Dielectric Constants of Some Alcohols
at Low Frequencies

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The dielectric constants of some aliphatic and aromatic alcohols have been measured with a parallel resistance impedance bridge at temperatures from 5° to 60° over the frequency range of 0.5 to 50 kilocycles/sec.

The dielectric constants for all the alcohols used, except for methanol, were independent of frequency within the present range, and agreed fairly well with the values by other investigators.

Only methanol showed a frequency dependence of dielectric constant below the frequency of about 10 kilocycles/sec. This dependence may be attributed to the electrode surface phenomena to be due to the electrolytic polarization of proton which takes part in the electrical conduction.

INTRODUCTION

The dielectric constants of alcohols have already been reported by many investigators, but the majority of the measurements was made at high frequency ranges. In view of the scarcity of the systematic data at lower frequencies, it is desirable to examine the static dielectric constants for some alcohols at various temperatures.

Hence, the dielectric measurements of alcohols at audio-frequencies was made to obtain the static dielectric constants and their temperature dependence.

At lower audio-frequencies it is often difficult to determine the dielectric constants of those conductive liquids as alcohols and glycols owing to the presence of the direct current conductance which arises from the proton conduction.

For the dielectric measurements of conductive liquids the conductance capacitance bridge by Cole and Gross[1] may be most suitable, but in this work a simple impedance bridge of parallel resistance type was employed and the operation of this bridge was sufficient for the present purpose.

This paper presents the static dielectric constants of thirteen different alcohols at the temperature range of 5° – 60° C and the apparent change of dielectric constant of methanol at audio-frequencies.

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EXPERIMENTAL

Materials

Materials used were nine aliphatic, one alicyclic and three aromatic alcohols.

Aliphatic : methanol, ethanol, n-propanol, i-propanol, n-butanol, i-butanol t-butanol, n-pentanol and i-pentanol.

Alicyclic : cyclohexanol.

Aromatic : phenyl carbinol, phenyl methyl carbinol, and benzyl carbinol.

Most of these alcohols were purified from research grade products by the method described in "Organic Solvents"[2] and several times distilled in an all-glass system.

Particularly aromatic alcohols were distilled under a reduced pressure of nitrogen to avoid any oxidation by air.

In each distillation the range of boiling point was retained within ±0.1°C. and only the middle fraction was used.

Apparatus and Procedure

The measurements of dielectric constant were made with an impedance bridge of parallel resistance type, involving the Wagner earthing device to eliminate the errors due to the stray capacity current. The frequency range was from 0.5 to 50 kilocycles/sec. The circuit diagram is shown in Fig. 1. In Fig. 1 G is the oscillator, and D the detector.
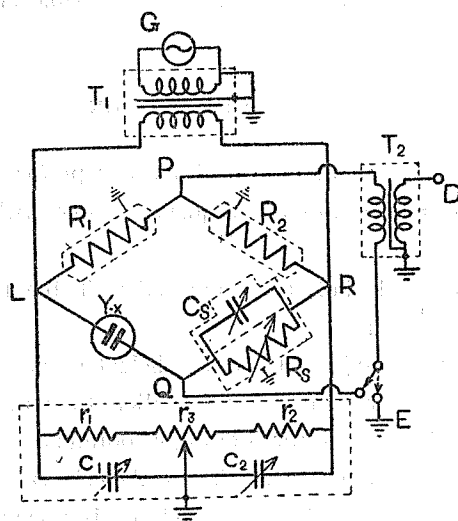

Fig. 1. The circuit diagram of the impedance bridge.
(For symbols see text)

T_1 and T_2 are the shielded coupling transformers made of permalloy cores.

R_1 and R_2 are the ratio arms of 10,000 ohms deposited type precision carbon

resistor. R_s is six decades resistors of 10 ohms - 10 megohms. C_s is a precision condenser with total capacitance of 1700 $\mu\mu$f. The resistances r_1 and r_2 of the Wagner arm are 12,000 ohms and r_3 is a 1,000 ohms variable resistor. C_1 and C_2 are 100 $\mu\mu$f. variable condensers. Unknown admittance is given by $Y_x = (1/R_x) + j\omega C_x$.

By the proper adjustment of C_s, R_s, r_3 and C_2, points P, Q and E are all brought to the same ground potential and there is no error due to the stray capacity current from P and Q to L and R through earthing respectively.

Hence, the equivalent capacitance C_x, resistance R_x and loss tangent $\tan \delta$ of the unknown impedance arm are given by the relations

$$C_x = \frac{R_2}{R_1} C_s , \qquad R_x = \frac{R_1}{R_2} R_s$$

$$\tan \delta = \frac{1}{\omega C_x R_x} = \frac{1}{\omega C_s R_s}$$

The measurable range of loss tangent on this bridge is $10^{-2} - 10^2$.
The measuring cell consists of two concentric platinum cylinders of 3.5 cm long, with diameters of 2.0 and 2.2 cm respectively.

Thirty five c.c. of liquid was required to fill this container and the capacity of the empty cell was about 30 $\mu\mu$f. The cell constant was determined accurately by several standard materials : carbon tetrachloride $\epsilon_{25^\circ} = 2.225^{3)}$, benzene $\epsilon_{20^\circ} = 2.283^{4)}$, diethylether $\epsilon_{20^\circ} = 4.355^{5)}$ mono-chlorobenzene $\epsilon_{25^\circ} = 5.611^{6)}$, dichloroethane $\epsilon_{25^\circ} = 10.16^{7)}$ and nitrobenzene $\epsilon_{25^\circ} = 34.89^{8)}$. The probable error of the dielectric constant measurement was 0.5 %.

RESULTS AND DISCUSSION

The dielectric constants ϵ for all the alcohols, except for methanol, were independent of frequency over the present frequency range within the experimental error.

The observed valus for alcohols are tabulated in Table 1, and compared with the values appearing in literatures.

Åkerlöf's data are often cited as the static dielectric constants of alcohols, but it seems that his values, on the whole, are smaller than those reported by other workers. Particularly the values for t-butanol obtained in this research were in excellent agreement with Harris, Haycock and Alder's values, which are considerably larger than Åkerlöf's data. t-Butanol used in this research showed the sudden change of dielectric constant at the melting point of 25.0°C and ϵ fell to the very small value in the solid state, as shown in Fig. 2. From this fact it was considered that t-butanol has no freedom of dipole orientation in the solid state and the sharp change of ϵ at the melting point presents a criterion of high purity of the specimen

Dielectric Constants of Some Alcohols

Table 1. The static dielectric constant of alcohols at the temperature range of 5—60°C.

Alcohol		Dielectric Constant ε Temperature in °C					Reference
		5	20	35	50	60	
	Methanol	36.45	33.30	30.48	27.84	26.23	This work
			32.35	29.84[a]	27.44	25.97	Åkerlöf[9]
		36.88	33.69[a]	30.74	28.06[a]	26.42[b]	Albright & Gosting[10]
		36.80[a]	33.7	30.70[a]	28.0		Saxton[11]
	Ethanol	27.58	25.09	22.63	20.40	19.05	This work
			25.00	22.88[a]	20.87	19.55	Åkerlöf[9]
		27.7[a]	25.1	23.2[a]	21.0		Saxton[11]
	n-Propanol	23.10	20.75	18.66	16.70	15.42	This work
			20.81	18.91[a]	17.11	15.88	Åkerlöf[9]
		23.38[a]	20.98[a]				Davidson & Cole[12]
			21.3				Brot et al.[13]
	i-Propanol	22.02	19.52	17.38	15.33	14.11	This work
			18.62	16.81[a]	15.06	14.03	Åkerlöf[9]
Aliphatic	n-Butanol	19.88	17.90	16.00	14.10	13.08	This work
			17.73[a]	15.92[a]			Harris et al.[14]
			18.5				Brot et al.[13]
	i-Butanol	20.66	18.08	15.95	13.75	12.52	This work
			16.68	14.63[a]	12.83	11.75	Åkerlöf[9]
			18.6				Brot et al.[13]
	t-Butanol	2.48[d]	12.27[c]	10.63	8.57	7.67	This work
			9.80[a,c]	8.89[a]	7.67	6.96	Åkerlöf[9]
			12.46[b,c]	10.64[a]	8.54[a]		Harris et al.[14]
	n-Pentanol	16.67	14.80	13.04	11.46	10.43	This work
			15.4				Brot et al.[13]
	i-Pentanol	17.59	15.64	13.82	11.77	10.77	This work
			15.7				Brot et al.[13]
Alicyclic	Cyclohexanol	17.48[a]	15.54[c]	14.37	12.50	11.36	This work
			16.8[e]				Brot et al.[13]
			16.12[a,c]	14.88[b]			Crowe & Smyth[15]
	Phenyl carbinol	15.21	13.63	12.15	10.96	10.22	This work
			13.6				Brot et al.[13]
Aromatic	Phenyl methyl carbinol	10.34[f]	9.23	8.36	7.74	7.22	This work
	Benzyl carbinol	13.98	12.31	10.75	9.50	8.78	This work

[a] Interpolated, [b] extrapolated, [c] value at 26°, [d] solid state, [e] value at 25°, [f] supercooled liquid state.
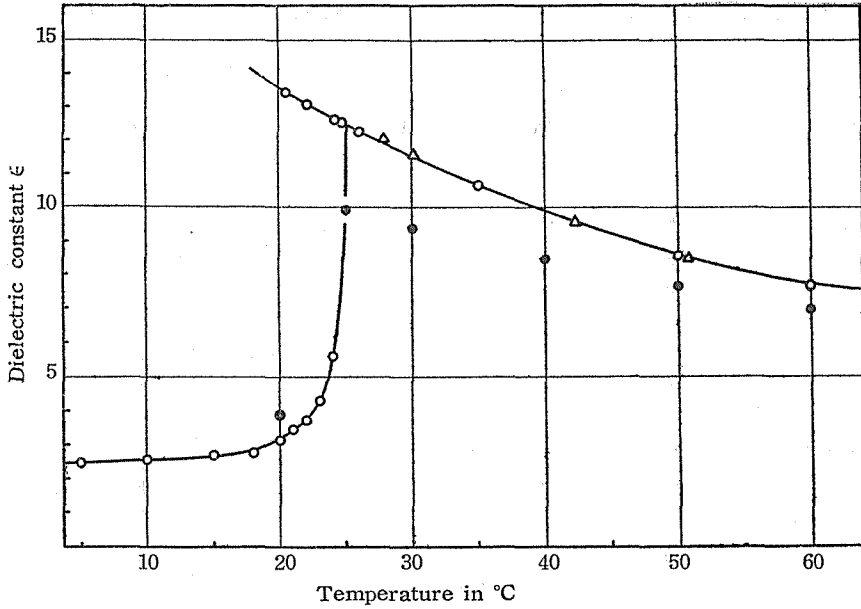
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Fig. 2.   Dielectric constant of *t*-butanol *versus* temperature.
(○ This work, △ Harris *et al.*[14], ● Åkerlöf[9])

used.   Probably Åkerlöf's values for *t*-butanol should be subject to revision.

It was recognized that only methanol exhibited a decreasing tendency of the dielectric constant with increasing frequency and ϵ converged to a certain constant value above *ca.* 10 kilocycles.   The values for methanol in Table 1 are these
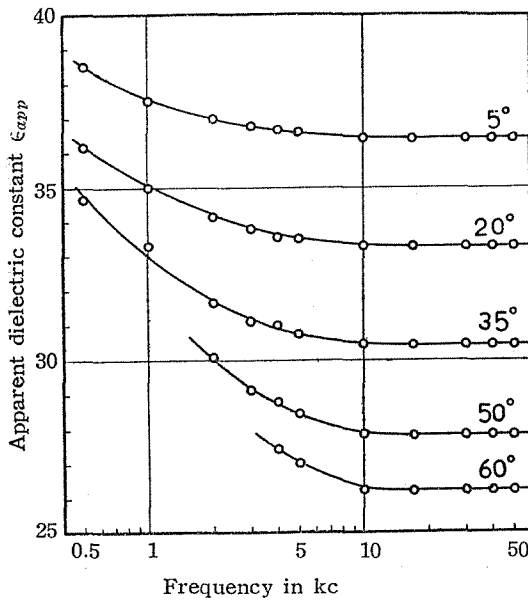

Fig. 3.   The variation of apparent dielectric constant ϵ_{app}
of methanol with frequency.

convergent values, which may correspond to the static dielectric constants. The variation of dielectric constant for methanol with frequency at each temperature is illustrated in Fig. 3. The resistance R_x for methanol observed together with the capacitance exhibited no appreciable change in the frequency range of this research. Strictly speaking, it appears that the resistance increased very slightly with increasing frequency.

The relation of the apparent dielectric constant ϵ_{app} and the static value ϵ_0 to the angular frequency ω was expressed by the following empirical formula

$$\epsilon_{app} = \epsilon_0 + k\omega^{-n}$$

where k and n are empirical constants.

The numerical values of constants k and n are given in Table 2.

Table 2. Two empirical constants K and n for the apparent dielectric constants of methanol at each temperature

t °C	$k \cdot 10^{-3}$	n
5	3.31	0.92
20	5.90	0.94
35	9.33	0.95

Such an apparent frequency dependence of dielectric constant has been reported for some other materials. In the case of aqueous ionic solutions it is well known that the apparent dielectric constant at lower frequency is strongly dependent on frequency and ionic concentration, and this effect is attributed to the electrode phenomenon which arises from the electrolytic polarization of ions on the electrode surface.

Ferry and Oncley[16] found the numerical values of $n = 1.5$ for the aqueous protein solutions.

Recently Johnson and Cole[17] have reported that the dielectric constant of pure formic acid shows a similar frequency-dependent character to the case of ionic solutions, and the values of n are 2.0 and 1.5 for liquid and solid states respectively.

Dannhauser and Cole[18] observed the frequency dependence of $n = 1.8$ for trifluoroacetic acid.

Although in these latter cases there is no electrolytic ion in an ordinary sense, the electrical conduction is caused by the proton transfer mechanism in the intermolecular hydrogen bonding. The present results for methanol may also be interpreted in terms of the electrolytic polarization effect of proton on the electrode surface as similarly as for formic acid, because the direct current conduction is due to the proton jumping.

Therefore it may be considered that the polarization impedance due to the

electrode process contributes to the observed capacitance in addition to the geometrical capacitance of the measuring cell.

Also in the case of ethanol the similar increasing tendency of dielectric constant with decreasing frequency was found very slightly at higher temperatures and lower frequencies.

There have been some attempts[17][19] to interpret the frequency dependence of dielectric constant at audio-frequencies in terms of the equivalent electrode impedance. However, no systematic interpretation concerning the mechanism of electrode impedance has been obtained.

The empirical relation of the apparent dielectric constant to frequency for methanol, that is the frequency dependence of $n \cong 1$, was not always explained by the equivalent circuit theory of electrode impedance by several workers mentioned above[17][19].

ACKNOWLEDGMENTS

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