Conductivity of Trifluoroacetic Acid in 1,2-Dichloroethane

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The conductivity of trifluoroacetic acid in 1,2-dichloroethane has been measured at 25°, 30° and 35°C over the concentration range 10^{-1}–$10^{-5}M$, under strictly anhydrous conditions. The results were treated by the Shedlovsky procedure. The equilibrium constants for the process $CF_3COOH \rightarrow CF_3COO^- + H^+$ at the three temperatures are 1.50×10^{-7}, 2.57×10^{-7}, 5.03×10^{-7}. The derived values of $\Delta G°$ are 38.9, 38.1, 37.2 kJ mol^{-1}, of $\Delta H°$ 49.7 kJ mol^{-1} and of $\Delta S°$ 192 JK^{-1} mol^{-1}.

Conductance measurements can provide valuable information on the nature of the polymerizing species in ionic polymerizations provided that they are conducted under rigorous experimental conditions so as to ensure that the only conducting species are those involved in the polymerization. As a preliminary step in the investigation of the polymerization of isobutyl vinyl ether by trifluoroacetic acid (TFA) in 1,2-dichloroethane (DCE), we have studied the conductance of TFA alone in the solvent.

The concentration dependence of the molar conductivity yielded the limiting molar conductivity Λ_0 and the overall dissociation constant, K_3, for the equilibria

$$\underset{\text{molecule}}{CF_3COOH} \overset{K_1}{\rightleftharpoons} \underset{\text{ion-pair}}{CF_3COO^-H^+} \overset{K_2}{\rightleftharpoons} \underset{\text{free ions}}{CF_3COO^- + H^+}$$

where

$$K_3 = K_1K_2 = \frac{[CF_3COO^-][H^+]}{[CF_3COOH]}$$

The temperature dependence of the conductivity gave thermodynamic parameters associated with this complete dissociation assuming that nonideality could be ignored.

EXPERIMENTAL

Trifluoroacetic Acid. This was refluxed for 24 hr over a prebaked molecular sieve (Union Carbide Linde 3A2) under dry nitrogen. The fraction boiling between 72.1-72.4°C was collected in a flask and transferred to the vacuum manifold. It was degassed and distilled into a storage vessel containing fresh prebaked drying agent, rejecting large initial and final fractions.

TFA was metered into ampuls with breakable internal seals by first distilling into a side arm constructed of calibrated high-precision capillary tubing, and distilling into ampuls which were then sealed off.

1,2-Dichloroethane. This was refluxed over Linde 4AXW molecular sieves and distilled, collecting the fraction boiling between 83.4–83.7°C. The remainder of the purification procedure was the same as for TFA, except that the solvent was metered directly into the conductivity cell using a vacuum buret. The error in measuring volume was ±0.05 cm^3 giving a maximum error of 0.1% in the volume of the solvent.

The concentrations of TFA in DCE given in Table I are those calculated using the room temperature volume of DCE as metered on the vacuum line. The temperature variation of the density of DCE is given by $\rho = 1.2553 - 1.468 \times 10^{-3} (T - 18.5)$ over the temperature range 18.5–27.15°C *(6)*. This would give an extra variation in volume over our tempera-

Table I. Conductivity and Molar Conductivity of TFA in DCE at Different Temperatures

Temp, °C, [TFA] × 10^3 mol l.$^{-1}$	25°C		30°C		35°C	
	$K \times 10^9$, ohm^{-1} cm^{-1}	$\Lambda \times 10^4$, ohm^{-1} cm^2 mol^{-1}	$K \times 10^9$, ohm^{-1} cm^{-1}	$\Lambda \times 10^4$, ohm^{-1} cm^2 mol^{-1}	$K \times 10^9$, ohm^{-1} cm^{-1}	$\Lambda \times 10^4$, ohm^{-1} cm^2 mol^{-1}
246.5	75.112	3.047	77.874	3.159	82.303	3.339
121.9	43.614	3.578	45.284	3.715	47.010	3.856
80.10	31.150	3.892	32.493	4.057	33.464	4.170
7.750	7.377	9.502	7.912	10.21	8.362	10.79
6.210	6.332	10.20	6.606	10.62	6.827	10.99
5.065	5.285	10.44	5.673	11.21	5.911	11.68
3.950	4.284	10.85	4.682	11.89	4.911	12.34
3.261	3.747	11.50	4.075	12.50	4.304	13.20
2.580	3.217	12.47	3.401	13.18	3.558	13.79
0.248[a]	1.309	52.77	1.458	58.79	1.669	67.32
0.189[a]	1.142	60.42	1.239	65.56	1.373	72.67
0.102[a]	0.836	81.96	0.928	90.98	1.020	100.00
0.098[a]	0.819	83.58	0.916	93.42	0.975	99.52
0.078[a]	0.722	92.50	0.804	103.0	0.901	115.5
0.051[a]	0.577	114.3	0.624	123.7	0.677	134.0
0.035[a]	0.485	138.6	0.530	151.4	0.587	167.8
0.025[a]	0.406	162.2	0.448	179.1	0.493	197.1

Conductance of pure DCE = 8.4×10^{-10} ohm^{-1}.
[a] Used for the Shedlovsky calculations.

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ture range of less than 0.1% leading to a maximum error in the concentration of 0.2%. We were prepared to tolerate this level of uncertainty in concentrations, which resulted from the use of a rigorous vacuum line technique since conductivity measurements in nonaqueous solvents only have validity if water is strictly excluded.

Conductivity Cell. This is shown in Figure 1. In the experiments described here, the side arm for isobutyl vinyl ether (IBVE) was not used. The electrodes were made of bright platinum 15 mm^2 cross-sectional area, and approximately 5 mm apart. The cell constant (0.2488 cm^{-1}) was determined using 0.010*M* aqueous KCl at 25°C. The same cell constant was used for the whole temperature range since the cell constant is insensitive to temperature (*1*).

All measurements were made using an oil bath thermostated to within ±0.02° using a Wayne-Kerr B221 Universal Bridge operating at 1592 Hz.

RESULTS

The experimental results at three different temperatures are given in Table I. Graphical methods (*10*) present the best means of evaluating the limiting conductance (Λ_0) and the dissociation constant (K_3); the methods of Shedlovsky (*4*) and Fuoss (*3*) are the most frequently employed. We have used the Shedlovsky procedure; this was considered more accurate for weakly dissociated solutes.

According to Fuoss (*2*), the conductance relationships deviate from linearity if the solute concentration is higher than $3.2 \times 10^{-7} D^3$ where D is the dielectric constant of the medium; since the dielectric constant of DCE is 10.36, only the results for the range of TFA concentrations from 2.5×10^{-5} to $2.48 \times 10^{-4}M$ were used for these calculations.

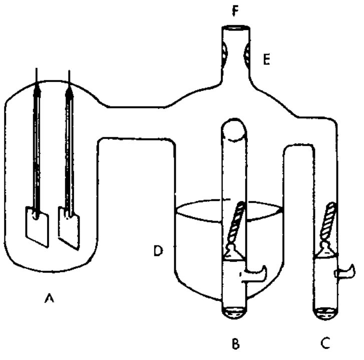

Figure 1. The conductivity cell

- A. Conductivity cell
- B. Isobutyl vinyl ether ampul
- C. Trifluoroacetic acid ampul
- D. Solvent and mixing vessel
- E. Seal-off poitn
- F. Connection to vacuum line

Table II. Dielectric Constant and Viscosity Values for DCE

Temp, K	Dielectric constant (*9*)^a	Viscosity, 10^{-3} P (*7*)
298.20	10.36	7.820
303.20	10.08	7.360
308.20	9.81	6.960

^{a} $\epsilon_{25} - d \log_{10}\epsilon/dT = 0.00240$.

Table III. Thermodynamic and Conductimetric Results

Temp, K	298.2	303.2	308.2
$K_3 \times 10^7$, mol l.$^{-1}$	1.50	2.57	5.03
Λ_0, ohm^{-1} cm^2 mol^{-1}	0.218	0.182	0.150
$\Delta G_d°$, kJ mol^{-1}	38.9	38.1	37.2
$\Delta H_d°$, kJ mol^{-1}	49.7	49.7	49.7
$\Delta S_d°$, J deg^{-1} mol^{-1}	192	192	192

The values of solvent dielectric constant (*9*) and viscosity (*7*) used are collected in Table II. A consistent minimum conductivity of 8.4×10^{-10} ohm^{-1} for DCE was obtained; this compares with the value of 3.4×10^{-10} ohm^{-1} obtained by Kraus and Fuoss (*8*). Any departure from this value was considered significant, and such runs were discarded.

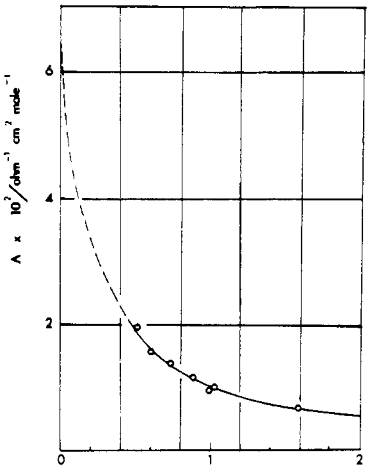

Figure 2. Molar conductance of trifluoroacetic acid in 1:2 dichloroethane at 35°C

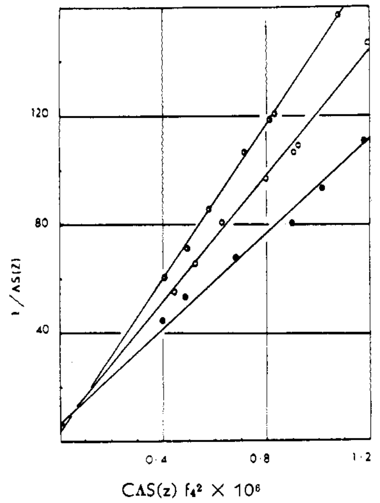

Figure 3. Shedlovsky plots of conductance data at different temperatures

◐ 25°C; ○ 30°C; ● 35°C

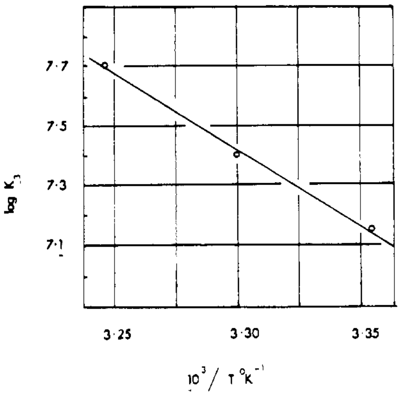

Figure 4. Temperature dependence of the overall dissociation constant

A Fortran IV program was written to evaluate Λ_0 from the results in Table I; it was based on assigning an initial value to Λ_0, estimated from the Λ vs. $[\mathrm{TFA}]^{1/2}$ plot (Figure 2). The iterative process converged rapidly, giving a true value of Λ_0, provided that the trial of Λ_0 was within a factor of 4 of the true value. Self-consistent values of Λ_0 and K were evaluated from the intercept and slope, respectively, of the plot shown in Figure 3 where the ordinate and abscissa have their usual significance (*10*). These results are given in Table III together with values of $\Delta H_3°$ obtained from the plot in Figure 4 and $\Delta G_3°$ and $\Delta S_3°$ evaluated by standard relationships.

No other data are available for comparison purposes, with the exception of a specific conductance value for $4 \times 10^{-2}M$ perchloric acid in dichloromethane of 9×10^{-8} ohm^{-1} cm^{-1} at 25°C quoted by Gandini and Plesch (*5*). This compares with our value of 2.8×10^{-8} ohm^{-1} cm^{-1} for TFA in DCE (with similar dielectric constant) at the same concentration and temperature. This parallels the known order of acid strengths of the two acids in water.

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Method for Determining Solubility of Slightly Soluble Organic Compounds

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A method for measuring the solubility of slightly soluble organic compounds is described. The procedure involves the quantitative extraction of the solute using nonpolar resins, elution of the sorbed solute, and analysis of the eluent. The accuracy of the method is comparable to other methods and does not suffer their limitations.

Solubility data for slightly soluble organic compounds are sparse in the literature because few general methods exist for obtaining the data. Moreover, those methods which do exist, such as radioactive isotopic labeling, ultraviolet spectrophotometry, and aqueous injection gas chromatography, all have limitations. Tracer techniques require sophisticated expensive equipment. Spectrophotometry possesses the requisite sensitivity for only certain classes of compounds and is often subject to interferences from other compounds which may be present in the solution. Direct injection of aqueous solutions into gas chromatographic columns often produces a large "tail" that masks the minor component being analyzed quantitatively.

This report describes a method for determining the solubility of nonionic organic compounds in water that circumvents many of these limitations of existing methods and uses only standard laboratory methods and equipment. The method involves the quantitative absorption of the dissolved organic compound on a macroreticular resin bed, followed by elution with an appropriate solvent and quantitative analysis of the eluent. The absorption of the solute on the resin serves the threefold purpose of separating the solute from the aqueous solution, concentrating the solute for increased sensitivity, and transferring the solute to a more convenient solvent for analysis. The method was tested on benzene, toluene, and chlorobenzene, the solubility of which has been measured using other techniques. For these compounds gas chromatography was a convenient analytical tool.

Macroreticular resins have been used to extract various organic compounds from water (*1*). Previous work in these laboratories has shown that a wide range of organic compounds are quantitatively extracted from water even when present at sub ppm concentration levels (*5*). Aliphatic compounds containing more than four or five carbon atoms and virtually all aromatic compounds are quantitatively absorbed. On the other hand, both inorganic and organic ions, such as Na^+ or Cl^-, pass unhindered through the resin bed. Thus it is possible to extract and analyze nonionic compounds in the presence of ions that might interfere with spectrophotometric methods.

PROCEDURE

A thermostated (21° ± 1°C) separatory funnel containing about 50 ml of distilled water and about 1 ml of the organic solute (A. R. Grade) was allowed to stand for 10–20 hr with occasional stirring in order to come to equilibrium. A weighed amount of the saturated solution was added dropwise to a 1-cm diam × 7-cm long column of XAD-2 macroreticular resin until 20–40 grams of solution had been removed. The tip of the separatory funnel was kept submerged under distilled water covering the resin bed to minimize the possibility of evaporation of the solute during the absorption step. About 30 ml of isopropyl ether was used to elute the sorbed compound from the column. By observing the water–ether interface as it proceeded down the column, it was possible to collect the first 10–20 ml of eluent. Separate experiments verified that the compounds tested were quantitatively retained by the resin and that the elution was complete after about 10 ml of eluent passed through the bed. After the eluent was weighed, about 10 pellets of molecular sieve were added to remove the small

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