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The radio frequency conductivity of some aliphatic alcohols at different temperatures

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Abstract. Activation energies for viscous flow and conductivity are computed from experimental values of RF conductivity (frequency 400 kHz) at different temperatures for eight polar liquids. It is observed that for aliphatic alcohols the activation energy for conductivity is greater than that for viscous flow. However, their ratio is slightly greater than unity and is different for different alcohols whereas for non-associating polar liquids the ratio is almost equal to unity. The dependence of conductivity on viscosity for the liquid alcohols does not follow the Walden's law but can be well represented by Adamczewskis relation.

Keywords. Activation energy; radio frequency; proton jumping; aliphatic alcohols; Walden's law.

1. Introduction

All liquids, including liquid dielectrics, easily become contaminated, and the nature of contamination will vary from one another. One form of contamination is the impurities inherent in the liquid dielectric and the other is water. The hygroscopic liquid dielectrics absorb water directly from the atmosphere and diminish the specific resistance of a dielectric. The aliphatic alcohols dissolve and dissociate impurities so efficiently that it is difficult to purify them to a state where they exhibit high level of resistivity; therefore, the aliphatic alcohols cannot be placed in the group of insulator. The evidence for the existence of free ions in organic polar dielectric liquids has been shown by many workers (Loheneysen and Nageral 1971; Rao and Raju 1970; Sen and Ghosh 1974). Considering the presence of free ions in the dielectric liquids the RF conductivity of the liquid dielectric could be expressed by the simple equation,

$$K' = N e (\mu_+ + \mu_-) \tag{1}$$

where K' is the RF conductivity, N is the number of ions per cc, e is the electronic charge and μ_+ and μ_- are the mobility of positive and negative ions respectively. The mobilities of the ions are not equal and differ due to their different mass. But the ions in a polar dielectric liquids are surrounded by neutral molecules making the mass of the positive and the negative ion almost equal. Therefore it may be assumed that μ_+ and μ_- are very nearly equal at a particular temperature. If it is assumed that

the mobility is the same for the positive and negative ions, the temperature dependence of ionic conductivity can be expressed by the equation

$$K' = A \exp(-W_e/kT) \text{ mhos/cm} \tag{2}$$

and $$A = Ne^2l^2f / 6kT,$$

where l is the distance between the two particles in the liquid f is the frequency of natural vibration of particles, k the Boltzmann constant, T the absolute temperature, and W_e is the activation energy necessary for separating an ion from the neighbouring molecule to which it becomes attached during its movement in the electric field. Equation (2) is often written in the logarithmic form

$$\ln K' = \ln A - \frac{W_e}{kT}. \tag{3}$$

The activation energy for viscous flow of the solvent may be calculated from the relation

$$\eta = B \exp(W_\eta/kT) \tag{4}$$

or $$\ln \eta = \ln B + \frac{W_\eta}{kT}. \tag{5}$$

where η is the viscosity of the liquid. B is the constant which is identified by Eyring (1936) with frequency factor (hN_a/V), where N_a is the Avagadros number, V is the molar volume and h is the Planck constant. From (3) and (5) and assuming

$$\frac{W_e}{k} \gg \delta(\ln A) / \delta(1/T) \text{ and } \frac{W_\eta}{k} \gg \delta(\ln B / \delta(1/T)),$$

we get $$\frac{\delta(\ln K')}{\delta(\ln \eta)} = -\frac{W_e}{W_\eta} = n, \tag{6}$$

where n is the constant and the ratio of the two activation energies.

As the problem of activation energy for viscosity and electrical conductivity is important to study the physical and chemical process in the liquid dielectrics, the present investigation has been undertaken to find out a relation between the two activation energies and to show that in associating liquids (alcohols) the successive proton transfer or proton jumping play an important role in the mechanism of RF conduction.

2. Experimental arrangement

The experimental arrangement for measuring the RF conductivity at 400 kHz range has been given in Sen and Ghosh (1972). The cell was made up of a pyrex glass tube of diameter 2 cm with a pair of stainless steel circular electrodes of diameter 1·5 cm separated by a distance of 1 cm. Before filling the dielectric liquids, the glass

cell was cleaned with chromic acid, then with distilled water and finally with benzene. The liquids under investigation such as methyl alcohol, ethyl alcohol, iso-propyl alcohol, *n*-butyl alcohol, iso-amyl alcohol, ethylene glycol, acetone and nitrobenzene were all of AnalaR grade obtained from Messrs British Drug House, London. The viscosities of the liquids were measured with an Ostwald viscometer. The temperatures in all the experiments were controlled within $\pm$ 1°C by a thermostat.

3. Results and discussion

The RF conductivity of all the liquids studied was measured at a wide range of temperature with an accuracy upto 3%. The plot of $\log_{10} K'$ against $(1/T)$ shows the dependence of the ionic conductivity on temperature and from the slope of the rectilinear plot, the activation energy for conductivity W_e has been calculated for all the liquids. Similarly from the linear plot of $\log_{10} \eta$ against $(1/T)$, the activation energy for viscous flow W_η has been determined. The values of W_e and W_η and their ratio $W_e/W_\eta = n$ are given in table 1. The variation of $\log_{10} K'$ against $\log_{10} \eta$ are shown in figure 1 for all the alcohols, and in figure 8 for nitrobenzene and acetone. This gives

Table 1. Value of W_e, $W\eta$ and their ratio for eight polar liquids at 400 kHz.

Liquids	Energy of activation eV				
	W_e	Literature value	$W\eta$	$\frac{W_e}{W_\eta}$	From slope
Methyl alcohol	0·114	0·047[a]	0·110	1·037	1·037
Ethyl alcohol	0·185	0·15[a]	0·146	1·27	1·27
Iso-propyl alcohol	0·241	0·295[b]	0·182	1·32	1·31
n-butyl alcohol	0·216	0·18[a]	0·177	1·22	1·25
Iso-amyl alcohol	0·174	0·16[a]	0·132	1·32	1·33
Ethylene glycol	0·273	—	0·266	1·02	1·04
Acetone	0·08		0·095	0·85	1·0
Nitrobenzene	0·14		0·16	0·89	0·98

[a]Nicolau *et al.* (1968).
[b]Sen and Ghosh (1978).

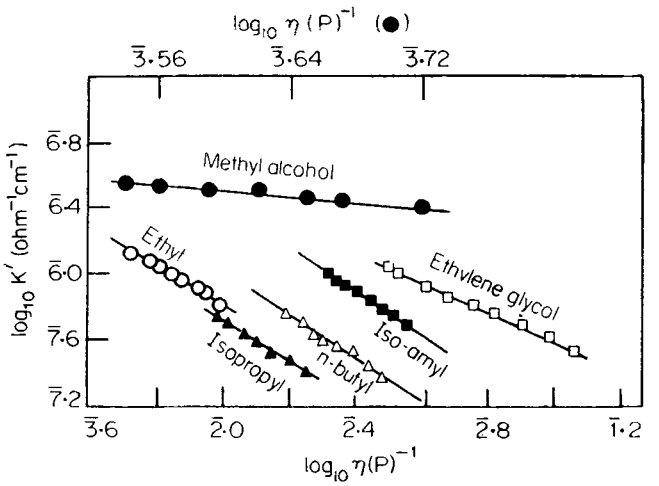


Figure 1. Plot of $\log_{10} K'$ in mhos/cm against $\log_{10} \eta$ in poise.

a linear relation of the type ($\log_e K' = G - n \log_e \eta$) where G is a constant and the slope n gives the ratio of two activation energies. It is observed from table 1 that the constant n is greater than unity ($n > 1$) and is different for different liquid alcohols whereas for non-associating liquids like nitrobenzene and acetone the constant n is equal to unity ($n \simeq 1$). Further from equation (4) we have

$$(\eta/B)^{-n} = [\exp (W_\eta/kT)]^{-n} \tag{7}$$

One can also write

$$K' = (AB^n)\ \eta^{-n}. \tag{8}$$

Equation (8) can be represented as

$$K' = f(\eta^{-n}) \tag{9}$$

where (AB^n) is a constant.

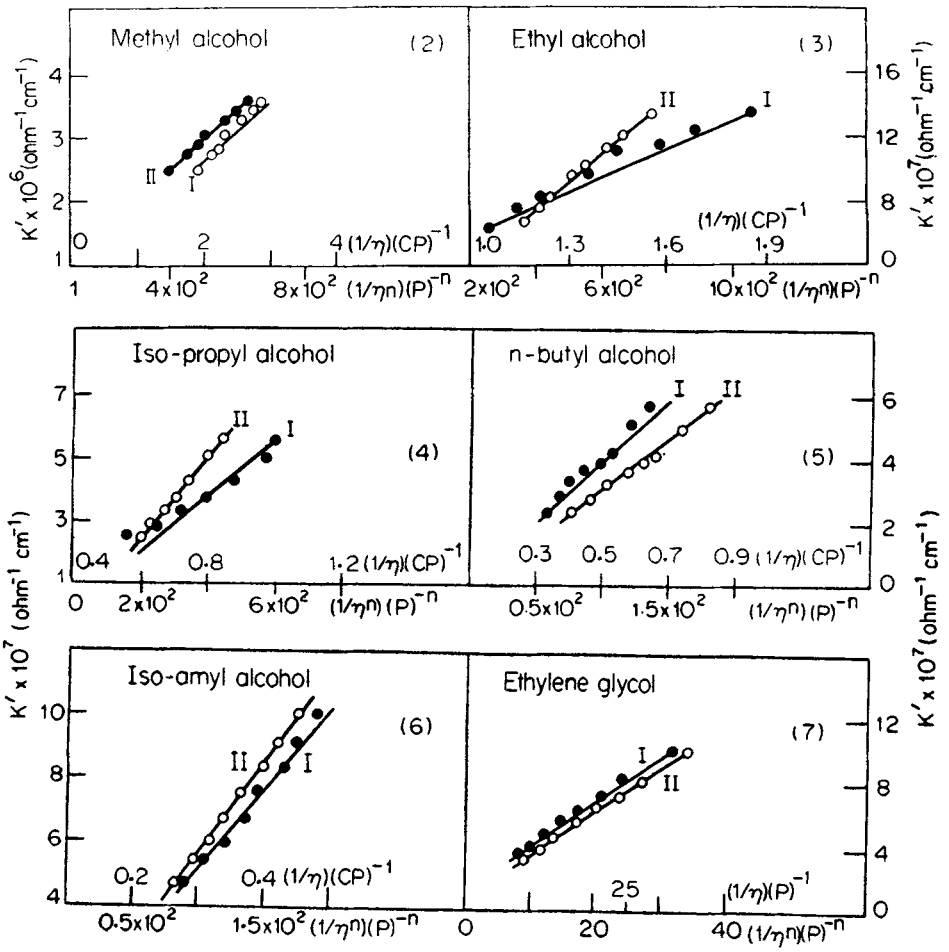
In order to examine the dependence of conductivity on the viscosity of each alcohol two separate plots (I & II) have been drawn as illustrated in figures 2 to 7. In the figures the linear plot I corresponds to Walden's law [$K' = f(\eta^{-1})$] and plot II corresponds to [$K' = f(\eta^{-n})$] which is similar to the relation given by Adamczewski (1969). The product of $K'\eta$ and $K'\eta^n$ and the constants A and B for all the alcohols at various temperatures given in table 2 show that the constant A is almost independent of tem-

Table 2. Values of $K'\eta$, $K'\eta^n$ and constants A and B at different temperatures.

	Methyl alcohol				Ethyl alcohol			
Temp. °K	$K'\eta \times 10^9$	$K'\eta^n \times 10^9$	$A \times 10^4$	$B \times 10^5$	$K'\eta \times 10^9$	$K'\eta^n \times 10^9$	$A \times 10^4$	$B \times 10^5$
303	13·18	6·32	1·734	8·261	6·16	1·80	7·76	5·625
308	12·88	6·08	1·776	8·213	6·59	1·83	8·13	5 591
313	12·83	6·01	1·740	8·164	6·79	1·86	7·82	5·557
318	13·18	6·12	1·789	8·115	7·03	1·80	8·20	5·59
323	12·88	6·00	1·759	8·067	6·92	1·80	7·75	5·493
333	12·58	5·8	1·712	7·971	7·07	1·80	7·63	5.42
	Iso-propyl alcohol				*n*-butyl alcohol			
303	4·46	1·26	2·448	4·37	7·07	2·95	9·18	3·63
308	4·56	1·25	2·422	4·35	7·40	3·00	9·43	3·61
313	4·56	1·20	2·407	4·32	8·12	3·21	9·27	3·60
318	4·67	1·22	2·403	4·29	7·93	3·05	9·62	3·58
323	5·011	1·24	2·410	4·26	7·94	3·00	9·34	3·56
333	5·30	1·23	2·40	4·20	8·50	3·07	9·32	3·53
	Iso-amyl alcohol				Ethylene glycol			
303	16·98	5·64	3·809	3·146	3·26	3·04	1·137	7·115
308	17·78	5·73	3·925	3·132	3·75	3·41	1·167	7·092
313	17·46	5·40	3·99	3·118	3·80	3·43	1·204	7·088
318	18·37	5·61	3·88	3·116	3·64	3·25	1·206	7·082
323	19·27	5·73	3·99	3·113	3·53	3·14	1·159	7·078
333	20·18	5·73	3·91	3·108	3·40	3·0	1·137	7·072
338	20·43	5·65	3·99	3·105	3·31	3·0	1·19	7·067

Table 3. Values of $K'\eta$ and constant A and B at different temperatures.

	Acetone				Nitrobenzene		
Temp. (°K)	$K'\eta\times10^{9}$	$A\times10^{5}$	$B\times10^{5}$	Temp. (°K)	$K'\eta\times10^{9}$	$A\times10^{5}$	$B\times10^{5}$
260	4·05	3·18	5·67	296	3·36	3·35	3·9
273	4·24	3·35	5·54	323	3·28	3·12	3·8
303	4·13	3·18	5·35	338	3·25	3·18	3·74
313	4·00	3·02	5·29	358	3·27	3·48	3·65
323	4·04	3·08	5·25	383	3·24	3·07	3·6
				393	3·24	3·0	3·56



Figures 2–7. Dependence of RF conductivity K' (mhos/cm) on inverse of viscosity (in poise^{-1}). Curve I. Conductivity vs $1/\eta$. Curve II. Conductivity vs $1/\eta^{n}$.

perature whereas B varies slightly. Table 3 and figure 9 also show that the value of $K'\eta$ for nitrobenzene and acetone are almost constant at different temperatures and obey the Walden's law. Equation (9) therefore seems to be more appropriate for alcohol molecule. The hydroxyl group in an alcohol molecule may be regarded as

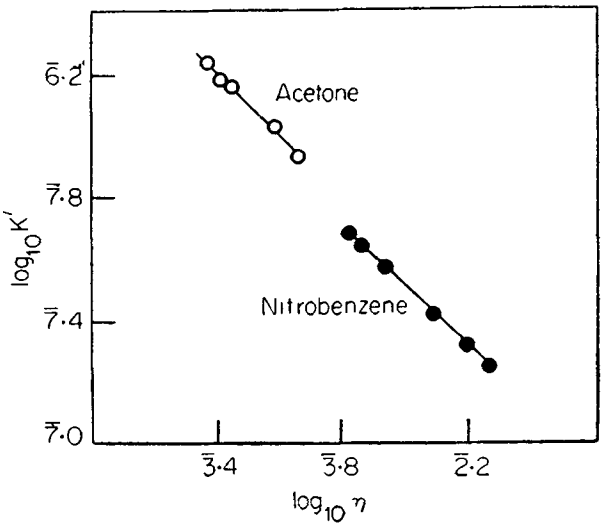


Figure 8. Plot of $\log_{10} K'$ in mhos/cm against $\log_{10} \eta$ in poise.

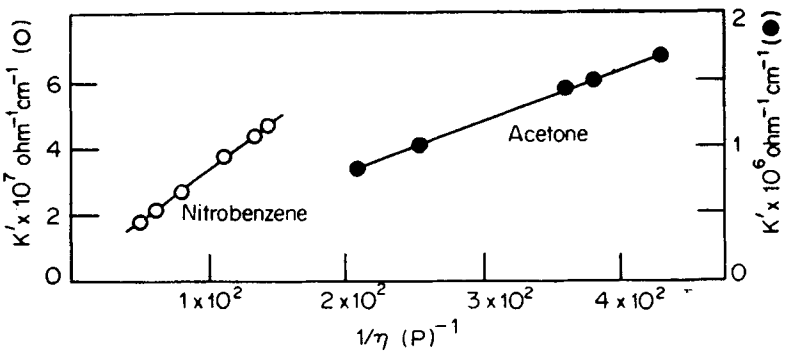


Figure 9. Dependence of RF conductivity K' (mhos/cm) on inverse of viscosity $1/\eta$ poise^{-1}.

an $\overline{O}$ ion containing a proton. The positive charge associated with the embedded proton together with an equal negative charge, gives to the (OH) group a dipole moment. It is well-known that in liquid alcohol some dipoles become linked to form a chain through intermolecular hydrogen bonding and the electrical conduction in alcohol has been accounted for by a proton transfer or by a proton jumping process. Watson (1963), Nowak (1963) and Zijac (1967) suggested that when $n \simeq 1$, the electrical conduction is due to the mobility of the negative ion and $n > 1$ the electrical conduction is due to the mobility of the positive ion. Therefore the observed value of n which is greater than the value of unity for alcohols implies that the RF conduction mechanism in aliphatic alcohols is possibly due to proton transfer or due to the proton jumping process.

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