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LETTER TO THE EDITOR

Broad-band dielectric spectroscopy on morpholine/*n*-butanol liquid mixtures

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Abstract. At 30 °C the complex (dielectric) permittivity of the system morpholine/*n*-butanol has been measured as a function of frequency ν ($5 \times 10^4 \text{ Hz} \leq \nu \leq 4 \times 10^{10} \text{ Hz}$) and mole fraction x ($0 \leq x \leq 1$). Within the frequency range under consideration all liquids show a relaxation region with an underlying unsymmetrical distribution of relaxation times. The static permittivity, the characteristic dielectric relaxation time, and the width of the relaxation time distribution function are discussed. Other than what is expected on the grounds of recent permittivity measurements at 100 kHz no unusual properties are found for the binary mixtures.

In view of novel ideas on the structure and molecular dynamics of hydrogen-bonded networks, there is currently wide interest in the properties of associating liquids [1-4]. Much attention is directed toward binary mixtures of alcohols, in particular with water as the second constituent [5-10]. Seshadri and Subrahmanyam recently measured excess compressibilities, β_E^E , and excess dielectric permittivities at 100 kHz, ϵ'^E , for the system morpholine/*n*-butanol [11]. At small values of the mole fraction x of morpholine ($x \approx 0.4$) these authors found abnormally high permittivity values. They concluded that a high degree of alignment of electric dipoles must exist in this composition range. Such strong effects of molecular ordering are expected also to have a noticeable influence on the relaxation behaviour of the liquids. Aiming at obtaining an explanation of the outstanding dependence upon composition of the ϵ'^E (100 kHz) values it seemed to us, thus, to be useful to measure dielectric spectra of the system morpholine/*n*-butanol over a wide range of frequencies.

Morpholine ($\text{NHCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2$, Fluka, puriss. p.a.) and *n*-butanol ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$, Aldrich, 99.8%) were used without additional purification. The mixtures were prepared by weighing appropriate amounts of the constituents into suitable flasks. With all liquids under consideration the specific electric DC conductivity, measured at frequencies between 50 kHz and 10 MHz, was smaller than 10^{-3} S m^{-1} .

The (relative) complex permittivity

$$\epsilon(\nu) = \epsilon'(\nu) - i\epsilon''(\nu) \quad (1)$$

of the samples has been measured as a function of frequency ν using well-tried frequency domain methods. Between 50 kHz and 13 MHz we utilized an automatically operating

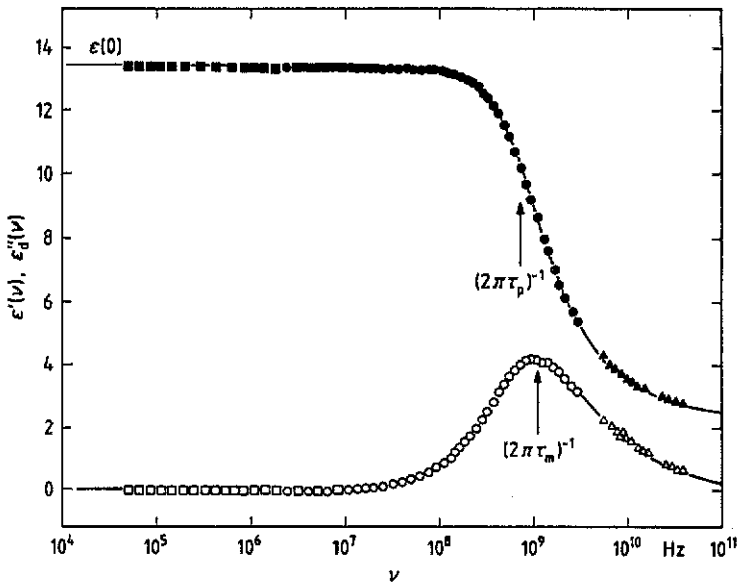


Figure 1. The real part $\epsilon'(\nu)$ (full symbols) and dielectric contribution $\epsilon''(\nu)$ to the negative imaginary part (open symbols) of the complex permittivity plotted as a function of frequency ν for a morpholine/*n*-butanol mixture with mole fraction $x = 0.25$ of morpholine at 30 °C. Different methods of measurements are indicated by different figure symbols (squares, input impedance measurements; circles, reflection coefficient measurements; triangles, double-beam interferometer measurements). The curves are graphs of the Davidson–Cole relaxation spectral function (equation (3)) with the parameter values found by a non-linear least-squares regression analysis.

impedance analyser (Hewlett–Packard 4192A) to perform input impedance measurements [12, 13] on specimen cells of the ‘cut-off’ variety [14]. These cells essentially consist of a coaxial line/circular cylindrical waveguide transition, the waveguide being excited below its cut-off frequency. Using the same type of cells between about 2 MHz and 3 GHz, reflection coefficient measurements [12, 13, 15], have been carried out with the aid of a computer-controlled network analyser (Hewlett–Packard 8753A). In the frequency range from 5 to 40 GHz we applied a travelling-wave method in which the wave transmitted through a liquid-filled cell of precisely variable length is balanced against a reference wave [14, 16]. Four microwave double-beam interferometers, each matched to a narrow frequency band, have been used.

With all measurements the temperature of the sample was controlled to within ± 0.05 K. The uncertainty in the frequency was smaller than 10^{-3} % below 3 GHz and smaller than 0.1% above 5 GHz. The accuracy of the $\epsilon(\nu)$ -values has been judged by test measurements on liquids with well-known dielectric spectra, by multiple data recording using different cells, and also by the fitting of data that had been measured by different techniques. In most of the frequency range the relative errors $\Delta\epsilon'/\epsilon'$ and $\Delta\epsilon''/\epsilon''$ in the complex permittivity data are smaller than $\pm 1\%$. Above 20 GHz, $\Delta\epsilon'/\epsilon'$ and $\Delta\epsilon''/\epsilon''$ are somewhat higher (± 3 %). Below 100 MHz the uncertainty in the imaginary part of $\epsilon(\nu)$ is given by $\Delta\epsilon'' = \pm 1$.

In figure 1 the complex dielectric spectrum is displayed for the morpholine/*n*-butanol mixture with mole fraction $x = 0.25$ of morpholine. Beside the real part ϵ' , only the

dielectric contribution $\varepsilon''_d(\nu)$ to the negative imaginary part of the spectrum is shown in this diagram. This has been calculated by subtracting from the total loss $\varepsilon''(\nu)$ the less interesting (small) conductivity contribution, using the relation

$$\varepsilon''_d(\nu) = \varepsilon''(\nu) - \sigma/2\pi\varepsilon_0\nu. \quad (2)$$

In this equation σ denotes the specific electric DC conductivity and $\varepsilon_0 = 8.854 \times 10^{-12} \text{ A s V}^{-1} \text{ m}^{-1}$.

At $x = 0.25$ the $\varepsilon'^E(100 \text{ kHz})$ values obtained by Seshadri and Subrahmanyam exhibit a pronounced relative maximum [11]. Our data obtained between 50 kHz and 40 GHz, however, do not show unusual properties. The real part of the complex spectrum is constant at low frequencies with a value between the static permittivities of the two constituents. There is a distinct dispersion ($d\varepsilon'(\nu)/d\nu < 0$) above 100 MHz. Correspondingly, dielectric loss is found ($\varepsilon''_d(\nu) > 0$) in the frequency range between about 100 MHz and 100 GHz.

Analysis of the complex permittivity spectrum shows that it can be well represented by the Davidson–Cole relaxation spectral function [17] which is given by the equation

$$\varepsilon'(\nu) - i\varepsilon''_d(\nu) = \varepsilon(\infty) + \frac{\varepsilon(0) - \varepsilon(\infty)}{(1 + i\omega\tau_p)^{1-b}}. \quad (3)$$

Herein, τ_p denotes the principal dielectric relaxation time, b measures the width of the underlying unsymmetrical relaxation time distribution function, and $\omega = 2\pi\nu$. The principal relaxation time τ_p of the Davidson–Cole function is also the largest time of the distribution function. Therefore, τ_p does not agree with the relaxation time τ_m (figure 1), which according to

$$\tau_m = (2\pi\nu_m)^{-1} \quad (4)$$

is defined by the frequency ν_m at which the dielectric loss adopts its relative maximum ($d\varepsilon''_d(\nu_m)/d\nu = 0$, $d^2\varepsilon''_d(\nu_m)/d\nu^2 < 0$).

Within the limits of experimental error, the Davidson–Cole spectral function can be used to represent analytically the spectra of all liquids measured in this study. However, with the pure alcohol and also with the solution of 7.2 % (mole/mole) of morpholine in *n*-butanol the agreement between the predictions of equation (3) and the measured permittivity values is not perfect. Small deviations for $\nu > \nu_m$ point to the existence of an additional high-frequency relaxation term. This finding corresponds to the dielectric spectra of isopropanol/water [7] and tert-butanol/water [9] mixtures at low water content. Also in conformity with the previous results on aqueous alcohol systems, however, the amplitude of this high-frequency relaxation term is too small to allow for a clear separation from the dominating Davidson–Cole term.

The extrapolated low-frequency ('static') permittivity $\varepsilon(0)$ is well defined by our measurements (figure 1). A plot of $\varepsilon(0)$ versus the mole fraction x of morpholine is given in figure 2. With increasing x the static permittivity monotonically decreases from the value for pure *n*-butanol ($\varepsilon(0, 0) = 17.27 \pm 0.5\%$) to that for pure morpholine ($\varepsilon(0, 1) = 7.50 \pm 0.5\%$). The $\varepsilon(0)$ values for the mixtures are somewhat smaller than predicted by the mixture relation that was used by Seshadri and Subrahmanyam to calculate the excess permittivity ε'^E . This mixture relation is given by the equation

$$\varepsilon(0, x) = (1 - x)\varepsilon(0, 0) + x\varepsilon(0, 1). \quad (5)$$

The resulting permittivity of binary liquid mixtures is usually found to be smaller than expected on the grounds of equation (5). One reason for this tendency is the fact that

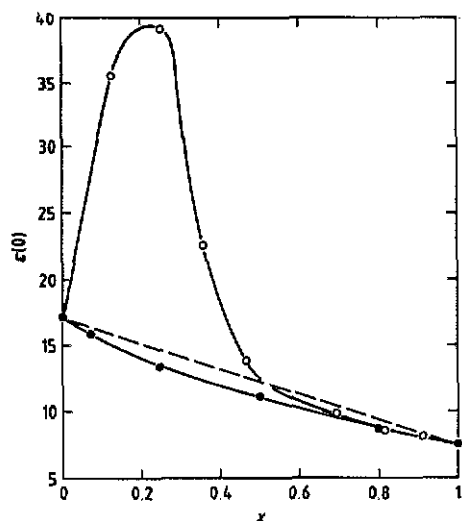


Figure 2. The static permittivity $\epsilon(0)$ (●) of morpholine/*n*-butanol mixtures at 30 °C displayed versus the mole fraction x of morpholine. The data obtained by Seshadri and Subrahmanyam (○, [11]) have been calculated using equation (5). For this purpose, the ϵ^E data have been taken from their figure 3 using a ruler. The broken line represents the mixture relation (equation (5)).

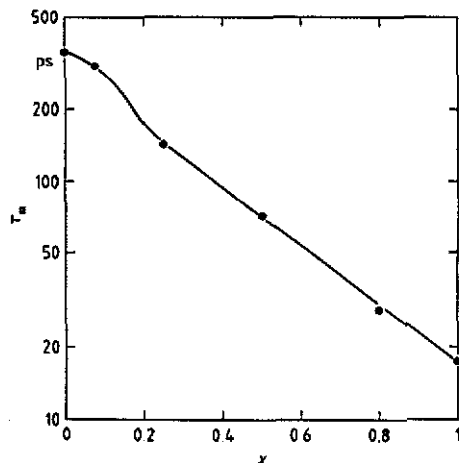


Figure 3. A semilogarithmic plot of the relaxation time τ_m (equation (4)) as a function of mole fraction x of morpholine for morpholine/*n*-butanol mixtures at 30 °C.

internal depolarizing electric fields are not taken into consideration in the mixture relation (5). For mole fractions $x < 0.4$ the $\epsilon(0)$ -values obtained by Seshadri and Subrahmanyam, also shown in figure 2, show behaviour substantially different to our results. We regret that we have no explanation for this.

The existence of only one relaxation region for the mixtures (figure 1) may be taken as an indication that the morpholine and *n*-butanol molecules form an almost homogeneous hydrogen bond network. As demonstrated by figure 3, the relaxation time τ_m also decreases monotonically from the pure alcohol value ($\tau_m = 357 \text{ ps} \pm 1\%$, 30 °C) to the value for pure morpholine ($\tau_m = 17.5 \text{ ps} \pm 1\%$, 30 °C). This behaviour seems to be characteristic for binary mixtures with distinctly different relaxation times of the pure constituents [7, 9]. Thus the dielectric relaxation time, also, gives no indication of the existence of special molecular complexes in the morpholine/*n*-butanol mixtures.

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