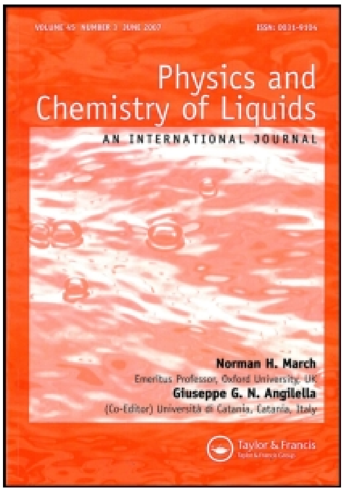

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DIELECTRIC STUDIES OF DILUTE SOLUTIONS OF BINARY MIXTURES OF N, N-DIMETHYLFORMAMIDE AND 1-HEXANOL IN THE NON-POLAR SOLVENT MESITYLENE

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The dielectric loss in the frequency range 200 MHz–10 GHz have been measured in dilute solutions of mesitylene for three binary mixtures of $\zeta = 0.25$, 0.50 and 0.75 MF of N, N-dimethylformamide (DMFA) in 1-hexanol. Similar measurements have also been carried out for dilute solutions of 1-hexanol $\zeta = 0$ and DMFA $\zeta = 1$ in mesitylene. The variation of static permittivity ε_s and dielectric loss ε'' of DMFA-Mesitylene systems as a funtion of ζ indicates a solute–solute type of molecular association between both components through a strong hydrogen bonding. The molecular association between DMFA and 1-hexanol is maximum around 1:1 ratio (i.e. $\zeta = 0.50$).

Keywords: Amides; dielectric; association

INTRODUCTION

Dielectric relaxation is a many particle phenomenon, and as such is a suitable tool for an insight into specific molecular interactions in polar liquids, as those leading to the formation of associates or other molecular aggregates. Relaxation time, as dynamical parameter, and relaxation strength, as structural or geometrical parameter, being related to a mean square moment, describe the behaviour of certain relaxing moities or relaxators, which generally consist of a number of molecules correlated by short range interactions.

The three kinds of amides (mono-, di- and un-substituted amides) have been extensively studied by dielectric spectroscopy already for a long time, regarding the pure liquids [1–4] as well as mixtures with water [5–7] or normal alcohols [8,9] or also non-polar solvents [9–12].

The influence of a *minor* dihydric alcohols component on the relaxation behaviour of a *major* component of 1-hexanol (protic/protic system) as a function of their total concentration in non-polar medium and of temperature was studied recently [13–15]. The diamide (aprotic)/water (protic) liquid mixtures attract current interest in view to be able to determine the own contribution of the dispersing medium in the resulting property [16].

Since there is relatively little work on diamide/alcohol system, a study of the combination diamide/hexanol is suggested, particularly since an alcohol of that kind (medium chain length) has not yet been used in that regard.

EXPERIMENTAL

The static permittivity ε_s was measured at 2 MHz using a dipolmeter type DM01 from "Wissenschaftlich-Technische Werkstatten GmbH" (WTW), Germany, to an uncertainty better than ±1%. An abbe refractometer (Carl-Zeiss Jena, model G) was used to measure the refractive index n_D of the Na-D line for the investigated solutions with an error of about $\pm 1.10^{-4}$.

The dielectric loss ε'' in the frequency range (0.2–10 GHz) was measured for the solutions under investigation using a microwave swept-frequency transmission. spectrometer. This spectrometer was established at the National Research Centre, Cairo, Egypt, similar to that described by Hanna and Hammel [17]. The method is based on recording the power transmitted through the dielectric as a function of frequency. The transmission through the pure solvent was taken as reference for the successive measurements of solutions with known concentrations of polar substances in the same non-polar solvent.

The dielectric loss values ε'' were calculated using the equation [18]

$$\varepsilon'' = \alpha(\varepsilon_0)^{1/2} C_0/(2\pi f) \qquad (1)$$

where f is the applied frequency, C_0 the velocity of light, ε_0 the dielectric permittivity of the solvent used and α is the attenuation coefficient which is given by

$$\alpha = 2.303\,(\mathrm{dB})_T/20\,L \tag{2}$$

where $(\mathrm{dB})_T$ is the difference between the transmitted power of solution and solvent and L is the length of the cell.

All the measurements were carried out at 20°C. Substances from Aldrich were used as obtained.

RESULTS

The dielectric data is regarded as a function of the total (molar) concentration c of the polar components, $c = c\,(\mathrm{DMFA}) + c\,(\mathrm{hexanol})$ for the same fixed DMFA/hexanol ratios, characterized in the following by $\zeta = c(\mathrm{DMFA})/c$. The polar/polar mixtures were chosen in mole fraction $\zeta = 1.00, 0.75, 0.50, 0.25$ and 0.00.

The values obtained for the dispersion step $S_{\max}$ (that is $\{\varepsilon_s\text{-}n_D{}^2\}$) for the investigated solutions are illustrated versus concentration c in mol.l^{-1} in Figure 1. Estimated or expected values of dispersion step ${}^{e}S_{\max}$, defined by equation (3) are added for comparison.

$${}^{e}S_{\max} = S_{\max}(\mathrm{hexanol}) + \zeta\{S_{\max}(\mathrm{DMFA}) - S_{\max}(\mathrm{hexanol})\} \tag{3}$$

Dielectric spectra $\varepsilon''(\nu)$ are illustrated, as an example, in Figure 2 for the two molar concentrations in mesitylene 0.28 and 0.61 mol. l^{-1} of the $\zeta = 0.00, 0.50$ and 1.00 systems. The striking feature is that at low frequencies the $\zeta = 0.50$ system exhibits a stronger absorption than both the corresponding DMFA or hexanol systems. Evidently, this system does not behave as an "ideal" 1:1 mixture of both components. The dielectric loss ε'' for two selected frequencies and different DMFA mole fractions ζ is given in Table I. Notwithstanding the suggestion to choose a two-terms description, the Cole-Cole function [19] allows for satisfactory formal fits within the frequency range studied, but that possibly the low

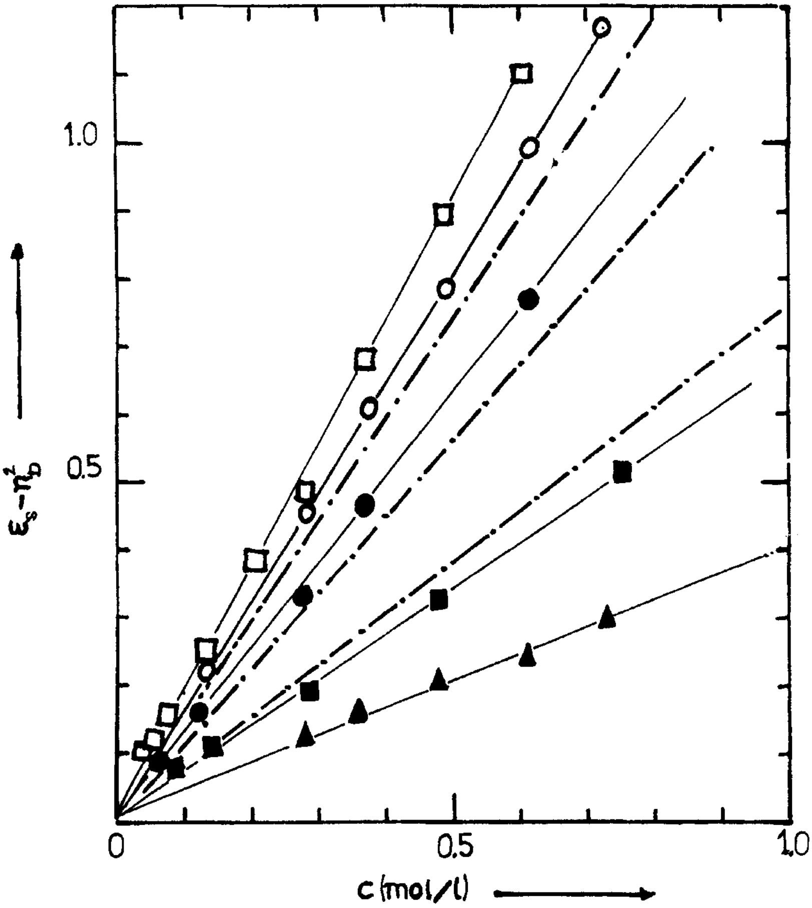

FIGURE 1 The dispersion step (ε_s-n_D^2) as dependent on molar concentration c at 20°C. $\zeta = 1$ □ 0.75 ○ 0.50 ● 0.25 ■ 0.00 ▲.

frequency features may be due to a physically distinguishable relaxation process characterized by a comparably relaxation time. Relaxation parameters, relaxation time τ, relaxation strength S and Cole-Cole distribution parameter α, obtained in that manner are given in Figure 3.

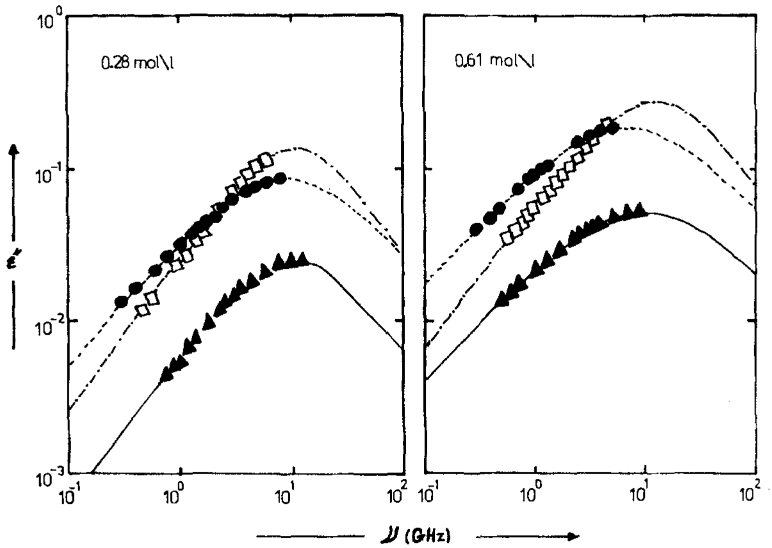

FIGURE 2 Imaginary part of permittivity ε'' vs. frequency ν (log-log plot) for $c = 0.28$ and 0.61 mol.l^{-1} for the three systems $\zeta = 1, 0.50$ and 0.00 *the same notation as in Figure 1.*

DISCUSSION

1. Static Dielectric Properties

Figure 1 shows a linear increase of S_{max} with increasing concentration c, at least in the range of concentration used, for all system under investigation. The slope for the $\zeta = 1$ system is of course higher than that for the $\zeta = 0$ system since the static permittivity $\varepsilon_s = 38.6$ for DMFA [20] and 13.15 for 1-hexanol [18]. The slope increases monotously with ζ. 'Ideal' according to Eq. (3) is shown as dashed line in Figure 1 for the three ternary systems. The S_{max} values deviated from the ideal behaviour for all ternary mixtures. The largest positive excess $\Delta S_{max} = S_{max} - {}^{e}S_{max}$ is found with the $\zeta = 0.50$ mixture ratio. More detailed information on the origin of ΔS_{max} may be obtained from the dynamic data.

TABLE I Dielectric loss values ε'' for two selected frequencies ν and different DMFA mole fraction ζ. For comparison with a linear variation of ε'' on the ζ scale, the excess value $\Delta\varepsilon'' = \varepsilon'' - {}^{c}\varepsilon''$ is given, where ${}^{c}\varepsilon'' = \varepsilon'' + \zeta\{\varepsilon''(\text{DMFA}) - \varepsilon''(\text{hexanol})\}$

ζ	*1.0*	*0.75*		*0.50*		*0.25*		*0.0*
ν *MHz*	ε''	ε''	$\Delta\varepsilon''$	ε''	$\Delta\varepsilon''$	ε''	$\Delta\varepsilon''$	ε''
				$c = 0.13$ mol/l				
800	0.0114	0.0158	0.0060	0.0092	0.0010	0.0061	−.0004	0.0048_7
5000	0.0519	0.0420	0.0011	0.0322	0.0023	0.0185	0.0004	0.0078_6
				$c = 0.28$ mol/l				
800	0.0205	0.0304	0.0138	0.0262	0.0136	0.0162	0.0075	0.0048
5000	0.1041	0.0932	0.0102	0.0776	0.0158	0.0403	−.0004	0.0195
				$c = 0.37$ mol/l				
800	0.0276	0.0426	0.0198	0.0391	0.0211	0.0237	0.0110	0.0083_5
5000	0.1387	0.1284	0.0178	0.1060	0.0235	0.0564	0.0020	0.0263
				$c = 0.48$ mol/l				
800	0.0376	0.0572	0.0264	0.0554	0.0314	0.0350	0.0178	0.0104
4500	0.1635	0.1593	0.0279	0.1357	0.0365	0.0705	0.0034	0.0349
				$c = 0.61$ mol/l				
800	0.0455	0.0731	0.0342	0.0762	0.0438	0.0480	0.0222	0.0192
4500	0.1932	0.2026	0.0465	0.1768	0.0578	0.0910	0.0091	0.0448

2 Dynamic Dielectric Properties

To explain the variation of dispersion step in terms of distinct species, a number of models have been developed [21,22]. These will be kept in mind in the discussion subsequent to the consideration of the dynamic data.

Figure 3 shows that an extrapolation of the Cole-Cole parameter α to $c \rightarrow 0$ leads to $\alpha \rightarrow 0$ for the two binary systems and also for $\zeta = 0.25$ system but seemingly not for the two ternary systems $\zeta = 0.50$ and 0.75 which may indicate complexation effect even at very low concentration. This could be considered as a hint at a particular low frequency relaxation contribution. It was already mentioned before that a two-term fit might be adequate; the present finding points in the same direction. However, because of the reasons given above the CC fit is retained.

Relaxation times for $\zeta = 0$ and $\zeta = 1.0$ systems seem to be independent of c as shown in Figure 3b. This behaviour is well known for non-associating liquids (such as DMFA) but not for associating substances (such as hexanol). This may indicate that there are still no

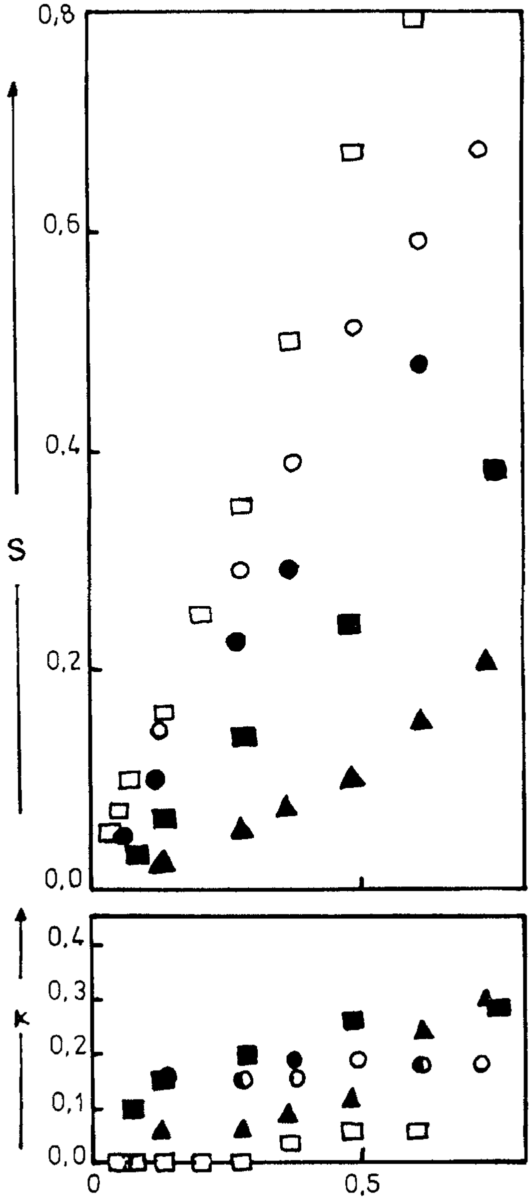

FIGURE 3 Relaxation parameters S, α and τ (Cole-Cole fit, $\alpha = 0$ means Debye behaviour) vs. concentration *c. the same notation as in Figure 1.*

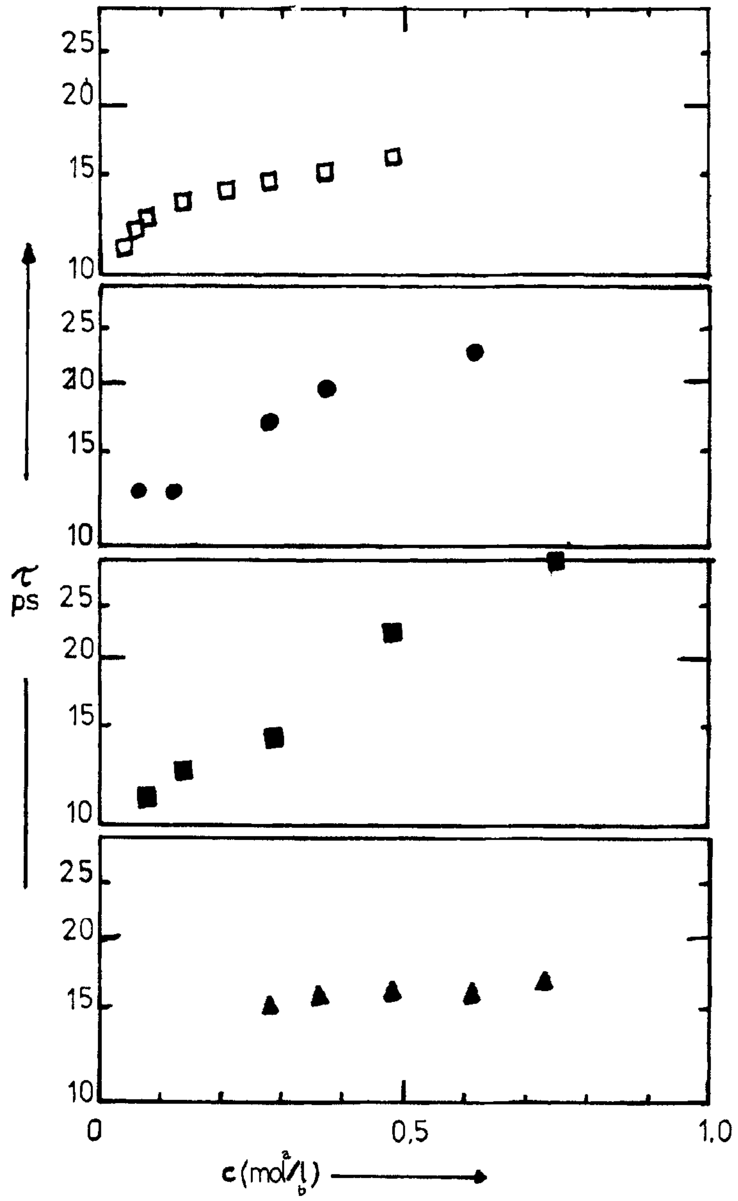

FIGURE 3 Continued

short range interactions between alcohol molecules in this range of low concentrations. Relaxation time in this case may be related directly to the alcohol's single molecule. Rather increasing of concentration leads to appearance of some other slower relaxation time which increases with concentration related to association process via hydrogen bonding as reported elsewhere [13].

For the three ternary systems, on the other hand, τ increases with increasing molar concentration c. The increase for $\zeta = 0.50$ is higher than for the other two ternary systems. In the dilute solution systems there is (i) an interaction amide-hexanol leading to a "slow" relaxation contribution, exhibiting (ii) maximum intensity around $\zeta = 0.5$ (1:1 "complexation"), which (iii) is likely to result from hydrogen bonding (as described).

From all these findings together, it could be concluded that the molecular association between DMFA and 1-hexanol arising from the hydrogen bonding between the hydrogen atom of hexanol molecule and the oxygen atom of DMFA molecule seems to be maximum around 1:1 interaction.

References

[1] Jörg, M., Ghoneim, A., Turky, G. and Stockhausen, M. (1995). *Phys. Chem. Liq.*, **29**, 263.

[2] Puranik, S. M., Kumbharkhane, A. C. and Mehrotra, S. C. (1993). *Indian J. Chem.*, **A 32**, 613.

[3] Brownsell, V. L. and Price, A. H. (1970). *J. Phys. Chem.*, **74**, 4004.

[4] Saha, U. and Acharyya, S. (1994). *Indian J. Pure&Appl. Phys.*, **32**, 346.

[5] Stockhausen, M., Utzel, H. and Seitz, E. (1982). *Phys. Chem.* (Neue Folge) **133**, 69.

[6] Karamyan, G. G. and Shakhparanov, M. I. (1981). *Zh. Strukt. Khim.*, **22**, 54.

[7] Verstakov, E. S., Yastremskii, P. S., Kessler, Yu. M., Goncharov, V. V. and Kokovin, V. V. (1980). *J. Struct. Chem.*, **21**, 639.

[8] Bennetto, H. P., Evans, G. F. and Shappard, R. J. (1983). *J. Chem. Soc.* Faraday Trans., 1 **79**, 245.

[9] Sharma, A. and Sharma, D. R. (1985). *Indian J. Pure&Appl. Phys.*, **23**, 418.

[10] Stockhausen, M. and Opriel, U. (1985). *J. Chem. Soc.* Faraday Trans., 1 **81**, 397.

[11] Firman, C. P., Eyring, E. M., Xu, M. H., Marchetti, A. and Petrucci, S. (1992). *J. Phys. Chem.*, **96**, 41.

[12] Dhull, J. S., Sharma, D. R., Gill, D. S. and Lakshminarayana, K. N. (1982). *Indian J. Phys.*, **B 56**, 334.

[13] Turky, G., Hanna, F. F., Ghoneim, A. and Stockhausen, M. (1994). *Z. Naturforsch.*, **49 a**, 503.

[14] Hufnagel, F., Hanna, F. F., Ghoneim, A., Saad, A. L. and Turky, G. (1992). *J. Chem. Soc.* Faraday Trans., **88**, 1819.

[15] Noreland, E., Gestblom, B. and Sjöblom, J. (1989). *J. Sol. Chem.*, **18**, 303.

[16] Ferriol, M., Siblini, A. and Noyel, G. (1995). *J. Mol. Liq.*, **63**, 239.

[17] Hanna, F. F. and Hammel, H. (1982). *Z. Phys. Chem.*, Leipzig., **263**, 323.

[18] Turky, G. (1993). Ph. D. Thesis, Cairo University, Egypt.
[19] Cole, K. S. and Cole, R. H. (1941). *J. Chem. Phys.*, **9**, 341.
[20] Jörg, M. (1992). Ph. D. Thesis, Münster University, Germany.
[21] Kilp, H. (1977). *J. Phys. Sci.* Instr., **10**, 985.
[22] Brot, C., Magat, M. and Reinisch, L. (1953). Kolloid Z., **134**, 101.