	Φ	γ	molality	Φ	γ
0.1	0.926	0.770	0.6	0.827	0.571	1.2	0.720	0.440
0.2	0.904	0.711	0.7	0.807	0.544	1.4	0.691	0.408
0.3	0.884	0.666	0.8	0.788	0.519	1.6	0.666	0.381
0.4	0.865	0.631	0.9	0.770	0.497	1.8	0.648	0.360
0.5	0.846	0.600	1.0	0.752	0.476	2.0	0.635	0.342

Table II. Electromotive Force Data for the System Hydrochloric Acid-Trichloroacetic Acid at 298.15 K

molalities			
HCl	HTCA	$\epsilon - \epsilon^\circ$	$\gamma_\pm$(HCl)
0.001 96	0.007 91	0.2836	0.911
0.003 30	0.006 60	0.2704	0.906
0.004 92	0.004 99	0.2603	0.902
0.006 65	0.003 23	0.2526	0.904
0.007 95	0.001 91	0.2480	0.906
0.019 81	0.077 69	0.1721	0.799
0.031 74	0.065 32	0.1603	0.795
0.047 94	0.048 56	0.1499	0.795
0.063 96	0.031 98	0.1426	0.795
0.076 07	0.019 46	0.1382	0.796
0.07 86	0.29 67	0.1074	0.720
0.12 69	0.24 48	0.0951	0.723
0.18 43	0.18 33	0.0853	0.730
0.24 70	0.11 68	0.0775	0.738
0.28 98	0.07 05	0.0731	0.746
0.15 32	0.56 93	0.0746	0.703
0.24 77	0.47 14	0.0617	0.713
0.36 21	0.35 22	0.0511	0.727
0.49 75	0.21 07	0.0419	0.746
0.57 90	0.12 59	0.0374	0.756
0.23 66	0.83 03	0.0495	0.760
0.38 81	0.67 60	0.0357	0.776
0.55 15	0.50 98	0.0261	0.786
0.73 56	0.32 24	0.0179	0.800
0.86 82	0.18 74	0.0130	0.811

Table III. Electromotive Force Data for the System Hydrochloric Acid-Trifluoroacetic Acid at 298.15 K

molalities			
HCl	HTFA	$\epsilon - \epsilon^\circ$	$\gamma_\pm$(HCl)
0.00205	0.00728	0.2845	0.900
0.00346	0.00619	0.2701	0.901
0.00509	0.00454	0.2604	0.900
0.00655	0.00309	0.2538	0.900
0.00791	0.00189	0.2485	0.901
0.0206	0.0763	0.1721	0.786
0.0344	0.0628	0.1587	0.788
0.0502	0.0478	0.1488	0.787
0.0655	0.0333	0.1418	0.787
0.0798	0.0195	0.1363	0.790
0.0766	0.2717	0.1104	0.713
0.1253	0.2241	0.0976	0.716
0.1856	0.1655	0.0867	0.725
0.2397	0.1129	0.0794	0.734
0.2855	0.0681	0.0741	0.744
0.1414	0.5539	0.0780	0.700
0.2504	0.4454	0.0627	0.707
0.3526	0.3444	0.0528	0.721
0.4737	0.2241	0.0439	0.739
0.5614	0.1376	0.0387	0.752
0.2212	0.8764	0.0508	0.755
0.2314	0.8668	0.0495	0.757
0.3673	0.7228	0.0368	0.772
0.5366	0.5434	0.0268	0.781
0.7138	0.3569	0.0188	0.794
0.8561	0.2075	0.0135	0.806

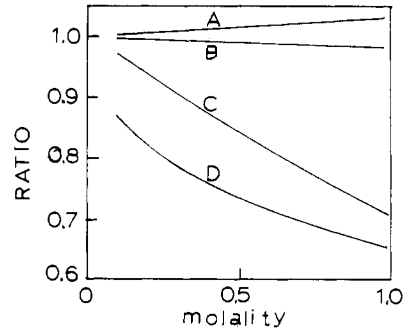

Figure 1. Ratios of acid-lithium salt osmotic coefficients: A, iodide; B, nitrate; C, trichloroacetate; D, iodate.

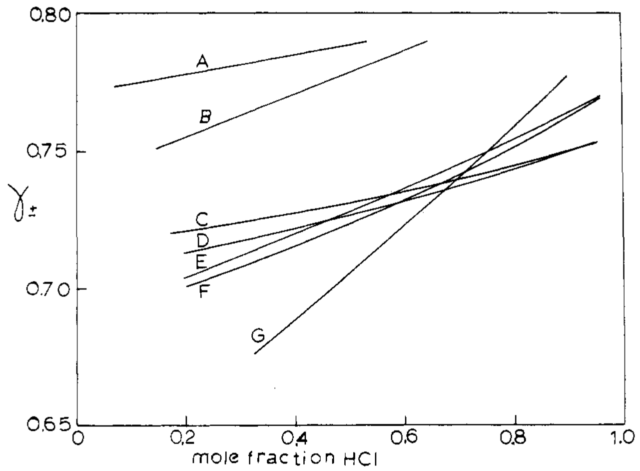

Figure 2. Activity coefficient of HCl ($\gamma_\pm$) in mixed aqueous solutions: A, with *p*-toluenesulfonic acid, μ = 1.0 *m*; B, with trifluoroacetic or trichloroacetic acid, μ = 1.0 *m*; C, with trichloroacetic acid, μ = 0.38 *m*; D, with trifluoroacetic acid, μ = 0.35 *m*; E, with trichloroacetic acid, μ = 0.7 *m*; F, with trifluoroacetic acid, μ = 0.7 *m*; G, with iodic acid, μ = 0.1 *m*.

Table IV. Activity Coefficients of Hydrochloric Acid in Mixtures of Sodium Trichloroacetate and Sodium Iodate at 298.15 K

molalities			
HCl	NaTCA	$\epsilon - \epsilon^\circ$	$\gamma_\pm$(HCl)
0.007 904	0.001 947	0.2539	0.903
0.006 280	0.003 093	0.2660	0.899
0.004 867	0.004 696	0.2792	0.896
0.003 184	0.006 338	0.3013	0.891
molalities			
HCl	$NaIO_3$	$\epsilon - \epsilon^\circ$	$\gamma_\pm$(HCl)
0.007 413	0.001 756	0.2571	0.906
0.005 971	0.002 853	0.2683	0.904
0.004 614	0.004 525	0.2816	0.902
0.003 166	0.006 030	0.3010	0.902

If the concentrations are in excess of 0.1–0.2 *m*. Our earliest work (*1*) on HTCA, however, yielded an extrapolated value of K_a of the order of magnitude of 10^{-1} using very dilute solution data. This was in agreement with the values tabulated in ref 2 for the earliest work on this acid. An emf measurement in very dilute solutions seemed necessary to determine whether yet another experimental technique would yield different results at different concentrations. The data of Table IV are for HCl-NaTCA and HCl-$NaIO_3$ systems at an ionic strength of

Table V. Activity Coefficients of Hydrochloric Acid as a Function of Composition in Aqueous Mixtures of Trichloroacetic Acid and Hydrochloric Acid at 298.15 K

	$m_2/(m_1 + m_2)^a$					
μ	0.00	0.20	0.33	0.50	0.67	0.80
1	0.809	0.809	0.799	0.785	0.775	0.759
0.9	0.795	0.786	0.775	0.756	0.745	0.730
0.8	0.783	0.769	0.758	0.737	0.725	0.711
0.7	0.772	0.756	0.745	0.727	0.712	0.703
0.6	0.763	0.750	0.736	0.724	0.713	0.704
0.5	0.757	0.746	0.735	0.726	0.716	0.709
0.4	0.755	0.746	0.737	0.729	0.721	0.718
0.3	0.756	0.751	0.748	0.741	0.737	0.735
0.2	0.767	0.767	0.767	0.766	0.763	0.762
0.1	0.796	0.796	0.796	0.796	0.796	0.796

[a] Mole fraction trichloroacetic acid.

Table VI. Activity Coefficients of Trichloroacetic Acid as a Function of Composition in Aqueous Mixtures of Trichloroacetic Acid and Hydrochloric Acid at 298.15 K

	$m_2/(m_1 + m_2)^a$					
μ	0.20	0.33	0.50	0.67	0.80	1.00
1			0.618	0.584	0.542	0.476
0.9	0.658	0.637	0.610	0.584	0.560	0.497
0.8	0.661	0.640	0.613	0.586	0.565	0.519
0.7	0.667	0.647	0.622	0.598	0.578	0.544
0.6	0.674	0.657	0.637	0.616	0.598	0.571
0.5	0.694	0.671	0.653	0.635	0.622	0.600
0.4	0.701	0.690	0.675	0.660	0.648	0.631
0.3	0.725	0.723	0.703	0.690	0.680	0.666
0.2	0.765	0.756	0.745	0.733	0.725	0.711
0.1						0.770

[a] Mole fraction trichloroacetic acid.

about 0.01 *m*. The values of $\gamma_{\pm}$(HCl) are observed to be lowered almost equally by NaTCA and $NaIO_3$. This result is consistent with all of the other data for very dilute solutions. At this point, it appears that we have sufficient evidence to establish that HTCA, and probably HTFA, is associated more in dilute solutions than would be expected from its association in more concentrated solutions. A possible explanation appears to be as follows. The association of HTCA occurs in two ways as has been previously postulated (*3*): the formation of the covalent oxygen–hydrogen bond in Cl_3CCOOH and a second interaction involving the hydrogen bonding of the proton to the trichloro group of the anion. If one makes the reasonable assumption that the tendency of protons to form ion pairs is less with the covalently bonded acid than with the anion but that a covalent bond with the hydroxyl group may be formed whether or not the anion is involved in a H···Cl ion pair, then, in dilute solutions where the ratio of anions to covalently bonded acid is larger, the ion pairing phenomenon will be more important. This causes $\gamma_{\pm}$(HTCA) to fall off rapidly and result in a rapid increase (*1*) in the value of an ionization quotient calculated from concentrations rather than activities. The presence of three chlorine atoms not only increases the inductive effect but also furnishes a triple degeneracy to the equivalent ion pairing configurations. In the measurements reported in Table IV in which the TCA anion is present in a larger concentration than the hydrogen ion, the effect should be greater than in pure dilute solutions of HTCA where the concentrations of cation and anion are identical.

The activity coefficients of a second solute in a solution may be calculated if the activity coefficients of the first solute are known as a function of composition and concentration. The equation which was derived in a previous publication (*9*) is

$$\ln \gamma_2 = \ln \gamma_2{}^0 + \int^{m_1} \left(\frac{d \ln \gamma}{dm_2}\right)_{m_1} dm_1$$

where the subscript 1 refers HCl and the subscript 2 to HTCA. The superscript 0 refers to pure solutions of HCTA. Values of activity coefficients of both solutes at even concentrations are taken from smoothed curves and presented in Tables V and VI. A comparison of these data with those in *p*-toluenesulfonic acid–HCl solutions indicates that HTCA is definitely a weaker acid than *p*-toluenesulfonic acid but not an extremely weak acid.

In summary, these experiments furnish further evidence that the small ionization constant calculated for trichloroacetic acid in very dilute solutions of the pure acid is probably due to a second type of ion pairing of the hydrogen and trichloroacetate ions. This treatment is entirely equivalent to that of Covington et al. (*2*) except that they did not specify the structure of the ion pair. This type of association is not as important in more concentrated solutions where HTCA appears to be an appreciably stronger acid by both Raman and emf measurements.

Registry No. HFTA, 76-05-1; HTCA, 7782-68-5; HCl, 7647-01-0; HIO_3, 76-03-9.

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