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Dielectric spectroscopy of dimethylsulfone solutions in water and dimethylsulfoxide

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ABSTRACT

In the present work, we provide a dielectric study on dimethylsulfone (DMSO2) solutions in water and dimethylsulfoxide (DMSO) in the frequency range from 100 MHz to 50 GHz and for temperatures from 298.15 to 318.15 K. The dielectric data are parametrized utilizing a Cole–Davidson spectral function, which presumes an unsymmetrical relaxation time distribution. The conductivity contribution to the total relaxation must be taken into account only in an aqueous solution of DMSO2. The concentration dependent static dielectric constant (ε_S), relaxation time (τ) and relaxation strength ($\Delta\varepsilon$) of these solutions have been determined.

1. Introduction

It is known that not only dimethylsulfoxide (DMSO) but also dimethylsulfone (DMSO2, also known as methylsulfonylmethane, MSM) are important and widely used solvents, which also have biomedical significance, especially their aqueous solutions [1].

It has been suggested that polar solvents such as DMSO2 and DMSO have a chemopreventive mechanism that affects the interaction of tumor cells with the host immune response. DMSO2 has been proven to have anti-inflammatory and antioxidant mechanisms in an in vitro study in which human neutrophils were artificially stimulated to produce oxidative compounds, including hydrogen peroxide, superoxide, and hypochlorous acid. After cell lines were treated with either DMSO or DMSO2, these free radical by-products were decreased [2,3].

DMSO2 has unusual physical and chemical properties. It has a relatively high boiling point and high thermal stability and is fairly non-reactive. It virtually resists all but the strongest reducing agents. It is also a much weaker base than DMSO and only slightly protonated in concentrated sulfuric acid solution.

The dipole moments and especially the dielectric constants of DMSO and DMSO2 indicate that they are quite polar, which suggests strong intermolecular interactions in the liquid phase. DMSO and DMSO2 are important and widely used solvents [4], the latter being especially valuable for high temperature reactions. They can dissolve a wide range of solutes and are miscible with many other solvents; this is true not only for polar compounds but also for some of low polarity.

Recently, in our laboratory aqueous solutions of dimethylsulfone and diethylsulfone (DESO2) have been studied by means of densimetry, surface tension, and calorimetry. The solution densities have been defined and the apparent and partial molar volumes of DMSO2 and DESO2 are calculated in the temperature range of 293.15–323.15 K. It was revealed that in both cases the increase of sulfone concentration leads to the reduction of the surface tension. This is more expressed in the case of DESO2 than in the extension of the sulfone hydrocarbon chain [5].

In [6] an ab initio study on the properties of the dimethyl sulfone and dimethyl sulfoxide functional groups was proposed. Structural, energetic, and charge distributions of the radical, positive, and negative species have been studied at DFT, MP2, MP4, and QCISD level of theory.

Dielectric relaxation studies in the microwave region on liquid systems are an efficient tool to investigate the structure and dynamics of molecular interactions. More detailed DRS studies of dialkylsulfoxide/water mixtures have been presented in [7–10]. The sulfones are a second, closely related, family of compounds that differ from the sulfoxides by having two oxygen atoms, rather than one, attached to the sulfur atom. The close similarity between these two families of chemicals makes their systematic comparison particularly interesting.

In the present work dielectric relaxation spectroscopy has been used to study dynamic and structural parameters of binary DMSO2/water, DMSO2/DMSO and ternary DMSO2/DMSO/water systems.

2. Experimental details

Dimethylsulfoxide (ACS reagent, >99.9%) and dimethylsulfone (98%) were purchased from Sigma Aldrich and were used without further purification. The solutions were prepared by weight using distilled and deionized water. All concentrations in this work are expressed in molality (mol/kg).

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The complex permittivity, $\varepsilon^*(\nu)$, including dielectric dispersion and adsorption spectra for DMSO2/water, DMSO2/DMSO and DMSO2/DMSO/water solutions in a large concentration range (up to 3 mol/kg in water, molal concentration of DMSO2) has been measured as a function of frequency between 100 MHz and 50 GHz at four temperatures between 298.15 K and 318.15 K. Dielectric spectra were recorded by a coaxial reflection technique based on a microwave PNA-L network analyzer (Agilent Technologies). The probe was fixed in a glass cell thermostatted with an accuracy of ±0.02 K to 298.15, 308.15 and 318.15 K, respectively. Reflected waves were sampled at $0.1 < \nu < 50$GHz and were converted to dielectric spectra using software based on the Nicolson–Ross method. The method requires a three-point calibration at each frequency, made with an open circuit, a short circuit, and with pure water as a calibration fluid. Several spectra were recorded for each sample and were averaged.

In addition, the conductivity κ was determined by a conductivity meter (Jenway 4330) to the accuracy of ±0.5% at 298.15 K.

3. Results and discussion

Measured dielectric spectra of the DMSO2 in water and DMSO at various concentrations at 298.15 K are shown in Figs. 1 and 2. The figures display the real part $\varepsilon'(\nu)$ and imaginary part $\varepsilon''(\nu)$ of the complex permittivity $\varepsilon^*(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu)$, respectively. The spectra comprise about 1000 data triples $\{\nu, \varepsilon'(\nu), \varepsilon''(\nu)\}$ in the range 100 MHz $\le \nu \le$ 50 GHz. It can be seen from Figs. 1 and 2 that the position of the peak in the plot of the imaginary part of permittivity vs. frequency shifts toward low frequency with an increasing concentration of DMSO2. It shows that the relaxation time increases with the increase of DMSO2 in these mixtures.

Data analysis is performed by simultaneously fitting the real and imaginary part of the complex permittivity spectrum ($\varepsilon^*(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu)$) to various models based on a sum of n Havriliak–Negami (HN) equations

$$\varepsilon^*(\nu) = \sum_{j=1}^{n} \frac{\Delta\varepsilon_j}{\left(1 + \left(i2\pi\nu\tau_j\right)^{1-\alpha}\right)^{\beta}} + \varepsilon_\infty \tag{1}$$

Or its variants the Debye (D), the Cole–Davidson (CD) or Cole–Cole (CC) equations with adjustable α and β parameters. In Eq. (1) $\Delta\varepsilon_j$ defines the amplitudes of the individual processes of relaxation times τ_j, ε_∞ is the high frequency limit of the permittivity, and α and β parameters represent a possible asymmetric broadening of spectrum. At static conditions the dielectric behavior is characterized by the relative static dielectric constant. ε_S is defined as the zero-frequency limit of the real part, $\varepsilon'(\nu)$ of the complex permittivity.

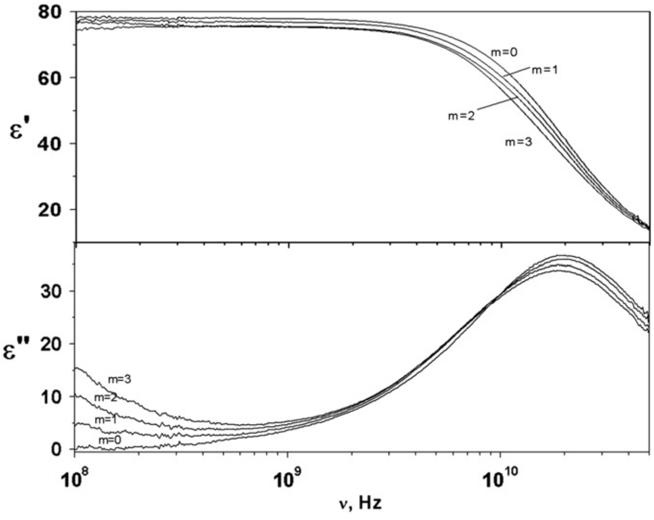

Fig. 1. Complex permittivity spectra of DMSO2/water mixtures at 298.15 K at various concentrations (m(DMSO2) ≤ 3 mol/kg).

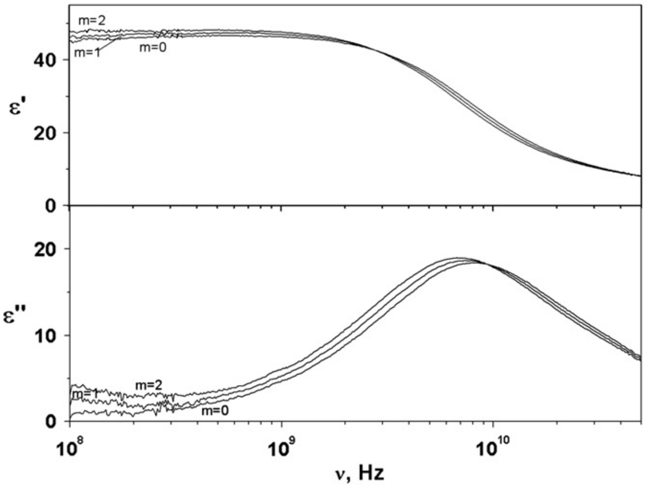

Fig. 2. Complex permittivity spectra of DMSO2/DMSO mixtures at 298.15 K at various concentrations (m(DMSO2) ≤ 2mol/kg).

In the frequency and concentration range under consideration the dielectric spectra of DMSO2/water and DMSO2/DMSO mixtures are monomodal. In this case monomodal spectra can be described by one Cole–Davidson type in the whole concentration range. The conductivity contribution to the total relaxation must be taken into account in an aqueous solution of DMSO2. In this case the relaxation is affected by the conductivity of the solution (the value of the conductivity, κ, of 3 mol/kg DMSO2 in water is 1.0 mS/cm). Meanwhile, the value of the conductivity for DMSO2 solutions in DMSO is in the microsiemens region (100–200 μS/cm).

The dielectric parameters, the static dielectric constant (ε_S), the relaxation time (τ), the relaxation strength ($\Delta\varepsilon$), the CD parameter (β), the high frequency limiting dielectric constant (ε_∞, approximated by Maxwell as $\approx 1.1n_D^2$) and the mean relaxation time $<\tau_{CD}>$ of the CD distribution ($<\tau_{CD}> = \beta \cdot \tau_{CD}$) obtained from the dielectric relaxation spectra of DMSO2/water and DMSO2/DMSO mixtures at various temperatures are summarized in Tables 1–3.

The concentration dependent static dielectric constant (ε_S), the relaxation strength ($\Delta\varepsilon$) and the mean relaxation time ($<\tau_{CD}>$) for DMSO2/water solutions have been presented in Figs. 3–5. The values of dielectric constant for the DMSO2/water mixtures decrease with increasing concentration of DMSO2 in solution at all temperatures (Fig. 3). The permittivity values of these solutions are found to have a

Table 1
Parameterization of dielectric spectra of DMSO2/water mixtures at 298.15 K.

m(DMSO2) mol/kg	ε_s	$\Delta\varepsilon$	τ_{CD}, ps	β	$<\tau_{CD}>$	$\varepsilon_\infty = 1.1n_D^2$	κ, μS/cm
0	78.35	76.40	8.39	0.987	8.28	1.95	8.8
0.05	78.39	76.44	8.92	0.868	7.74	1.95	45.5
0.1	78.36	76.40	9.07	0.868	7.87	1.96	62.0
0.3	78.05	76.09	9.14	0.866	7.92	1.96	156
0.5	77.81	75.84	9.32	0.856	7.98	1.97	233
0.7	77.50	75.53	9.41	0.853	8.03	1.97	303
1.0	77.08	75.10	9.56	0.847	8.09	1.98	403
1.3	76.82	74.84	9.85	0.836	8.24	1.98	500
1.5	76.50	74.51	9.96	0.833	8.30	1.99	557
1.8	76.19	74.20	10.21	0.823	8.40	1.99	637
2.0	75.85	73.85	10.20	0.822	8.38	2.00	693
2.2	75.51	73.51	10.12	0.823	8.33	2.00	740
2.3	75.56	73.56	10.33	0.823	8.50	2.00	764
2.5	75.38	73.38	10.32	0.817	8.43	2.00	813
3.0	75.56	73.55	11.24	0.799	8.98	2.01	912