Main Dielectric Dispersion Region of Mixtures of some Long-Chain Alcohols with Non-Polar Solvents

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The dielectric constant ε' and dielectric loss ε'' are measured for concentrated solutions of n-dodecanol and n-octanol with five non-polar solvents at five frequencies between 2 and 400 MHz at three temperatures between 20 and 60 °C. The effective dipole moments have been calculated and found to decrease with increasing dilution. The relaxation times of the concentrated solutions are lower than that of the pure alcohols, decrease with dilution and are dependent on the nature of the non-polar solvents.

Introduction

The relaxation times of concentrated solutions of n-butanol in non-polar solvents have been studied before[1] and it is aimed in this communication to find out whether the behaviour of the long-chain alcohols is similar to, or different from that of n-butanol.

Experimental

ε' and ε'' have been measured at three temperatures between 20 and 60 °C at 100, 200 and 400 MHz using the second method of Drude to an accuracy of 2%. The description and calibration of the apparatus is given in[1].

Pure n-dodecanol and n-octanol were obtained from B. D. H. Poole, England, carefully dried and fractionally distilled before use. As non-polar solvents, pure CCl_4, benzene, heptane, decalin and medical paraffin oil were used.

Results and Discussions

1. Dipole Moment

The effective dipole moments (μ_0) for the investigated concentrated solutions of n-dodecanol and n-octanol in non-polar solvents are calculated in the same way as given before[1]. The values obtained are plotted in Fig. 1 versus the dipole concentration N_1, together with the values obtained before for the pure alcohols. It is clear that μ_0 for the different mixtures decreases with increasing dilution. It seems that μ_0 depends essentially upon the dipole concentrtaion. It is to be added that μ_0 approaches at lower concentrations the value μ obtained from dilute solutions[2], which is 1.70 D. For butanol solutions[1], μ_0 approaches the value 1.84 D. Anyhow, this does not mean that the associates are fully decomposed, as it was found before[3] that at still increasing dilution, μ_0 reaches a minimum which indicates that non-polar associates are dominant.

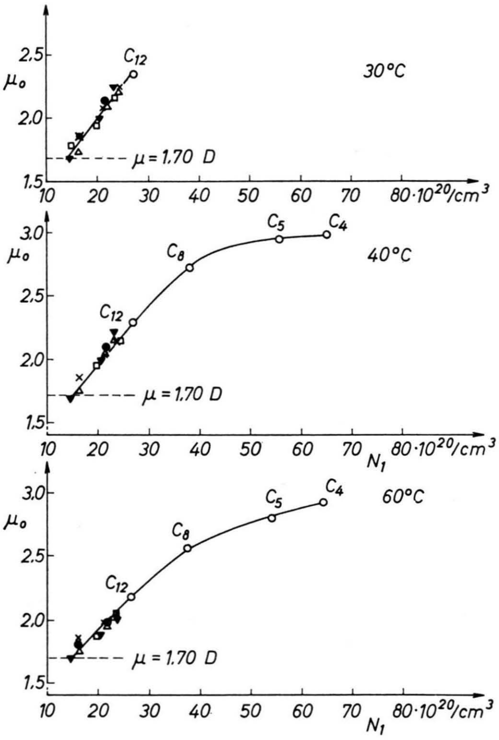

Fig. 1 a. Effective dipole moment μ_0 calculated by the Onsager equation versus the concentration N_1 of the OH-group for pure normal alcohols 0 and for mixtures of n-dodecanol with: ● Oil, △ Decalin, ▼ Heptane, □ Carbontetrachloride, × Benzene at 30, 40 and 60 °C. μ is the dipole moment of the alcohols in dilute solutions.

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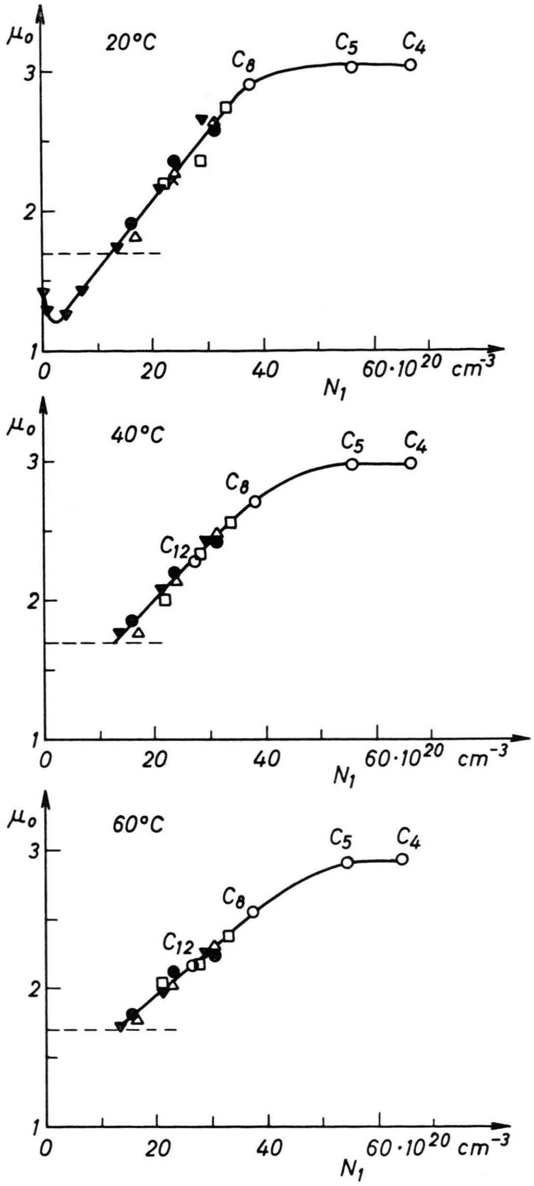

Fig. 1 b. Effective dipole moment μ_0 calculated by the Onsager equation versus the concentration N_1 of the OH group for n-octanol solutions. Same notations as in Figure 1 a.

This behaviour was observed in our laboratory in the case of dilute n-octanol solutions[4] as shown in Figure 1. μ_0 for the mixtures decreases with increasing temperature which means that the polar associates are decreased, but the decrease is about the same as that for the pure alcohol.

2. Dispersion and Absorption

It is to be emphasized that the main absorption region of pure normal alcohols and of their concen-

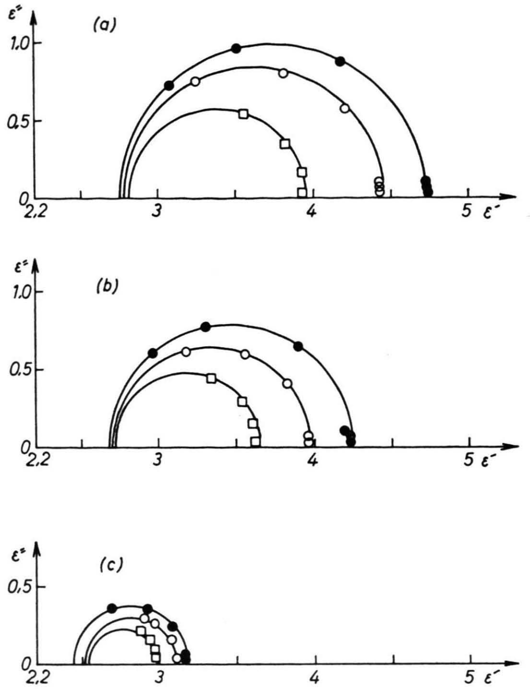

Fig. 2 a. Cole-Cole semi-circles for the main absorption region of n-dodecanol in decalin at concentrations: (a) 87%, (b) 80%, and (c) 60% by weight of alcohol. ● 20 °C, ○ 40 °C, and □ 60 °C.

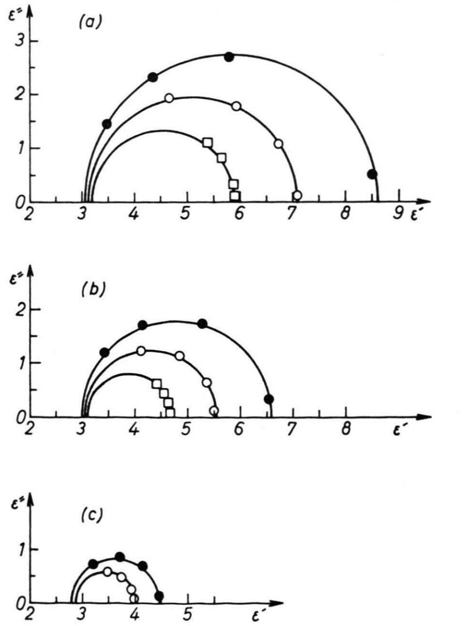

Fig. 2 b. Cole-Cole semi-circles for the main absorption region of n-octanol in CCl_4 at concentrations: (a) 80%, (b) 60%, (c) 40% by weight of alcohol. ● 20 °C, ○ 40 °C, and □ 60 °C.

trated solutions in non-polar solvents is found in all cases till now to follow a Debye curve[5–10]. So, the three measured values of ε'' at 100, 200, and 400 MHz are sufficient to define this absorption curve using the COLE-COLE[11] semicircle method or the familiar DEBYE equation[12].

Examples of the Cole-Cole semicircles are given in Figure 2. It is to be noted that the accuracy of the analysis at 60 °C is less than at 20 and 40 °C because the measured values of ε'' lie on one side of the curve before the maximum. The relaxation times obtained at 30 and 40 °C for the different mixtures of n-dodecanol and those obtained at 20 and 40 °C for n-octanol mixtures are given in Tables 1 and 2. It is to be noted that for the same dipole concentration N_1, the relaxation time τ is dependent on the nature of the non-polar solvent.

Therefore, it is appropriate to compare the variation in the relaxation time τ with that of viscosity η. This is shown in Figure 3. It is found that when the viscosity of the mixture is lower than that of the pure alcohol, then τ decreases with the decrease of the viscosity, whereby the solvents of lower viscosities lead to longer relaxation times. At higher temperatures (60 °C), the decrease in τ with the decrease in viscosity is small.

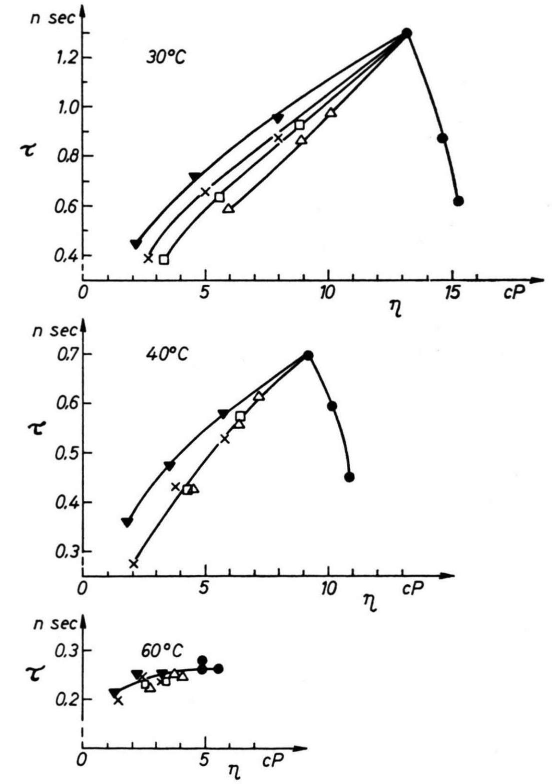

Fig. 3 a. τ versus the viscosity η for n-dodecanol mixtures with non-polar solvents. Same notations as in Figure 1 a.

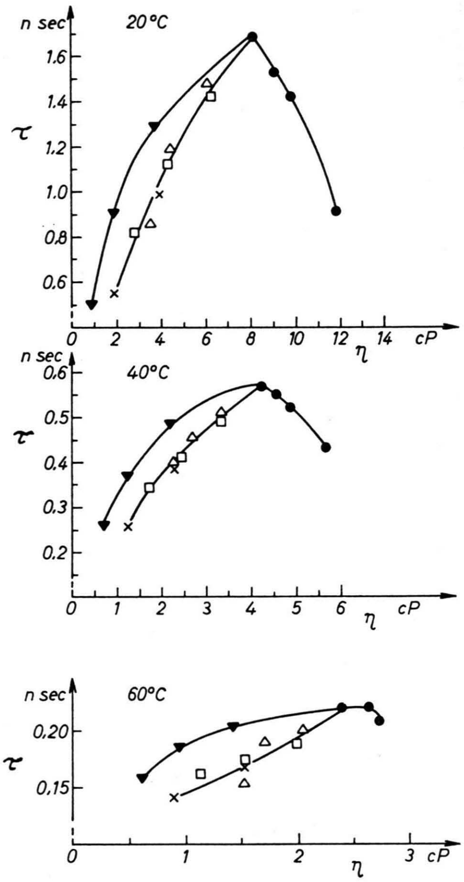

Fig. 3 b. τ versus the viscosity η for n-octanol mixtures with non-polar solvents. Same notations as in Figure 1 a.

The mixtures with paraffin oil are more viscous than the pure alcohols, and in spite of that the relaxation time decreases with the addition of more oil, i. e. with the increase in viscosity. This behaviour was found before by KLAGES[9] in the case of n-dodecanol mixtures with oil.

From the temperature dependence of the relaxation time, the activation energy ΔH and activation entropy ΔS have been calculated after EYRING and KAUZMANN[13] for the different mixtures. The results are given in Tables 1 and 2. For the solvents of lower viscosity than the pure alcohols, ΔH and ΔS are less than that of the pure alcohol and decrease with dilution. On the other hand, ΔH and ΔS increase a little with dilution in the case of paraffin

Table 1 a. Mixtures of n-dodecanol with non-polar solvents at 30 °C. N_1 is the dipole concentration, η, ε_0 and $n_D{}^2$ are the viscosity, static dielectric constant and square of the refractive index respectively. μ_0 is the effective dipole moment, τ is the relaxation time, ΔH is the activation energy and ΔS is the activation entropy.

Solvent	N_1 10^{20} cm^{-3}	η cP	ε_0	n_D^2	μ_0 D	τ ns	ΔH kcal/mole	ΔS cal/mole/deg
n-Dodecanol pure	27.0	13.26	5.53	2.0779	2.33	1.30	10.8	17.7
Heptane	23.80	7.97	4.76	2.0561	2.24	0.94	8.1	9.5
	20.80	4.65	3.84	2.0395	1.99	0.71	6.2	3.9
	14.95	2.14	2.80	2.0051	1.67	0.44	4.3	−1.4
Benzene	24.05	7.94	4.83	2.0854	2.22	0.86	7.8	8.9
	21.80	4.98	4.24	2.0982	2.08	0.65	6.3	4.3
	16.45	2.65	3.36	2.1261	1.86	0.39	3.8	− 2.9
CCl_4	23.80	8.81	4.64	2.0788	2.17	0.93	8.3	10.4
	20.20	5.60	3.74	2.0822	1.94	0.64	6.1	3.9
	15.35	3.31	3.12	2.0880	1.78	0.38	—	—
Decalin	23.60	10.21	4.73	2.0828	2.20	0.97	8.4	10.2
	21.80	8.94	4.24	2.0886	2.09	0.87	7.6	8.1
	16.55	5.92	3.17	2.1054	1.74	0.60	6.6	5.3
Paraffin oil	21.80	14.66	4.30	2.0909	2.12	0.88	6.5	4.4
	16.40	15.25	3.33	2.1083	1.85	0.63	6.7	5.6

Table 1 b. Results at 40 °C. Same notations as in Table 1 a.

Solvent	N_1 10^{20} cm^{-1}	η cP	ε_0	n_D^2	μ_0 D	τ ns
n-Dodecanol pure	26.80	9.25	5.22	2.0653	2.28	0.70
Heptane	23.70	5.73	4.53	2.0446	2.20	0.58
	20.70	3.56	3.72	2.0283	1.98	0.47
	14.82	2.78	2.78	1.9937	1.69	0.35
Benzene	23.90	5.79	4.50	2.0753	2.14	0.53
	21.70	3.74	4.01	2.0851	2.03	0.43
	16.35	2.07	3.26	2.1115	1.84	0.27
CCl_4	23.70	6.45	4.46	2.0670	2.15	0.57
	20.05	4.29	3.68	2.0693	1.94	0.42
Decalin	23.50	7.19	4.46	2.0730	2.15	0.61
	21.70	6.41	3.98	2.0776	2.02	0.56
	16.45	4.44	3.11	2.0935	1.74	0.42
Paraffin oil	21.65	10.15	4.08	2.0794	2.07	0.59
	16.30	10.84	3.23	2.0967	1.84	0.45

oil. This was noticed before by Klages[9] in the case of n-decanol mixtures with oil.

From this study it can be concluded that the relaxation times of the concentrated solutions of the long chain alcohols are always lower than that of the corresponding pure alcohols, contrary to what was found in the case of the concentrated solutions of the short chain alcohols (n-butanol[1]) where the relaxation times first increase with the addition of all the solvents and then decrease with continuous dilution.

Acknowledgment

We should like to thank Prof. Dr. R. N. Sedra, Professor of Physics, Cairo University, for his kind interest in this work.

Table 2 a. Mixtures of n-octanol with non-polar solvents at 20 °C. Same notations as in Table 1 a.

Solvent	N_1 10^{20} cm^{-3}	η cP	ε_0	n_{D}^2	μ_0 D	τ nS	ΔH k cal/mole	ΔS cal/mole/deg
n-Octanol pure	38.20	8.26	10.35	2.0433	2.90	1.65	9.6	14.4
Heptane	29.50	3.67	7.10	2.0178	2.64	1.27	8.3	10.5
	21.40	1.95	4.24	1.9937	2.16	0.89	7.3	7.9
	13.73	0.99	2.808	1.9690	1.73	0.48	5.2	1.9
	7.05	—	—	—	1.43	—	—	—
Benzene	31.3	4.09	7.50	2.0750	2.61	0.99	7.9	9.6
	23.7	1.99	4.98	2.1151	2.22	0.55	5.3	2.2
CCl_4	33.8	6.34	8.60	2.0532	2.75	1.42	9.1	13.1
	28.4	4.38	6.60	2.0650	2.56	1.12	8.2	10.6
	21.9	2.89	4.49	2.0794	2.18	0.82	7.3	8.0
Decalin	31.20	6.18	7.48	2.0670	2.61	1.48	9.1	13.0
	23.80	4.58	5.03	2.0912	2.26	1.19	8.3	10.6
	17.06	3.66	—	2.1141	1.82	0.86	7.1	7.1
Paraffin oil	31.20	9.12	7.25	2.0736	2.59	1.53	8.5	11.0
	23.60	9.96	5.29	2.0950	2.35	1.42	9.1	13.0
	15.90	11.92	—	2.1220	1.92	0.91	—	—

Table 2 b. Results at 40 °C. Same notations as in Table 1 a.

Solvent	N_1 10^{20} cm^{-3}	η cP	ε_0	n_{D}^2	μ_0 D	τ ns
n-actanol pure	37.90	4.26	8.62	2.0221	2.71	0.56
Heptane	29.20	2.23	5.82	1.9937	2.43	0.48
	21.10	1.27	3.81	1.9684	2.07	0.37
	13.50	0.77	—	1.9432	1.67	0.25
Benzene	30.75	2.30	6.35	2.0506	2.46	0.38
	23.20	1.24	4.44	2.0822	2.15	0.26
CCl_4	33.30	3.36	7.10	2.0306	2.57	0.49
	28.10	2.44	5.55	2.0392	2.32	0.41
	21.60	1.73	3.98	2.0506	2.00	0.34
Decalin	30.70	3.34	6.30	2.0443	2.46	0.51
	23.50	2.68	4.40	2.0678	2.12	0.46
	16.85	2.31	—	2.0909	1.77	0.40
Paraffin oil	30.80	4.60	6.22	2.0506	2.43	0.55
	23.30	4.89	4.57	2.0721	2.20	0.52
	15.73	5.68	—	2.0993	1.86	0.43

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