Main Absorption Region of some Pure Normal Alcohols and of Mixtures of Butyl Alcohol with Non-Polar Solvents

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The dielectric constant ε' and dielectric loss ε'' are measured for pure n-butyl, n-amyl, n-octyl, n-dodecyl alcohols and for concentrated solutions of n-butyl alcohol in four non-polar solvents at three frequencies between 100 and 400 MHz at three temperatures between 20 and 60 °C. The effective dipole moment has been calculated for the concentrated solutions and the results obtained are discussed. The relaxation times of the concentrated solutions of n-butyl alcohol are in general higher than that of pure n-butyl alcohol (contrary to what was found before in case of n-decyl alcohol) but decreases with increasing dilution.

Introduction

Alcohols present an interesting problem in liquid structure due to the possibility of forming associates by hydrogen bonding. Investigations on them have been carried out since 1927 [1]. Further measurements [2-9] over a wide frequency region have shown that the anomalous dispersion and absorption is represented by three regions (the long-wave side region is called the main absorption region) overlapping one another. Each of them is represented by one relaxation time and the behaviour in dilute solutions is different from that of pure alcohols [4].

Experimental

ε' and ε'' have been measured at 100, 200 and 400 MHz using the second method of DRUDE [10]. Few measurments have been carried out also at 250 MHz. The apparatus is similar to that used for determining ε' and ε'' of rubber [11] with the one exception that instead of the rubber plate, a small glass condenser filled with the liquid under test is put across the wires. To measure at different temperatures, warm air is blown at this condenser and the temperature of the liquid is measured by a thermocouple. The apparatus has been calibrated using pure n-octyl alcohol. The curves found in literature [12] for ε' and ε'' versus $\log \lambda$ for n-octyl alcohol at 20 °C are shown in Fig. 1 together with our measured values which lie very well on the curves.

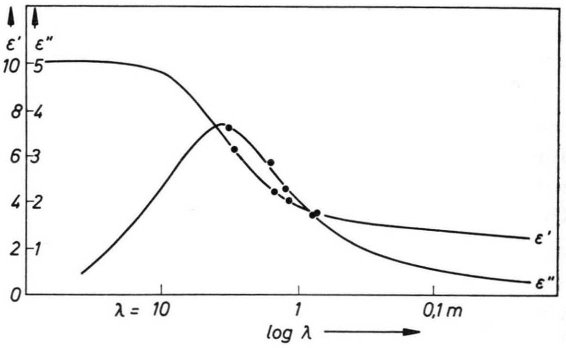

Fig. 1. Dispersion ε' and absorption ε'' of n-octanol at 20 °C [12]. ● Own measurements.

The static dielectric constant ε_s has been measured at 70 kHz by a Schering bridge, the refractive index n_D by an Abbé refractometer, the viscosity η by a Höppler viscometer and the density ϱ by a Mohr-balance.

Pure n-butyl, n-amyl, n-octyl and n-dodecyl alcohols were obtained from B.D.H. Poole, England and were carefully dried before use. As non-polar solvents, pure CCl_4, tetralin, decalin and medical paraffin oil were used.

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Results and Discussions

1. *Dipole Moment*

The effective dipole moment μ_0 for the investigated pure alcohols and for the concentrated solutions of n-butanol in non-polar solvents are calculated from ε_s and $n_D{}^2$ using the Onsager relation[13]

$$\frac{(\varepsilon_s - n_D{}^2)\,(2\,\varepsilon_s + n_D{}^2)}{\varepsilon_s\,(n_D{}^2+2)^2} = \frac{4\,\pi\,N\,\mu_0{}^2}{9\,k\,T}$$

where: N is the number of molecules per C. C., k is Boltzmann's constant, and T is the absolute temperature.

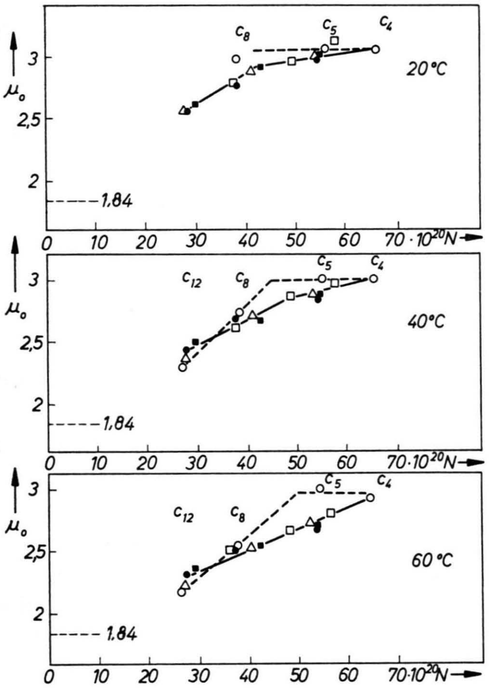

Fig. 2. Effective dipole moment μ_0 calculated by Onsager equation versus the concentration N of the OH-group for pure alcohols (○) and for solutions of n-butanol in: □ CCl_4, ■ Tetralin, △ Decalin, and ● Paraffin oil at 20, 40 and 60 °C.

The results obtained are drawn in Fig. 2 versus the dipole concentration N at the different temperatures. As shown, μ_0 for the small alcohol molecules (around 3 Debye) is temperature independent while that of the larger molecules (n-octyl and n-dodecyl alcohols) decreases regularly with the decrease in N and is temperature dependent. The value of μ_0 (3 Debye) obtained for the small molecules is higher than that found for single molecules (1.70 D) indicating that associates are present, but as the dipole concentration is high (around 60×10^{20} cm^{-3}) the molecules may not be able to change their positions and so μ_0 is not temperature dependent. On the other hand, μ_0 for n-octyl and n-dodecyl alcohols decreases with increase in temperature indicating that polar associates are decreased. Using the data found in literature[14] for ε_s and ε_∞, μ_0 is calculated for the normal alcohols between C_3 and C_{10} at 20 °C using Onsager equation and for all investigated molecules it was found that μ_0 has the same value for small alcohol molecules between C_3 and C_6 and then decreases regularly with the dipole concentration, i. e. in agreement with our results. Also, KLAGES[15] found that μ_0 for normal alcohols between C_{10} and C_{16} depends upon the dipole concentration but he did not examine lower alcohols.

μ_0 for the concentrated solutions of n-butanol in non-polar solvents calculated after Onsager equation are in general somehow lower than that of pure alcohols having similar dipole concentration. μ_0 decreases with the decrease in N but not in a regular way. It seems that the relation between μ_0 and N can be represented by two straight lines at 20 °C and 40 °C and one straight line at 60 °C. It is interesting to find that the extrapolation of the curves at the three temperatures gives the same value of μ_0 which amounts to 1.84 Debye.

It could be concluded that for the small alcohol molecules up to hexanol where the concentration of the dipoles is very high, the molecules associate in a manner different to that found in case of the alcohols higher than hexanol.

2. *Dispersion and Absorption*

a) Pure alcohols

Figure 3 gives the measured values of ε' and ε'' for n-butyl, n-amyl, n-octyl, and n-dodecyl alcohols at three different wavelengths and three temperatures. The values of ε' and ε'' obtained at the three frequencies together with the static dielectric constant are sufficient to define the Debye curve of the main absorption region and to determine the relaxa-

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tion time τ. This is attained either by the Cole-Cole semicircle method[16] or using the familiar Debye equation[17]. The values of τ are plotted versus N in Figure 4. It is to be noticed that τ decreases with increasing temperature and increases with chain length. Moreover, the dependence of τ on the size of the molecule is less distinct at higher temperatures. Some values of τ found in literature[12] are added to Figure 4. They agree very well with our results.

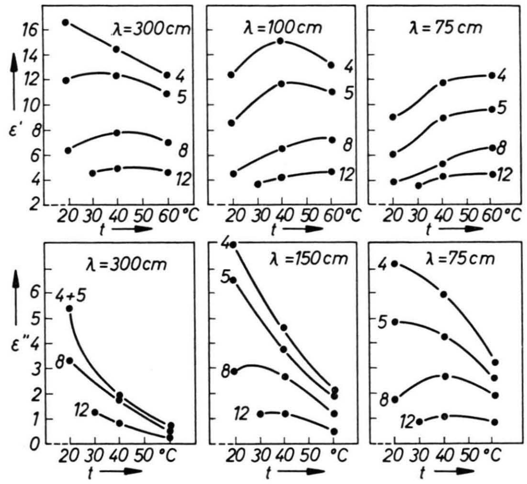

Fig. 3. Measured values of ε' and ε'' of pure normal alcohols. The ciphers give the number of the carbon atoms in the molecule.

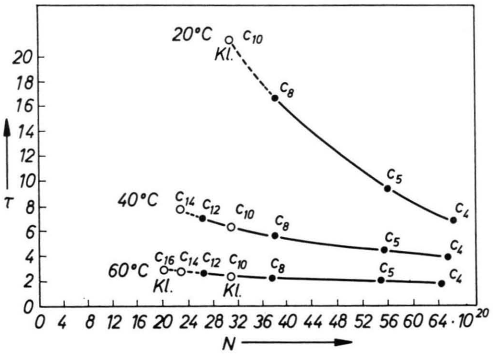

Fig. 4. The relaxation time τ of the main absorption region of pure normal alcohols versus the dipole concentration N. ● Own results and ○ data found in literature[12].

From the temperature dependence of the relaxation time, the activation energy has been calculated after EYRING and KAUZMANN[18]. In the temperature range used (20 – 60 °C) $\log T\tau$ is plotted versus $1/T$ for the mentioned molecules and a straight line is obtained in each case. From the slope of these straight lines, the heat of activation ΔH and hence the entropy of activation ΔS have been calculated. The results are given in Table 1. It is to be noticed that ΔH and ΔS increase with increasing chain length. ΔH is represented graphically versus the number of carbon atoms in Figure 5. Some literature values[12] are added also to our calculated values and it is clear that the increase in ΔH is slow for molecules having more than 10 carbon atoms.

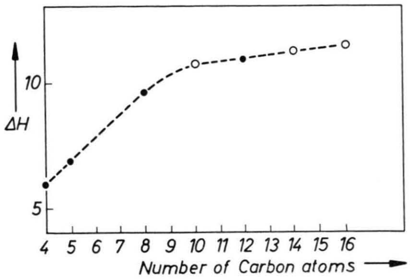

Fig. 5. Activation energy ΔH vs. the number of carbon atoms. Same notations as in Fig. 4.

It is also interesting to study the variation of τ with the viscosity η. From Fig. 6 it is seen that the relation between τ and η is almost linear till octyl alcohol and that at higher temperatures, the decrease in τ with decreasing viscosity is not much.

To sum up, τ for small and big alcohol molecules are single-valued (i. e. no distribution of relaxation times) and increase with chain length but are much too large to correspond to the orientation of a single

Alcohol	ε_∞	$\tau \cdot 10^{10}$ (sec) 20 °C	30 °C	40 °C	60 °C	ΔH kcal/mole	ΔS cal/mole/deg
n-butyl	—	6.68	—	3.82	1.66	6.03	4.00
n-amyl	—	9.30	—	4.30	1.99	6.88	6.29
n-octyl	3.10	16.54	—	5.64	2.19	9.62	14.40
n-dodecyl	2.90	—	13.0	7.01	2.58	10.80	17.68

Table 1. Main absorption region of normal primary alcohols. High frequency limiting value of dielectric constant ε_∞, relaxation time τ, activation energy ΔH and activation entropy ΔS.

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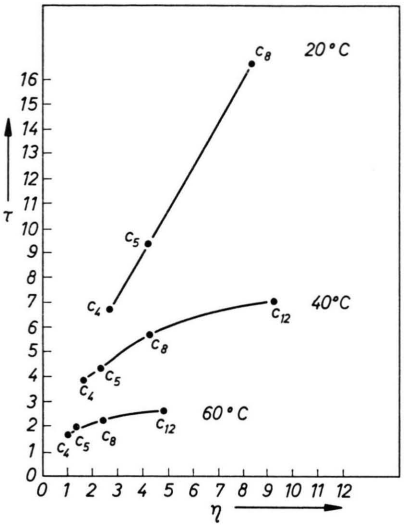

Fig. 6. τ versus the viscosity η at 20, 40 and 60 °C for pure normal alcohols.

molecule and may be expected for associates resulting from the strong hydrogen bonding between the OH-groups. As in previous interpretations[19], τ is attributed to breaking of the hydrogen bonds followed by ROH rotation. The relaxation time is long[18] because of the time required to break the hydrogen bond, dependent upon the length of the chain of the rotating ROH, but uninfluenced by all but the nearest portions of the molecular aggregate and essentially single valued.

b) n-Butanol mixtures with non-polar solvents

ε′ and ε″ have been measured and the data analysed in the same way as before. An example of the analysis is given in Fig. 7 and the results obtained for τ are plotted versus N in Figure 8. It is astonishing to find that the relaxation times increase by the addition of all the solvents and then decrease by continuous dilution. With the exception of 40% butanol mixtures with tetralin and CCl_4, the results obtained are contrary to what was found by us in case of n-octanol and n-dodecanol[20] and by KLAGES[12] in case of n-decanol where the relaxation times of all solutions are lower than those for pure alcohols.

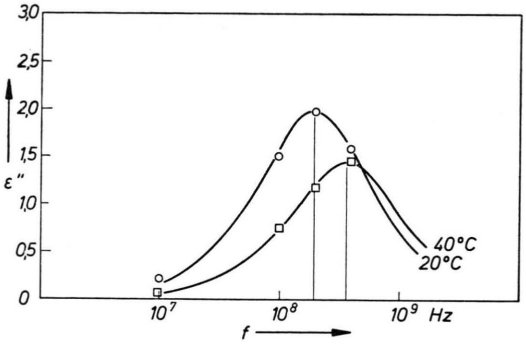

Fig. 7. Absorption curve of n-butanol in paraffin oil (concentration 40.5% alcohol) at 20 and 40 °C.

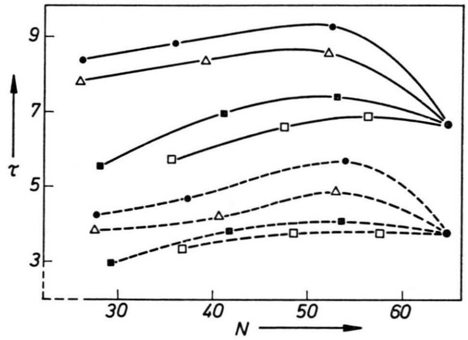

Fig. 8. τ versus N for n-butanol and its concentrated solutions in non-polar solvents. Same notations as in Fig. 2. ——— at 20 °C and – – – – at 40 °C.

As τ is solvent dependent, so, its variation with the viscosity is studied. It is noticed that although most of the decalin, tetralin and CCl_4 mixtures have viscosities lower than that for pure n-butanol, yet τ is higher than that for pure butanol and decreases

Table 2. Mixtures of n-butanol with non-polar solvents N is the dipole concentration at 20 °C, ΔH is the activation energy and ΔS is the activation entropy.

Solvent	N 10^{20} cm^{-3}	ΔH kcal/mole	ΔS cal/mole/deg
CCl_4	57.5	4.10	−2.50
	48.6	4.02	−2.75
	36.8	3.10	−5.50
Tetralin	54.3	4.57	−1.15
	42.4	4.33	−1.80
	29.5	3.74	−3.40
Decalin	53.0	5.12	0.45
	40.6	4.85	−0.35
	27.4	4.66	−0.70
Paraffin oil	54.0	3.75	−4.40
	37.3	4.66	−1.06
	27.7	5.56	2.00
n-Butanol (pure)	66.5	6.03	4.00

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with the decrease in viscosity. Paraffin oil mixtures have also higher values of τ but they decrease with the increase in viscosity in agreement to what was found by KLAGES[15] in case of decyl alcohol.

The activation energy ΔH and activation entropy ΔS for the investigated mixtures are given in Table 2. They are lower than that for pure n-butanol and decrease with the decrease in N with the exception of paraffin oil mixtures where they increase with the decrease in N. The behaviour of paraffin oil is different from the other solvents which is an indication that due to the viscous flow another molecular process takes place other than the orientation of the molecule.

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Zum Kornwachstum beim reinen und dotierten polykristallinen Selen

C. WEYRICH

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Grain Growth of Pure and Doped Polycrystalline Selenium

Samples of vitreous high-purity selenium as well as vitreous chlorine- and thallium-doped selenium have been brought into the polycrystalline form by annealing. The dependence of grain size on annealing time t_u was measured. In high-purity selenium and in chlorine-doped selenium the mean grain diameter increases essentially $\sim t_u^{1/2}$, in thallium-doped selenium $\sim t_u^{1/2}$, as is expected from the laws of grain growth. The proportionality between electrical conductivity and specific grain surface reported by other authors could not be verified.

1. Einführung

Trotz zahlreicher Untersuchungen bereitet die Deutung der Eigenschaften des Selens, insbesondere seines Leitungsmechanismus, heute noch große Schwierigkeiten.

Die exponentielle Abhängigkeit der Defektelektronenbeweglichkeit von der reziproken Temperatur im trigonalen einkristallinen Selen — trigonales Selen ist immer p-leitend — deutet STUKE[1] durch einen Hopping-Prozeß: Die Ladungsträger müssen bei ihrer Bewegung im Kristall Potentialschwellen, die durch Sperrschichten an den Versetzungen zustande kommen, überwinden. Die Ladungsträgerkonzentration ist nahezu temperaturunabhängig und läßt sich nur durch plastische Verformung erhöhen.

Trigonales polykristallines Selen erhält man durch Tempern von glasigem Selen unterhalb des Schmelzpunktes. Die elektrische Leitfähigkeit durchläuft dabei in Abhängigkeit von der Temperdauer ein Maximum, dessen Höhe und Lage von der thermischen Vorgeschichte und der Art und der Stärke der Dotierung abhängt. GOBRECHT, TAUSEND und PLÜMECKE[2] finden, daß die Kornoberfläche für den Leitungsmechanismus eine große Rolle spielt, insbesonders, daß die Leitfähigkeit nach dem Maximum proportional der sich ebenfalls verringernden spezifischen Kornoberfläche (=Kornoberfläche pro Volumeneinheit) abnimmt. Das bedeutet, daß die Kornoberflächen gegenüber dem Korninneren niederohmige Gebiete darstellen, entlang derer der Leitungsmechanismus bevorzugt stattfindet.

In der vorliegenden Arbeit wurde das Kornwachstum von Reinstselen (99,999%), sowie 123 ppm chlordotiertem und 350 ppm thalliumdotiertem Selen untersucht. Die Messungen erfolgten nicht wie bei [2] unter Ausnutzung des Reflexionsdichroismus, sondern durch Abbildung von Oberflächen im Durchstrahlungselektronenmikroskop.

2. Kornwachstumsgesetze[3]

Die Korngröße beim Polykristall nimmt bekanntlich im Laufe der Temperung zu. Größere Körner wachsen stets auf Kosten kleinerer, wobei sich die Korngrenzen auf ihren Krümmungsmittelpunkt hin bewegen, und zwar um so schneller, je größer die

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