On the Dielectric Constant of Trifluoroacetic Acid[1]

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Simons and Lorentzen[1a] have reported dielectric constants for trifluoroacetic acid, measured at 1000 c./sec., which increase with temperature from 26.2 at $-11°$ to 43.4 at 27.7°. These values are much larger than those of 6.07 at 10° to 6.60 at 70° reported by Smyth and Rogers[2] for acetic acid, which one might expect to have more similar properties, and the temperature dependence is the opposite of that normally found for liquids of high dielectric constant.

The observed values might be explained as the result of a monomer–dimer equilibrium quite different from that in either acetic or formic acid, but it also seemed to us quite possible that they resulted from electrode polarization effects at low frequencies because of appreciable specific conductance of the liquid, as found in formic acid, for example.[3]

Measurements were therefore undertaken on both acetic and trifluoroacetic acids over a frequency range 20 c./sec. to 5 mc./sec. and at temperatures from the respective melting points to about 50°. The bridge used has been described elsewhere.[4]

A stainless steel cell with coaxial cylindrical electrodes[5] was employed. Interchangeable inner cylinders giving electrode separations of either 3.2 or 1.6 mm. were used to distinguish surface and intrinsic properties of the sample measured. Acetic acid was prepared by essentially the method of Eichelberger and LaMer[6] and finally distilled directly into the test cell from the all-glass apparatus using ungreased joints. The starting material for preparation of trifluoroacetic acid was a sample of better than 99% stated purity,[7] which was dried by refluxing over P_2O_5 and then redistilled directly into the cell. Melting points agreed with the literature values to 0.1°; specific conductances at 25° were of the order 5–10 × 10^{-8} mho/cm. for acetic acid, 3–5 × 10^{-7} mho/cm. for trifluoroacetic acid. The latter slowly attacked the cell, but this caused only slight rises in observed conductance.

The dielectric constant results for acetic acid were found to confirm those of Smyth and Rogers and extensive study was therefore unnecessary. The values for trifluoroacetic acid increased markedly for frequencies below 1 kc./sec., as shown by the data of Fig. 1 which were taken with the 1.6-mm. electrode separation. Measurements with 3.2 mm. separation gave the same values within experimental error above 5 kc./sec., and similar but considerably smaller increases at lower frequencies.

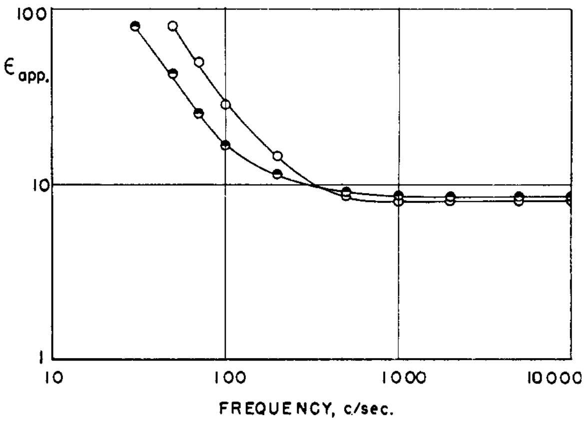

Fig. 1.—Dependence of apparent dielectric constant on frequency for trifluoroacetic acid: ◓, 19.7°; ○, 46.9°.

An analysis of electrode impedance errors[3] predicts that for identical electrodes at varying separations the increase in apparent capacitance should vary as the square of the specific conductance of the sample and in inverse ratio to the electrode spacing. This was found to be approximately true for these measurements, exact agreement not being expected because a different inner electrode was used to change the separation. The dependence of the increase in apparent dielectric constant on frequency was approximately as $f^{-1.8}$. This indicates that the electrode polarization effect was equivalent to a complex impedance, rather than a pure capacitance which would give a dependence as f^{-2}, and is similar to observations of Shaw[8] and Wolf.[9]

We conclude that the frequency independent values observed above a few kilocycles are characteristic of the liquid, and such values interpolated at several temperatures are listed in Table I, together with values for acetic acid. These show that the fluorine derivative has a somewhat higher dielectric constant, with a normal negative temperature coefficient, rather than the slight positive one observed for acetic acid. Attempts to account for the differences on the basis of associative equilibria or electronic polarization have been inconclusive.

Table I

Dielectric Constants of Acetic and Trifluoroacetic Acids

Temp., °C.	Dielectric constant			
	Acetic acid		Trifluoroacetic acid	
	Smyth and Rogers	This work	Simons and Lorentzen	This work
−10	..	..	..	9.16
0	..	..	29.5	8.90
+10	6.07	..	34.5	8.65
20	6.13	6.18	39.0	8.42
30	6.20	6.27	44.5^a	8.22
40	6.27	6.36	...	8.02
50	6.36	6.45	...	7.83
60	6.47	6.54^a	...	..

[a] Extrapolated value.

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[1] Supported in part by O. N. R.

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[5] P. M. Gross, Jr., and R. C. Taylor, This Journal, **72**, 2075 (1950).

[6] W. C. Eichelberger and V. K. LaMer, *ibid.*, **55**, 3633 (1933).

[7] Supplied through courtesy of Minnesota Mining and Mfg. Co.

[8] T. M. Shaw, *J. Chem. Phys.*, **10**, 609 (1942).

[9] I. Wolf, *Phys. Rev.*, **27**, 755 (1926).