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Dielectric relaxation study of diethylsulfoxide/water mixtures

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Complex dielectric spectra of diethylsulfoxide (DESO)/water mixtures at 25°C over the entire concentration range of DESO, in the frequency range $0.2 \leq \nu/\text{GHz} \leq 89$ have been measured. In general, a description of the complex permittivity spectra requires a consideration of different types of relaxation processes depending upon DESO concentration. For the lower DESO concentration range the relaxation contribution to the spectrum is described by two Debye terms, whereas for higher concentration three Debye terms are used. For both at mol fraction equals to 0.9 and pure DESO as well Cole–Davidson type is valid. In addition, the data on the dimethylsulfoxide (DMSO)/water system obtained in this work well agree with those known from literature. The concentration dependent excess dielectric constant, excess inverse relaxation time and Kirkwood correlation factor of the mixtures have been determined.

Keywords: dielectric relaxation; Kirkwood correlation factor; diethylsulfoxide; dimethylsulfoxide

1. Introduction

Dielectric relaxation studies in microwave region on liquid systems are an efficient tool to investigate the structure and dynamics of molecular interactions [1,2]. Dielectric relaxation spectroscopy (DRS) technique covers a broadband frequency window and therefore enables the investigation of a diverse range of processes including relatively fast reorientations of small molecules or side chain molecular groups. Especially important to reveal reorientational dynamics of the solvent which directly associated with the microscopic structure of material, is the higher frequency range from 0.1 to 89 GHz set-up.

The interest in the study of DESO/water mixtures comes from both physicochemical peculiarities [3–7] and recently recognised biomedical significance of this system [8,9]. DESO, like DMSO, exhibits strong self-associative effects, even stronger than in DMSO and the existence of intense intermolecular DESO–DESO interactions, involving also $\text{SO} \cdots \text{HC}$ hydrogen bonding has been suggested. Spectroscopic results together with thermodynamic measurements of DESO–water mixtures suggested very strong deviations from ideality, like in DMSO–water solutions, but to a greater extent [3–5].

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More detailed DRS studies of DMSO/water mixtures have been presented in [10–13], whereas, so far dielectric relaxation properties of DESO/water system have not been investigated.

Compared to other techniques, DRS is especially advantageous for an investigation of the cooperative nature of hydrogen-bonding liquids because it monitors the collective motion of a molecular ensemble through the response of the total dipole moment of the sample to a time dependent electric field. In general, DRS method reveals association as far as distinguishable by a slow enough moment fluctuation of the respective moieties. The both DMSO–water and DESO–water systems are complex in this respect since both mixture components are capable of self-association via dipole–dipole interactions and hydrogen bonds. In addition, one has to evaluate heteroassociation effects.

Dielectric relaxation properties of DESO–water system in fact has not been investigated so far. In addition, much less is known about the dynamics of the aqueous solutions of DMSO. For DMSO–water system, broad spectra can be described by two Debye type components. However, Cole–Cole or Cole-Davidson(CD) functions have been used as well [10–13].

Comparison of these two systems in respect of the length of alkyl moiety will add our knowledge about hydrophobic effects for aqueous solutions of non-electrolytes in general. Moreover, the results obtained will be used to explain the mechanism of biomedical actions of these systems.

Also on the basis of existing data on the physicochemical properties of DESO/water system more reasonable physically realistic relaxation models explaining the concentration dependence of complex permittivity spectra measured up to 89 GHz over the entire mixing range are considered.

2. Experimental section

DMSO is commercially available (Aldrich), DESO was synthesised and purified according to reference [14]. The solutions were prepared by weight using Millipore water. We have determined $\varepsilon^*(\nu)$ of DESO/water mixtures at the molar fraction of DESO, $X_{\text{DESO}} = 0.02, 0.05, 0.1, 0.25, 0.46, 0.6, 0.73, 0.9$ and 1 at 25°C in the frequency range $0.2 \leq \nu/\text{GHz} \leq 89$. Time Domain Reflectometry (TDR) was employed in the frequency range $0.2 \leq \nu/\text{GHz} \leq 25$, and TDR data were combined with those obtained with the three waveguide interferometers in the Ku, A, and E band covering $13 \leq \nu/\text{GHz} \leq 89$. Temperature control was made with an accuracy $\pm 0.02^\circ\text{C}$ for TDR measurements and $\pm 0.03^\circ\text{C}$ for interferometry.

In addition, the dielectric loss spectra $\varepsilon''(\omega)$ of all systems were measured in the frequency range up to 72 GHz, using various apparatus developed in the Muenster laboratory, Germany. Different coaxial and waveguide setups based on either a resonator perturbation method or a reflection measurement of the sample cell were utilised [6,7].

Properties such as density d and refractive index n were measured in addition (the densities of the mixtures, as well as pure compound, were measured using a vibrating tube densimeter, type Anton Paar DMA 4500, capable of an accuracy to $\pm 5 \times 10^{-5} \text{ g cm}^{-3}$, a refractometer to an accuracy $\pm 5 \times 10^{-4}$ was used to measure the refractive index). All measurements were made at 25°C and the temperature was controlled thermostatically.

3. Results and discussion

Data analysis is performed by simultaneously fitting the real and imaginary part of the complex permittivity spectrum ($\epsilon^*(\nu) = \epsilon'(\nu) - i\epsilon''(\nu)$) to various conceivable relaxation models.

$$\epsilon^*(\nu) = \sum_{j=1}^n \frac{\Delta\epsilon_j}{(1 + i2\pi\nu\tau_j)^{\beta_j}} + \epsilon_\infty. \tag{1}$$

The j th dispersion step is defined by its relaxation time, τ_j ($\tau_j > \tau_{j+1}$), and amplitude $\Delta\epsilon_j$, ϵ_∞ is the high frequency limit of the permittivity. In the present cases, it can be fitted by a sum of (maximum three) Debye type functions or, alternatively, by a CD function, respectively. Here β is the CD skewness parameter $0 < \beta \leq 1$, where $\beta = 1$ means Debye type.

In Figure 1 the $\epsilon^*(\nu)$ spectra of the DESO/water mixtures at 25°C at $X_{\text{DESO}} = 0.25$ and 0.73 are displayed to visualise the quality of the data and the excellent fit.

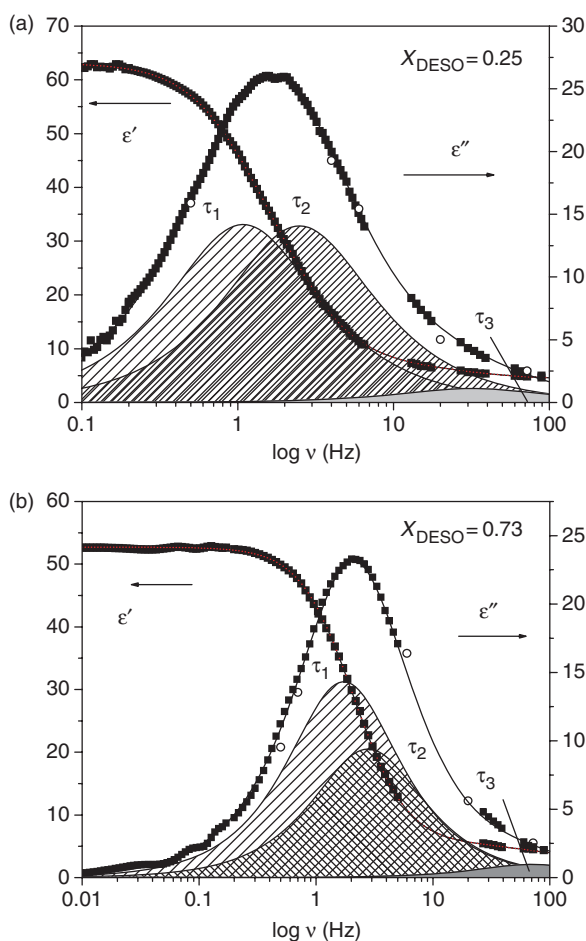


Figure 1. Dielectric permittivity, $\epsilon'(\nu)$, and loss $\epsilon''(\nu)$, spectra of diethylsulfoxide/water mixtures at 25°C with $X_{\text{DESO}} = 0.25$ (a) and $X_{\text{DESO}} = 0.73$ (b), determined with TDR and waveguide interferometry (●), and determined with different coaxial and waveguide setups (○).

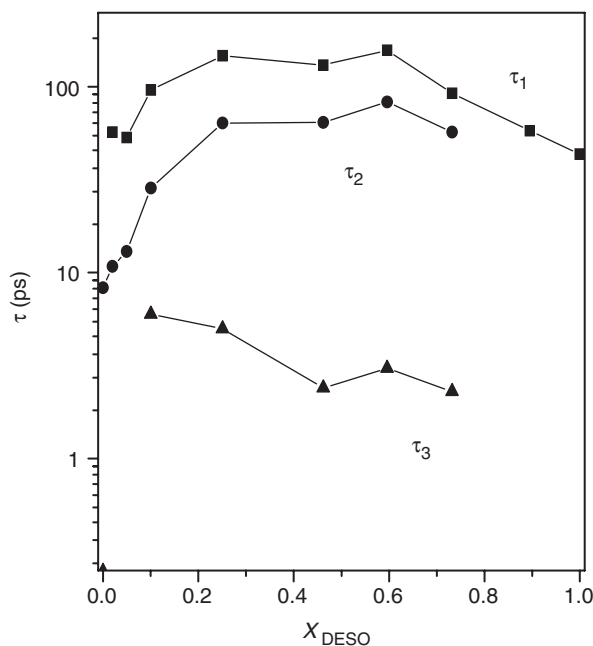


Figure 2. The relaxation times, τ_j ($j=1, 2$, and 3), for DESO/water mixtures at 25°C plotted against molar fraction of DESO, X_{DESO} .

For the investigated DESO/mixtures measured up 89 GHz, the results of the spectrum analysis can be summarised as follows: in the lower concentration range of DESO, up to $X_{\text{DESO}}=0.05$, a superposition of two Debye equations gives the best fit, whereas in the concentration range $0.1 \leq X_{\text{DESO}} \leq 0.7$ three Debye terms were used, in the DESO-rich region $X_{\text{DESO}} \geq 0.9$ up to pure DESO CD type gives satisfactory fitting. The latter well agrees with the dielectric loss spectrum of pure DESO $\varepsilon''(\nu)$ reported earlier [6,7].

Figure 2 shows the relaxation times of DESO/water mixtures, τ_j , for the individual processes ($j=1, 2$, and 3) as a function of molar fraction, X_{DESO} . For the main dispersion step ($j=1$), τ_1 exhibits remarkable increase when the concentration of DESO varies in the range of molar fraction from 0.25 to 0.6, which then decreases coming to the pure DESO. This behaviour conforms well with other physicochemical properties observed at this concentration range, such as cryoprotective ability. Indeed, recently our investigations have shown that DESO/water system could provide amorphous, glassy systems, thus avoiding ice crystallisation, in a wide range of concentrations ($0.1 \leq X_{\text{DESO}} \leq 0.5$) and even at very low cooling rates [8]. The glass-forming tendency of these solutions is discussed in terms of existing competitive interactions between molecules of DESO, on the one hand, and DESO and water molecules, on the other hand. The results are well explainable on the basis of the model structure of DESO/water solutions, deduced by Raman and infrared studies [3]. Obviously, the simultaneous existence of strong DESO– H_2O and DESO–DESO interactions suggest the coexistence of many types of structural molecular aggregates. Therefore, it is expectable that the dielectric relaxation behaviour of aqueous solution of DESO describes with different relaxation models.

In the water-rich region of $0 < X_{\text{DESO}} \leq 0.05$ a superposition of two Debye terms might be as a result of on the one hand a cooperative relaxation of the hydrogen-bond

system which is forming mainly with the participation of water molecules, and on the other hand due to the motion of two ethyl chains located in the intercluster cavity of water structure. Then with the increase of DESO concentration $0.1 \leq X_{\text{DESO}} \leq 0.7$, an additional third Debye term appears. In this range of concentration, an existence of competitive interactions between molecules of DESO, on the one hand, and DESO and water molecules, on the other hand are responsible for a superposition of three Debye-type functions due to strong intermolecular interaction occurring between DESO and water molecules. It is interesting to note that the dependence of τ_1 on X_{DESO} reveals maximum (Figure 2) at about the same concentration range where glass-forming tendency is more pronounced.

The static dielectric constant ϵ_S , high frequency limiting dielectric constant ϵ_∞ , relaxation time and excess properties are listed in Table 1.

The values of static dielectric constant of DESO/water and DMSO/water mixtures with mole fraction of dialkylsulfoxides (DASO) at 25°C are plotted in Figure 3. The values of static dielectric constant decrease with increasing concentration of DASO in both the studied binary mixtures. The permittivity values of both mixtures at all studied concentrations are found to have a non-linear variation. This non-linear variation of permittivity with concentration indicates the interaction between the components in the mixtures. It is worthy to note that this decrease is more significant water for DMSO/water system rather than for DMSO/water system despite of the fact that the value of dielectric constant for pure merely do not differ.

The variation of the high frequency limiting dielectric constant ϵ_∞ (approximated by Maxwell as $\approx 1.1 n_D^2$) of the binary mixtures with mole fraction of DASO is shown in Figure 4. As it follows from Figure 4, the ϵ_∞ value increases with increase in X for both DMSO and DESO. The information related to interaction of liquids A and B may be obtained by excess properties related to the permittivity and relaxation times in the mixture [15–18]. The excess permittivity ϵ^E is defined as:

$$\epsilon^E = (\epsilon_0 - \epsilon_\infty)_m - [(\epsilon_0 - \epsilon_\infty)_A X_A + (\epsilon_0 - \epsilon_\infty)_B X_B], \quad (2)$$

where X – mole fraction and suffices m, and A, B represents mixture, liquid A – DASO and liquid B – Water, respectively. The excess permittivity may provide qualitative information about multimers formation in the mixture as follows:

- (1) $\epsilon^E = 0$ indicates that the liquid A and B do not interact at all;
- (2) $\epsilon^E < 0$ indicates the liquid A and B interaction in such a way that the total effective dipoles get reduced. The liquid A and B may form multimers leading to the less effective dipoles; and
- (3) $\epsilon^E > 0$ indicates the liquid A and B interaction in such a way that the total effective dipole moment increases. There is a tendency to form multimers, dipole aligned in parallel direction.

Similarly, the excess inverse relaxation time is defined as:

$$\left(\frac{1}{\tau}\right)^E = \left(\frac{1}{\tau}\right)_m - \left[\left(\frac{1}{\tau}\right)_A X_A + \left(\frac{1}{\tau}\right)_B X_B\right], \quad (3)$$

where $(1/\tau)^E$ is the excess inverse relaxation time, which represents the average broadening of dielectric spectra. The inverse relaxation time analogy is taken from spectral line broadening (which is inverse of the relaxation time) in the resonant spectroscopy.

Table 1. Values of static dielectric permittivity ϵ_s , high frequency dielectric constant ϵ_∞ , excess dielectric constant ϵ^E , relaxation time τ , and excess inverse relaxation time $(1/\tau)^E$ for DASO/water mixtures at different mole fraction X of DASO at 25°C.

X	ϵ_s	$\epsilon_\infty \approx 1.1 n_D^2$	ϵ^E	τ (ps)	$(1/\tau)^E$
DESO					
0.000	78.36	1.96	0.00	8.32	0.000
0.0202	76.09	2.06	-1.68	-	-
0.0502	73.67	2.08	-3.10	17.73	-0.059
0.101	70.93	2.16	-4.20	35.00	-0.082
0.252	63.11	2.28	-7.01	94.23	-0.085
0.462	58.20	2.34	-4.85	99.16	-0.065
0.596	54.37	2.35	-4.14	78.91	-0.050
0.732	52.70	2.37	-1.21	78.18	-0.036
0.895	49.90	2.37	1.53	57.89	-0.016
1.000	44.82	2.38	0.00	43.36	0.000
DMSO					
0.000	78.36	1.96	0.00	8.32	0.000
0.0504	76.59	2.02	-0.19	13.84	-0.045
0.101	76.22	2.09	1.02	18.72	-0.060
0.249	72.87	2.22	2.37	40.88	-0.079
0.402	67.64	2.30	2.05	46.97	-0.072
0.497	64.11	2.32	1.59	42.96	-0.064
0.602	60.23	2.35	1.10	34.26	-0.051
0.706	56.24	2.37	0.49	28.72	-0.038
0.899	49.44	2.39	-0.05	18.53	-0.006
1.000	46.20	2.40	0.00	18.86	0.000
DMSO*					
0.000	78.36	1.96	0.00	8.27	0.000
0.019	77.75	1.99	-0.03	10.04	-0.020
0.064	77.13	2.04	0.72	15.92	-0.054
0.120	76.25	2.11	1.56	24.59	-0.072
0.205	74.23	2.19	2.16	38.58	-0.081
0.357	69.70	2.28	2.37	50.38	-0.077
0.507	64.02	2.33	1.42	44.08	-0.064
0.694	58.38	2.36	1.69	33.12	-0.044
0.920	51.50	2.39	1.96	22.78	-0.015
1.000	47.00	2.40	0.00	18.53	0.000

Note: *For comparison, data from [10] are presented.

The information regarding the dynamics of liquids A and B interaction from this excess property is as follows:

- (1) $(1/\tau)^E = 0$: there is no change in the dynamics of liquid A and B interaction;
- (2) $(1/\tau)^E < 0$: the liquid A and B interaction produces a field such that the effective dipoles rotate slowly; and
- (3) $(1/\tau)^E > 0$: the liquid A and B interaction produces a field such that the effective dipoles rotate fastly, i.e. the field will co-operate in the rotation of dipoles.

The evaluated values of excess parameters (ϵ^E and $(1/\tau)^E$) of the binary mixtures are listed in Table 1 and plotted in Figure 5.

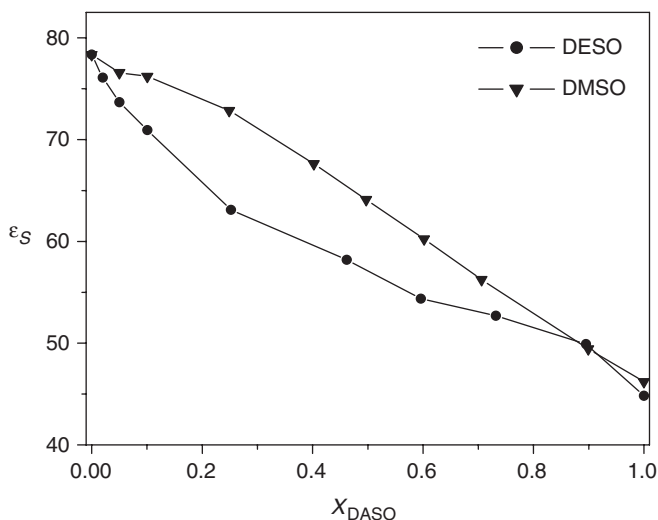


Figure 3. The static dielectric constant ϵ_s for DESO/water and DMSO/water mixtures against mole fraction of dialkylsulfoxides at 25°C.

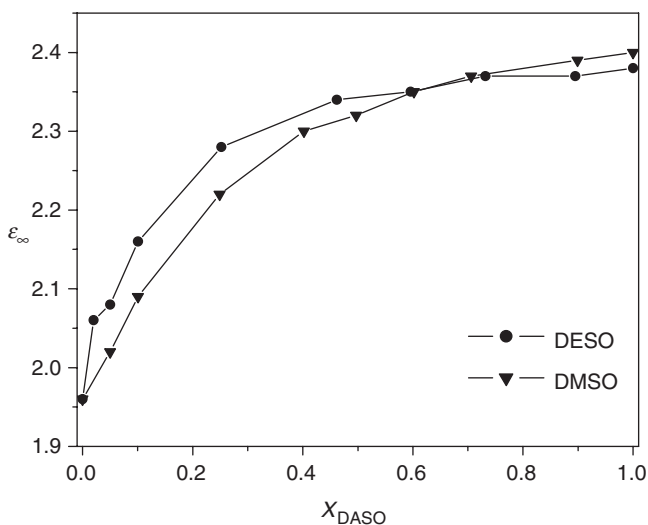


Figure 4. The high frequency limiting dielectric constant ϵ_∞ for DESO/water and DMSO/water mixtures against mole fraction of dialkylsulfoxides at 25°C.

The inverse relaxation time values are negative for all concentrations and both systems studied indicates slower rotation of the dipoles, due to the solute–solvent interaction from the hydrogen bonded structures, which produces a field in such a way that the effective dipole rotation is hindered.

It is interesting to note that although pure DMSO and DESO are characterising with merely same physicochemical features their aqueous solutions do behave differently: the ϵ^E

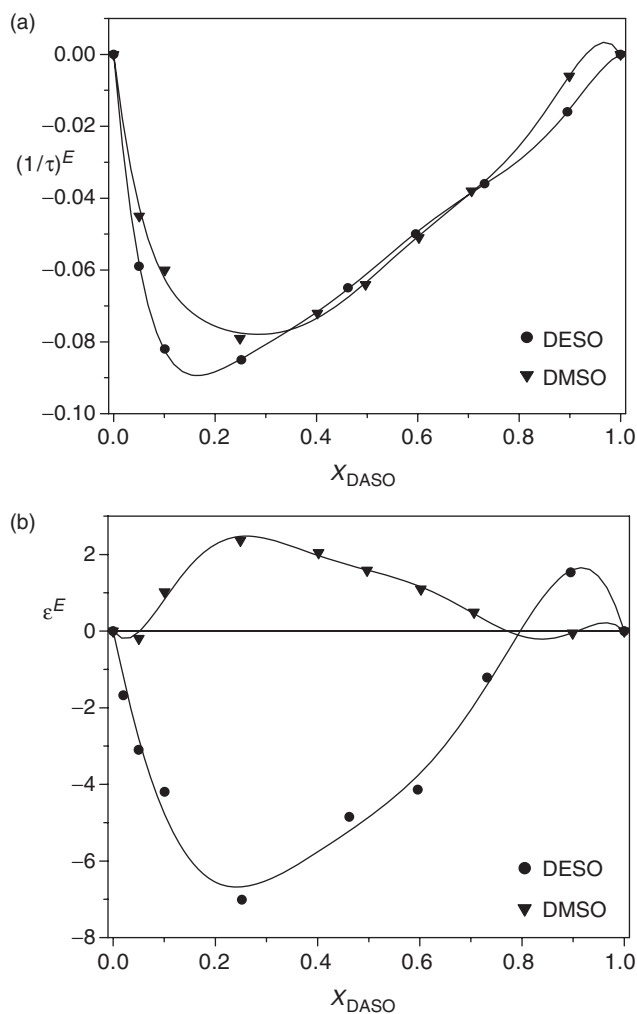


Figure 5. (a) Excess inverse relaxation time $(1/\tau)^E$, and (b) excess permittivity ε^E against mole fraction of dialkylsulfoxides at 25°C. — is smoothed curve obtained by using Equation (4) for fitting the experimental data for this work.

values of DMSO/water mixtures were found positive at all concentrations, but opposite trend in ε^E values (negative) was observed in case of DESO/water mixtures. The experimental values of both the excess parameters were fitted to the Redlich–Kister equation:

$$P^E = (X_A \cdot X_B) \sum_n K_n (X_A - X_B)^n, \quad (4)$$

where P is either ε^E or $(1/\tau)^E$, and $n=5$.

The structural information about the liquids from the dielectric relaxation parameter may be obtained using the Kirkwood correlation parameter g . This factor is a measure for preferential local ordering of molecular dipole moments and thus a hint at the formation of self-aggregates.

For pure liquid the g factor may be obtained using the equation [7,19]:

$$g = \frac{(\epsilon_S - \epsilon_\infty)(2\epsilon_S + \epsilon_\infty)9\epsilon_0kT}{\epsilon_S(\epsilon_\infty + 2)^2N_A\mu^2c}, \tag{5}$$

where ϵ_∞ is the high-frequency dielectric constant, approximated by Maxwell as $\approx 1.1 n_D^2$, k is the Boltzmann constant, N_A is the Avogadro number, c is the concentration of the dipoles ($c = d/M$, accessible from the density and the molar weight M , of the pure liquids), ϵ_S is the dielectric constant ($\epsilon_S = S + 1.1 n_D^2$), ϵ_0 is the permittivity of empty space (8.86×10^{-12} F/m), μ is the dipole moment in a gas phase (for DASO ~ 3.9 D, for water 1.82 D) [7,15,19].

The modified forms of the above equation are used to study the orientation of the electric dipoles in binary mixtures of polar solvents; two equations used are as follows:

$$\left(\frac{\mu_A^2 d_A}{M_A} \phi_A + \frac{\mu_B^2 d_B}{M_B} \phi_B \right) g^{eff} = \frac{(\epsilon_{Sm} - \epsilon_{\infty m})(2\epsilon_{Sm} + \epsilon_{\infty m})9\epsilon_0kT}{\epsilon_{Sm}(\epsilon_{\infty m} + 2)^2N_A}, \tag{6}$$

where g^{eff} is the effective Kirkwood correlation factor for a binary mixture, μ , d , M and ϕ are the dipole moment, density (1.096 g cm^{-3} for pure DMSO, and $1.01017 \text{ g cm}^{-3}$ for pure DESO at 25°C), molecular weight and volume fractions of liquid A and B, respectively. The value of g^{eff} varies between g_A and g_B .

$$\left(\frac{\mu_A^2 d_A g_A}{M_A} \phi_A + \frac{\mu_B^2 d_B g_B}{M_B} \phi_B \right) g_f = \frac{(\epsilon_{Sm} - \epsilon_{\infty m})(2\epsilon_{Sm} + \epsilon_{\infty m})9\epsilon_0kT}{\epsilon_{Sm}(\epsilon_{\infty m} + 2)^2N_A}, \tag{7}$$

g_f is the corrective Kirkwood correlation factor for binary mixture.

The values of g^{eff} and g_f for various compositions are given in Table 2 and graphically represented in Figure 6.

The values of g^{eff} decrease from $g(\text{H}_2\text{O})$ to that of $g(\text{DASO})$. Since always $g > 1$, a preferentially parallel orientation of molecular dipoles is likely to occur.

Table 2. Values of effective averaged Kirkwood correlation factor g^{eff} and corrective Kirkwood correlation factor g_f for DASO/water mixtures at different volume fraction ϕ of DASO at 25°C .

ϕ	g^{eff}	g_f	ϕ	g^{eff}	g_f
DESO			DMSO		
0.000	2.63	1.00	0.000	2.63	1.00
0.107	2.48	0.98	0.173	2.42	1.04
0.235	2.45	1.01	0.307	2.28	1.09
0.395	2.35	1.04	0.566	1.96	1.17
0.662	2.09	1.07	0.726	1.71	1.19
0.833	1.96	1.12	0.796	1.59	1.18
0.895	1.84	1.10	0.856	1.46	1.16
0.941	1.79	1.11	0.904	1.34	1.12
0.980	1.71	1.10	0.972	1.15	1.05
1.000	1.53	1.00	1.000	1.06	1.00

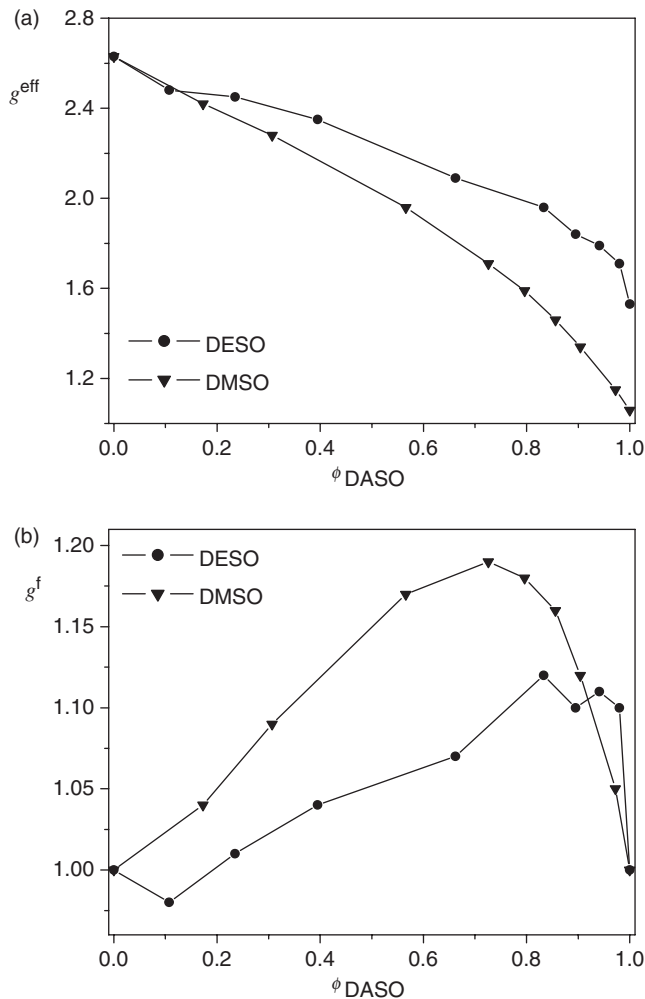


Figure 6. (a) Kirkwood effective correlation factor g^{eff} , and (b) corrective Kirkwood correlation factor g_f against volume fraction of dialkylsulfoxides at 25°C.

The g_f values for the mixtures are greater than unity, and deviation from unity indicating strong interaction between two components.

4. Conclusion

Dielectric relaxation parameters, excess dielectric constant, excess inverse relaxation time and Kirkwood correlation factor have been first reported for DMSO/water mixtures for various concentrations. The results obtained have shown the quite difference between dielectric relaxation behaviour of DESO/water and DMSO/water binary systems, and are well explainable on the basis of the model structure of non-electrolyte/water solutions. The presence of H-bonds, dipole–dipole and hydrophobic interactions in these systems is also considered.

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