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Dielectric relaxation in phenyl alcohols at low temperatures

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Abstract.

The complex dielectric constant of three phenyl alcohols has been measured at frequencies between 1 Kc/s and 3 Mc/s over a temperature range of -60°C to -20°C in order to compare the relaxation behaviour with that of monohydric aliphatic alcohols. To ascertain the effect of the proximity of the phenyl and hydroxyl groups the substances chosen were 3-Phenyl Propanol, 2-Phenyl Ethanol and 1-Phenyl Propanol. The shape of the Cole-Cole diagrams and the activation energy is discussed.

INTRODUCTION.

Previous research into the dielectric behaviour of monohydric alcohols at low temperatures has revealed a typical pattern of behaviour [1, 2, 3]. A major dispersion region having a single relaxation time is accompanied by one or more minor dispersion regions having much smaller relaxation times. The main relaxation time is generally assumed to be due to the reorientation of dipoles by the breaking and re-forming of hydrogen bonds linking the hydroxyl groups [4]. Experimental results indicate that the activation energy increases with length of the chain in primary alcohols and increases further if the chain is divided [2].

The purpose of the investigation described here is to determine whether the typical dielectric behaviour is maintained if a phenyl group is substituted in the alcohol. Measurements were made on 3-Phenyl Propanol, 2-Phenyl Ethanol and 1-Phenyl Propanol in which the phenyl group is attached to the third, second and first carbon atoms respectively.

EXPERIMENTAL DETAILS

The materials were dried by standing over anhydrous calcium sulphate and then distilled under vacuum.

Measurements were carried out at temperatures between -60°C and -20°C using totally enclosed guard ring cell immersed in a constant temperature bath. Dielectric constant and loss were measured at frequencies between 1 Kc/s and 3 Mc/s.

3-Phenyl Propanol.

The Cole-Cole diagram for this substance is found to be fundamentally similar to that of other alcohols. At -60°C a main dispersion (with a single relaxation time of 18.5×10^{-6} sec) has $\epsilon_s = 23.7$ and $\epsilon_{\infty} = 4.2$. A high frequency dispersion reduces this to $\epsilon_{\infty} = 3$. The relatively high static dielectric constant suggests association.

2-Phenyl Ethanol.

This substance melts at -26°C but was found to supercool readily. A Cole-Cole diagram for the liquid at -59.5°C consists of a main dispersion with a single relaxation time of 14.7×10^{-6} sec., $\epsilon_s = 24.8$ and $\epsilon_{\infty} = 4.6$. A high frequency dispersion reduces ϵ_{∞} to 3.0. The large static dielectric constant again suggests association.

1-Phenyl Propanol.

A Cole-Cole diagram for this substance is asymmetric and is found to conform closely to a continuous distribution of relaxation times giving rise to the Cole-Davidson relationship¹.

$$\epsilon = \epsilon_{\infty} + \frac{\epsilon_s - \epsilon_{\infty}}{(1 + j \omega \tau)^{\beta}}$$

A table of Cole-Davidson parameters for the material at various temperatures found to fit the experimental points is given below.

Temperature ($^{\circ}\text{C}$)	ϵ_{∞}	ϵ_{∞}	β	Critical frequency ($1/2 \pi \tau$) Kc/s.
-30	9.55	3.15	0.72	270
-35.1	10	2.9	0.72	100
-40.2	10.65	2.9	0.65	26.5
-45.1	11.2	2.9	0.66	8.3
-50	12.25	2.9	0.66	1.5

The lower static dielectric constant suggests a reduced degree of association.

TEMPERATURE DEPENDENCE OF RELAXATION TIME.

The slope of a graph of the logarithm of the relaxation time plotted against the reciprocal of the absolute temperature is a measure of the heat of activation ΔH .

Values obtained from the experimental results were as follows:

	ΔH
3 Phenyl Propanol	14.7 K Cal/Mole
2 Phenyl Ethanol	14.5 K Cal/Mole
1 Phenyl Propanol	25.5 K Cal/Mole

The large value for 1 Phenyl Propanol suggests a much higher hinderance to dipole rotation.

CONCLUSION.

The measurements on 2-Phenyl Ethanol and 3-Phenyl Propanol indicate that the substitution of a phenyl group on the second or third carbon atom of an alcohol does not prevent it from displaying the typical dielectric behaviour. There is little difference in activation energy for the two positions.

1-Phenyl Propanol differs greatly in so far as it displays a distribution of relaxation times, a higher activation energy and a lower static dielectric constant. All these effects are presumably due to the close proximity of the phenyl and hydroxyl groups.

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Résumé.

La constante diélectrique complexe de 3 alcools phénoliques a été mesurée à des fréquences situées entre 1 Kc/s et 3 Mc/s et dans un domaine de température de -60°C à -20°C afin de comparer le comportement de leur relaxation avec celui des alcools aliphatiques monohydriques. Pour confirmer l'effet de la proximité des groupes phényl et hydroxyl, les substances choisies étaient 3-phénylpropanol, 2-phényléthanol et 1-phénylpropanol. Nous discutons la forme des diagrammes de Cole-Cole et la valeur de l'énergie d'activation.
