Dielectric Properties of Solutions of a Binary Mixture Resorcinol/n-Dodecanol in Heptane

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The static and broadband dynamic dielectric properties of the title mixtures, which contain the diol to an only minor fraction, are reported for the whole concentration range (alcohol mole fraction 0.1 to 1). As with similar systems, the diol leads to increased association effects.

In previous publications we reported about the dielectric properties of mixtures of n-hexanol and some aromatic diols with mesitylene [1] and n-hexanol or n-dodecanol mixed with some aliphatic diols and diluted with heptane [2]. The present communication deals with mixture of a long chain alcohol, n-dodecanol "D", with an aromatic diol "R" (resorcinol, 1,3-dihydroxy benzene). Heptane "H" was used as a nonpolar diluent. Static and dynamic dielectric properties of this system have been measured over the concentration range (total alcohol mole fraction) $x = 0.1 - 1$ at three temperatures. Since the results are closely similar, the 20 °C values only are reported here. The dihydric/monohydric ratio is fixed and equals $r_{21} = 1/19$.

The static permittivity was determined at 2 MHz using a WTW dipolemeter with an uncertainty of 2%. The refractive index n_D was measured with an Abbe refractometer. The dielectric loss ε'' was measured over a wide frequency range (10 MHz–3 THz). At frequencies between 100 MHz and 11 GHz, a swept frequency transmission spectrometer was used [3]. In the high frequency region, four spot frequencies (138, 238, 429 and 671 GHz) were used. The 138 GHz frequency was generated by a Hughes oscillator [4], the other three frequencies were delivered by a Laser system [5, 6]. The values are uncertain to about 5%. The density and viscosity were measured by a pycnometer and capillary viscometer, respectively.

The normalized static-optical dispersion step $S/N = (\varepsilon_s - n_D^2)/N$ at 20 °C is illustrated in Fig. 1 for the investigated system RDH together with data for comparable systems, with another diol, EDH and HDH taken from [7]. Here, the number density N of dipoles, i.e. of OH groups is taken as a measure for the total alcohol content. The data for the mixture n-dodecanol–heptane (ODH) are added to show the effect of addition of diol to this mixture.

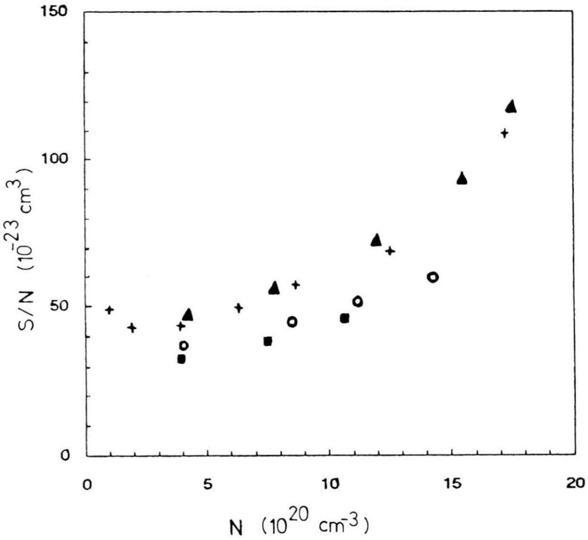

Fig. 1. Normalized dispersion steps S/N against number density N of dipoles, 20 °C.

■	n-dodecanol/heptane	ODH
○	1,2-ethanediol/n-dodecanol/heptane ($r_{21} = 1/9$)	EDH
+	resorcinol/n-dodecanol/heptane ($r_{21} = 1/19$)	RDH
▲	1,6-hexanediol/n-dodecanol/heptane ($r_{21} = 1/9$)	HDH

It is clear from Fig. 1 that the addition of a diol to the normal alcohol increases the dispersion step which is proportional to the apparent dipole moment squared (μ_{app}^2). The increase of μ_{app} for the investigated system RDH approaches that of HDH although the concentration of the resorcinol is only half that of 1,6-hexanediol. The increase of the values of S/N for EDH is relatively small, which could be due to the breaking of existing hydrogen bonds in the alcohol multimers and formation of ethanediol centered complexes.

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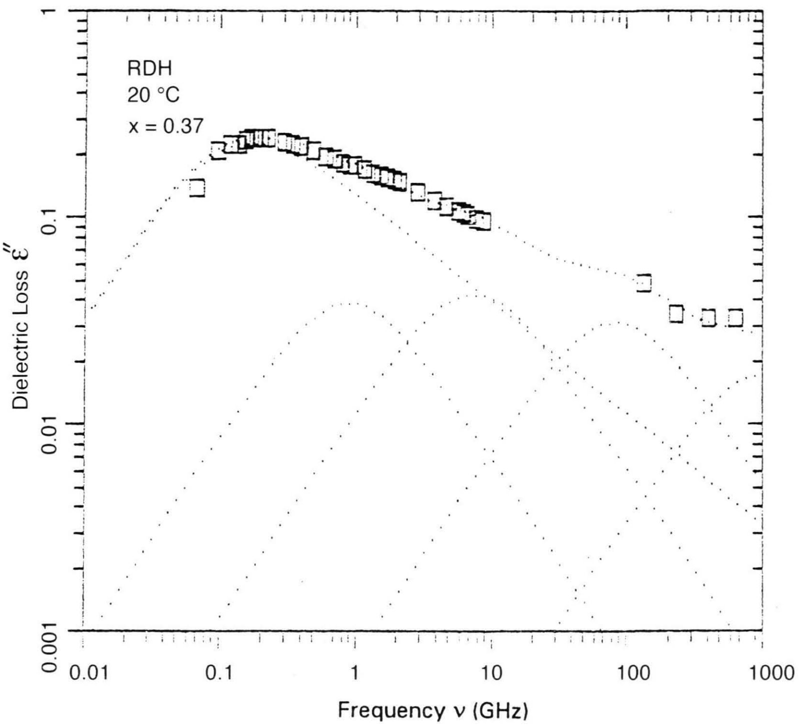

Fig. 2. Absorption spectrum for RDH ($x = 37$ mol%) at 20 °C. Fitting of the experimental data ε'' values using one Cole-Davidson and four Debye terms.

Table 1. Relaxation times τ_i, normalized relaxation strengths S_i/x, Cole-Davidson distribution parameter β and viscosity η for the system RDH (5 mol% resorcinol +95 mol% n-dodecanol) in n-heptane at 20 °C. [The mole fraction x denotes the total alcohol content.]

x mol%	η mPas	β	$\tau_1\beta$ ps	τ_2 ps	τ_3 ps	τ_4 ps	τ_5 ps	S_1/x	S_2/x	S_3/x	S_4/x	S_5/x	$\Sigma\,(S_i/x)$
100	–	0.94	2788	173	23	–	–	3.58	0.38	0.26	–	–	4.22
80	13.06	0.87	2326	168	22	–	–	3.40	0.38	0.25	–	–	4.03
65	7.45	0.73	1739	172	22	–	–	3.00	0.31	0.26	–	–	3.57
50	4.68	0.63	1263	169	20	1.7	0.16	2.27	0.27	0.27	0.13	0.08	3.02
37	2.09	0.54	793	173	21	1.8	0.16	1.60	0.20	0.22	0.16	0.09	2.27
16	0.86	0.38	344	169	21	1.8	0.17	1.06	0.16	0.23	0.16	0.11	1.72
10	0.64	0.33	263	169	22	1.8	0.16	0.92	0.10	0.25	0.18	0.13	1.58

The dielectric absorption spectra $\varepsilon''(\nu)$ for the investigated concentrations are broader than a Debye curve, as commonly found with alcoholic systems. This suggests to fit the data by a Cole-Davidson (CD) function [8]. The fit quality was improved by employing an additional superposition of Debye type spectral components. Relaxation parameters for 20 °C are given in Table 1 for the different concentration. An example of the analyses for the concentration $x = 0.37$ is shown in Figure 2.

It is clear from Table 1 that the effective relaxation time $\tau_1\beta$ of the main term and its normalized relaxation strength S_1/x increase with increasing concentration. The relaxation times of the second spectral component τ_2 at the different concentrations deviate by $<2\%$ from a mean value 170 ps, but its relaxation strength S_2/x has the same trend as S_1/x, i.e. it increases with increasing concentration. On the other hand, the relaxation times and the normalized relaxation strengths S_i/x for terms with relatively short relaxation times remain practically independent of concentration, so they are not related to the association process.

One must be very cautious in the assignment of relaxation processes to the different terms obtained from the analysis. There is no doubt that the first term characterized by τ_1 β and S_1/x is related to the association process. It reflects probably the time dependent association-dissociation equilibrium. The fraction of associated alcohol, which is proportional to S_1/x, becomes dependent on the alcohol concentration. The relaxation time τ_2 may describe the switch-over process from one hydrogen bond to another within the cluster. The terms with short relaxation times ($\tau_3 - \tau_5$) may be related to segmental motion in single molecules or polar group rotation or librational motion.

The data reported here show the alteration of the dielectric properties when a small fraction of a monohydric alcohol is replaced by a dihydric one, which similarly has been found for related systems. The increase in static permittivity is essentially due to the increasing strength of the main relaxation term (S_1/x in Table 1), thus to intensified association. To summarize, the effect of resorcinol is relatively strong, comparable to that of 1,6-hexanediol, in contrast to the weak effect of 1,2-ethanediol [2].

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