

# Dielectric constant of dimethyl sulfoxide–monohydric alcohol mixture solution at the microwave frequency



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## ABSTRACT

Dielectric spectra of dimethyl sulfoxide (DMSO)–monohydric alcohol (C1–C4) mixtures, over the entire mole fraction range, have been measured using the dielectric relaxation spectroscopy (DRS) at frequencies from 20 MHz to 20 GHz at room temperature. The mixture behavior is described according to four Davidson–Cole terms whose evolution with composition is analyzed. Numbers of hydrogen bonds and bonding energies between alcohol–alcohol and DMSO–alcohol pairs are estimated from the dielectric constants using the Luzar model. The average number of hydrogen bonds associated with DMSO decreases with increasing mole fraction of DMSO. The binding energy for alcohol–alcohol ( $E_{11}$ ) and DMSO–alcohol ( $E_{12}$ ) interactions decreases with the increased numbers of carbon atoms in the alcohols.

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## 1. Introduction

Microwave irradiation has been successfully applied in organic chemistry, such as microwave-accelerated catalysis, microwave-applied cycloaddition reaction and polymers [1]. The effects of microwave radiation on compounds mainly depend on their dielectric properties. Selection of a proper solvent of suitable polarity with special physicochemical parameters is important for many processes, accelerating or inhibiting chemical reactions, and/or changing their kinetics and mechanism. Mixed solvents are of current interest to meet the required solvent polarity with quite different physicochemical properties [2,3].

Because of DMSO is widely used in biological studies, chemical materials, medical, and other fields, many authors [4–6] have studied its properties. As an aprotic polar solvent, DMSO can dissolve most organic compounds, as well as many inorganic substances. Due to the partial negative charge on the oxygen atom in  $S=O$ , DMSO can form strong hydrogen bonds with water [7]. Using a mean field approximation for hydrogen-bonded mixtures; Luzar [8] has proposed a theoretical model that qualitatively agrees with experimental results for DMSO–water mixtures. Zijie Lu [7] has studied DMSO–water mixtures by dielectric relaxation spectroscopy, and found the average number of hydrogen bonds per molecule is fewer than for pure water.

Monohydric alcohols other polar solvents, which are used in oils, resins, and antifreeze as a kind of organic solvent [9]. Methanol is used as a cleaning agent and analytical reagent; ethanol is now used in fuel; propanol is used to produce synthetic spices, and butanol is used in manufacturing plastic and rubber products. Research on these systems has focused on the hydroxyl group–OH, which forms many complex molecular clusters and network structures in mixtures. Dielectric research [10–15] has found mixture systems with both structure breaking and structure making.

Many experimental systems have been implemented to determine the contribution of the interaction of molecules. These include, NMR [16], X-ray [17], CD [18], fluorescence [19], UV–Raman [20], infrared and dielectric spectroscopy [21,22]. Further, ab initio calculations and molecular dynamics simulations have been used [22]. Compared to other techniques, DRS is especially advantageous for investigating the cooperative nature of hydrogen-bonding in 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. Christa Trandum [23] has reported the intermolecular interaction in the DMSO–*t*-Butylanol–water system. Although there are abundant literatures concentrate on several studies of aqueous DMSO [4,24,25,26], the structure for the DMSO–alcohol mixtures may be more complex.

In this paper, we study the dielectric relaxation of DMSO–monohydric alcohol system by using the DRS. This system consist three pairs of hydrogen-bond, the interaction for alcohol–alcohol (pair 1), DMSO–alcohol (pair 2) and DMSO–DMSO (pair 3),

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**Table 1**  
Sample information.

Item	DMSO	Monohydric alcohol
The source	Chengdu Kelong Chemical reagent factory	
Mass fraction purity <sup>a</sup>		≥99.5%
Purification methods		No further purification

<sup>a</sup> Given in the certificate of analysis.

respectively. We choose methanol, ethanol, 1,2-propanol, and 1,2-butanol as the representative of monohydric alcohol. At the same time, hydrogen bond energy between alcohol molecules ( $E_{11}$ ) and between DMSO and alcohol molecules ( $E_{12}$ ) is reported. This provides molecular parameters related to solute-solvent interaction, and also complements the mixture dielectric properties theory.

## 2. Experiments

All of the DMSO (≥99.5%) and the monohydric alcohols (≥99.5%) used in these experiments have been purchased from Chengdu Kelong Chemical Reagent Factory without further purification. The sample table of these compounds is presented in Table 1. The mixtures with full concentration range at 0.1 (mole fraction) intervals were prepared.

The complex permittivity spectra of the DMSO-alcohol mixtures in the frequency range from 20 MHz to 20 GHz were measured by Microwave Network Analyzer (PNA-N5227A) and an Agilent slim-form probe (85070E). The calibration of the system was performed with the aid of three standards: air, an Agilent standard short circuit, and pure water at 298 K. The whole measuring system was placed in an air-conditioned room maintained at  $298 \pm 0.5$  K. Each

sample was measured at least four times on different occasions. The real and imaginary parts  $\varepsilon'(\omega)$  and  $\varepsilon''(\omega)$  were evaluated using the Agilent Materials Measurement Software 85070 with accuracy  $\Delta\varepsilon'/\varepsilon' = 0.05$ ,  $\Delta\varepsilon''/\varepsilon'' = 0.05$ .

The experimental dielectric spectra was fitted in a complex non-linear least-squares routine by using various models represented by the Havriliak–Negami function [7,27]:

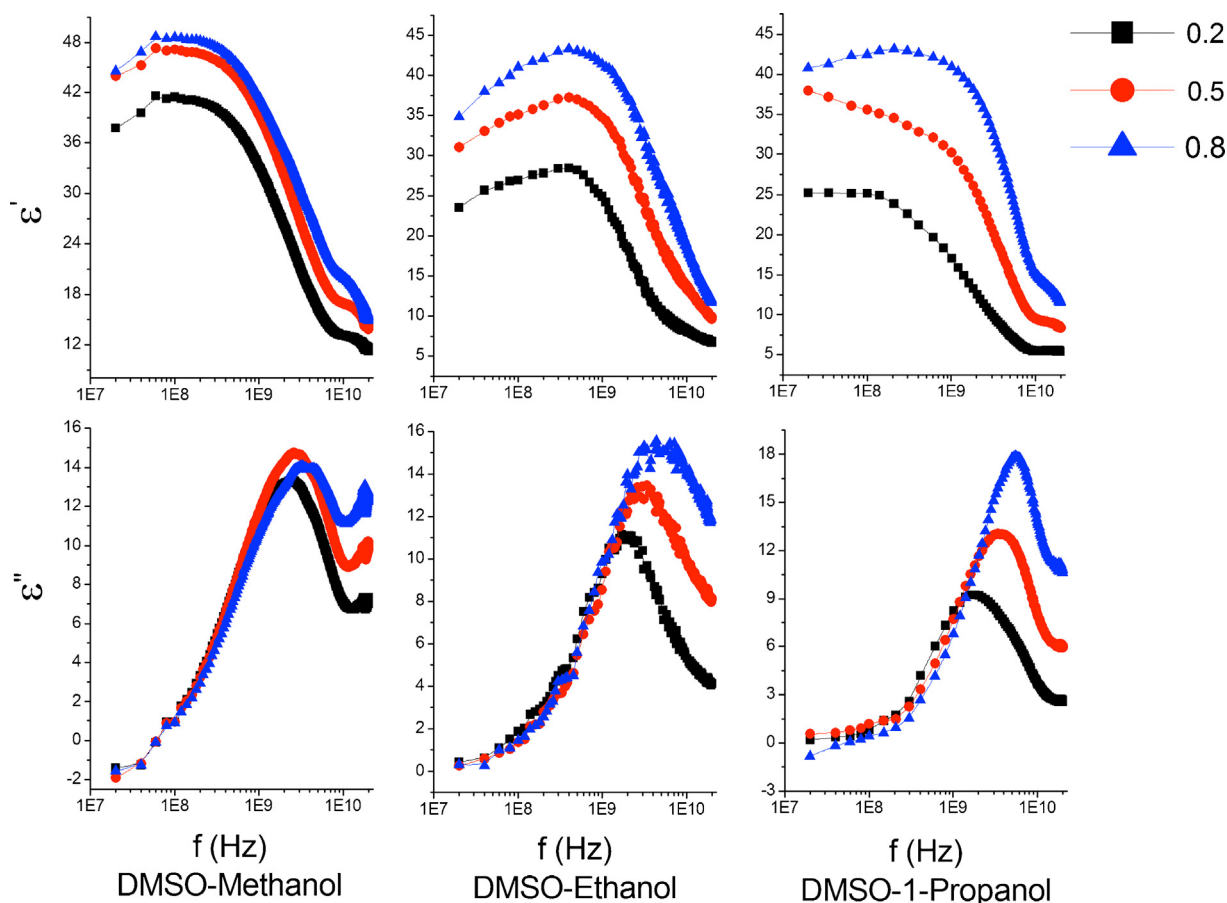
$$\varepsilon(\omega) = \varepsilon_{\infty} + \frac{\varepsilon_0 - \varepsilon_{\infty}}{[1 + (j\omega\tau)^{1-\alpha}]^{\beta}} \quad (1)$$

where  $\varepsilon_0$  is the static permittivity,  $\varepsilon_{\infty}$  is the high-frequency limiting permittivity, and  $\tau$  is the relaxation time.  $\alpha$  ( $0 \leq \alpha \leq 1$ ) and  $\beta$  ( $0 \leq \beta \leq 1$ ) are shape parameters describing symmetric and asymmetric distribution of relaxation times, respectively. Three well-known models are limiting cases of this general equation; they are the Debye equation ( $\alpha = 0$ ,  $\beta = 1$ ), the Cole–Cole equation ( $0 \leq \alpha < 1$ ,  $\beta = 1$ ), and the Davidson–Cole equation ( $\alpha = 0$ ,  $0 < \beta \leq 1$ ).

## 3. Results

The permittivity spectra of the DMSO-monohydric alcohol mixtures in the whole composition range at room temperature are shown in Fig. 1 and Fig. 2.

It can be seen from Fig. 1 and Fig. 2 that all of the real part  $\varepsilon'$  decreases with the increase of frequency. The imaginary part  $\varepsilon''$  increases with  $x_2$  at small DMSO content, and then decreases to the pure DMSO value, the position of its peak shifts toward higher frequency with increasing DMSO mole fraction; it shows that the relaxation time decreases with an increase of DMSO in the mixture.



**Fig. 1.** Complex permittivity spectra ( $\varepsilon'$  and  $\varepsilon''$ ) of DMSO-monohydric alcohol (methanol, ethanol and 1-propanol) mixtures at 298 K at  $x_2 = 0.2, 0.5, 0.8$ .  $x_2$  represents the mole fraction of DMSO.

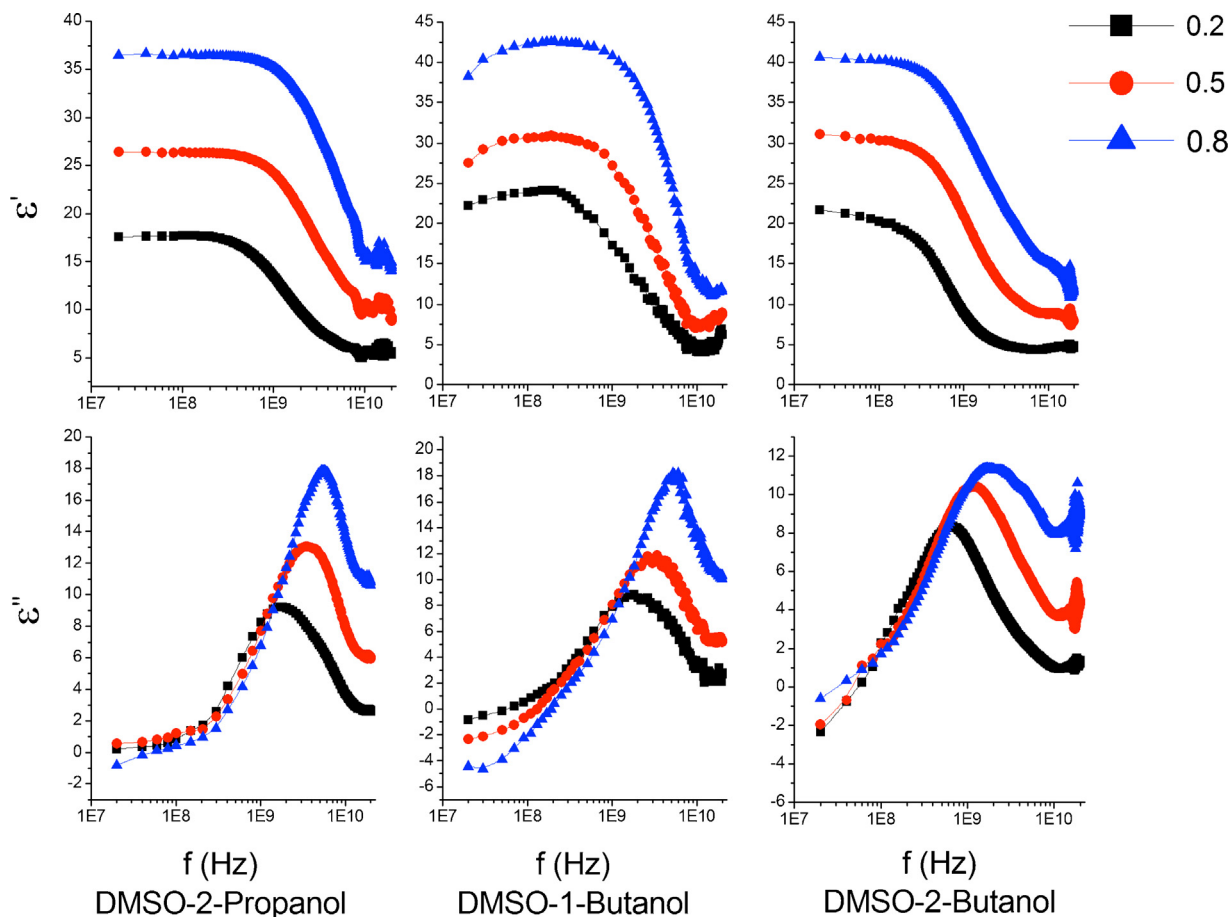


Fig. 2. Complex permittivity spectra ( $\epsilon'$  and  $\epsilon''$ ) of DMSO-monohydric alcohol (2-propanol, 1,2-butanol) mixtures at 298 K at  $x_2 = 0.2, 0.5, 0.8$ .  $x_2$  represents the mole fraction of DMSO.

In order to determine the dielectric relaxation parameters, we performed a curve-fitting procedure for the dielectric spectrum by Genetic Algorithm. From Figs. 1 and 2, the dielectric spectrum of the DMSO-monohydric alcohol is an asymmetric shape. The permittivity spectra  $\epsilon(\omega)$  at various compositions were then analyzed by simultaneously fitting  $\epsilon'(\omega)$  and  $\epsilon''(\omega)$  to Eq.(1) with adjustable  $\alpha$  and  $\beta$  [7]. Using the Havriliak–Negami function, we can obtain the minimum variance which fits a consistent set of relaxation parameters as a function of composition. Zijie Lu [7] has been successfully reported dielectric relaxation parameters in DMSO-water mixtures by using the Davidson–Cole function. Besides, in order to check more complicated spectral functions that might be related to more specific solution models, we also attempted to fit  $\epsilon(\omega)$  by a sum of multiple dispersion steps, where for each relaxation process a band shape defined by Debye, Cole–Cole, Davidson–Cole, or Havriliak–Negami function can be selected. However, we find the Davidson–Cole function is the most appropriate way for displaying the frequency dispersion of the data.

Fig. 3 shows that, the dielectric parameters of pure sample in this work are accord well with literature data [7]. Table 2 lists the literature results of  $\epsilon_0$  pure compounds and its evaluated data.

Table 3.

#### 4. Discussion

##### 4.1. The excess inverse relaxation time and the excess permittivity

The excess inverse relaxation time is defined as [27],

$$(1/\tau)^E = (1/\tau)_m - [(1/\tau)_1 X_1 + (1/\tau)_2 X_2] \quad (2)$$

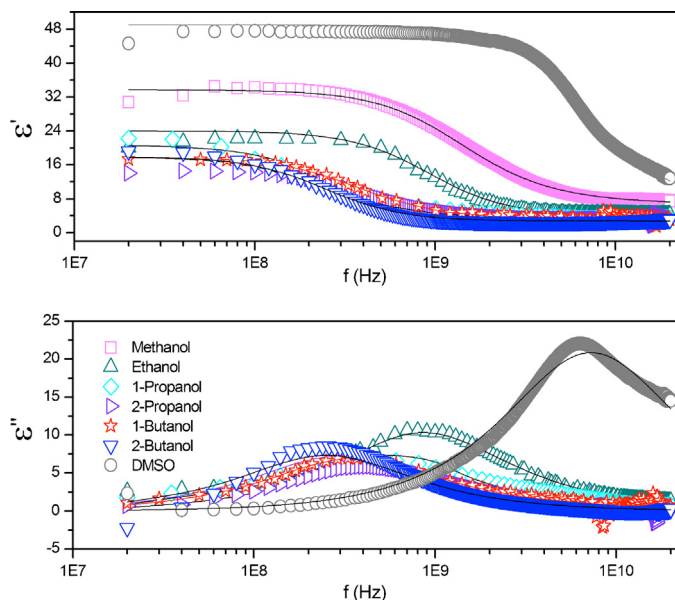


Fig. 3. Complex permittivity spectrum ( $\epsilon'$  and  $\epsilon''$ ) of pure solvent at 298 K. The symbols present the experimental result. The solid lines are fitted curve that accord well with Davidson–Cole function.

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

**Table 2**

The experimental relative permittivity and literature data for pure compounds at 298 K.

Pure solvent	$\epsilon_0 (\pm 5.3\%)$		Pure solvent	$\epsilon_0 (\pm 5.3\%)$	
	Literature	experimental		Literature	experimental
Methanol	32.6 <sup>a</sup>	33.1	Ethanol	24.32 <sup>b</sup>	22.8
1-Propanol	20.7 <sup>c</sup>	21.3	1-Butanol	17.6 <sup>d</sup>	17.8
2-Propanol	19.4 <sup>d</sup>	19.1	2-Butanol	18.0 <sup>d</sup>	17.6
DMSO	47.3 <sup>e</sup>	49.0			

<sup>a</sup> Reference [28].

<sup>b</sup> Reference [29].

<sup>c</sup> Reference [30].

<sup>d</sup> Reference [31].

<sup>e</sup> Reference [7].

And the excess permittivity is defined as,

$$\epsilon^E = (\epsilon_0 - \epsilon_\infty)_m - [(\epsilon_0 - \epsilon_\infty)_1 x_1 + (\epsilon_0 - \epsilon_\infty)_2 x_2] \quad (3)$$

In this formula,  $x_1$  and  $x_2$  represent the mole fraction of monohydric alcohol and DMSO respectively in the mixture.  $\epsilon^E$  related to  $\tau$  and  $\epsilon_0$  provides valuable information concerning interaction between the solute-solvent liquid mixtures. Due to intermolecular hydrogen bonding interaction, these properties are also useful for detection of the cooperative domain in the mixture and may evidence for formation of multimers in the mixture. According to definition formulas (2) and (3), the excess inverse relaxation time and excess permittivity in the whole composition range at room temperature 298 K are shown in Fig. 4.

As shown in Fig. 4(a),  $(1/\tau)^E < 0$  means the effective dipoles rotate slowly as the strength of the heterogeneous hydrogen-bond increases, and  $(1/\tau)^E > 0$  indicate the effective dipoles rotate rapidly. From Fig. 4(b),  $\epsilon^E > 0$  for methanol and ethanol indicate that there is formation of monomers and dimers.  $\epsilon^E < 0$  for 1,2-propanol and 1,2-butanol suggest that the DMSO-1,2-propanol and 1,2-butanol mixture may form multimers leading to the less effective dipoles. Both the values of static dielectric constant and dielectric relaxation time for the binary mixtures of hydrogen-bonded associative molecules cannot be assumed to be those given by a simple mole-fraction mixture law because the dielectric constant is highly sensitive to the hydrogen-bond structures of the unlike molecules in the mixtures.

#### 4.2. Luzar model

The significance of hydrogen bonds to the dielectric properties of the mixture can be studied using the Luzar model. Due to this model is successfully applied to a DMSO-water system and the statistical behavior of solute-solvent interaction assumes that only solute-solute and solute-solvent pairs are formed in the mixture. Thus, it is applicable for a polar-nonpolar mixture. We use the same model to explain the static dielectric permittivity of the mixture. The static electric permittivity in terms of the Kirkwood correlation factor “ $g_i$ ” for a mixture can be expressed as follows<sup>12</sup>:

$$[(\epsilon_0 - \epsilon_\infty)(2\epsilon_{0i} + \epsilon_{\infty i})/9\epsilon_0] = 4\pi/9kT \sum_{i=1}^2 g_i \rho_i \mu_i^2 \quad (4)$$

where  $i=1$  and 2 represent monohydric alcohol and DMSO, respectively;  $k$  is the Boltzmann constant,  $T$  is the temperature,  $\rho_i$  is the density,  $\mu_i$  is the corresponding dipole moment in the gas phase,  $\mu_1$  is the dipole moment for monohydric alcohol and  $\mu_2$  is the dipole moment for DMSO, and  $\epsilon_0$  and  $\epsilon_\infty$  are the static dielectric constant and dielectric constant at high frequency. With the  $i$ th liquid system,  $g_i$  is the Kirkwood correlation factor parameter affording information regarding the orientation of electric dipoles

**Table 3**

Dielectric parameters for DMSO-monohydric alcohol solution at full mole fraction range and measurement error effected with the uncertainty in frequency.

System <sup>a</sup>	Mole fraction of DMSO $x_2$ <sup>b</sup>	$\epsilon_0$ <sup>c</sup> ( $\pm 5.3\%$ )	$\epsilon_\infty$ <sup>c</sup> ( $\pm 5.3\%$ )	$\tau$ (ps) <sup>d</sup> ( $\pm 10\%$ )	$\beta$ <sup>e</sup> ( $\beta \pm 7\%$ )
DMSO-methanol	0.0	33.1	5.3	114.5	0.85
	0.1	33.9	4.4	107.7	0.84
	0.2	39.0	4.2	89.0	0.80
	0.3	42.5	4.3	85.0	0.76
	0.4	44.8	4.4	82.4	0.70
	0.5	45.8	4.2	80.7	0.68
	0.6	47.1	4.2	79.1	0.67
	0.7	49.2	3.3	75.9	0.66
	0.8	47.3	4.2	48.6	0.66
	0.9	45.8	4.1	45.9	0.66
	1.0	49.0	5.0	23.3	0.86
DMSO-ethanol	0.0	22.8	4.1	166.0	0.99
	0.1	26.3	4.8	115.9	0.85
	0.2	29.4	4.7	80.8	0.77
	0.3	31.7	4.6	66.9	0.73
	0.4	34.4	5.2	53.4	0.71
	0.5	37.4	3.7	45.8	0.67
	0.6	39.7	4.0	38.9	0.66
	0.7	41.6	4.0	33.3	0.67
	0.8	42.9	3.8	29.9	0.69
	0.9	45.4	4.0	24.4	0.75
DMSO-1-propanol	0.0	21.3	3.6	366.0	0.99
	0.1	22.7	3.8	132.7	0.91
	0.2	23.9	4.3	85.7	0.88
	0.3	26.0	4.3	66.1	0.84
	0.4	27.0	4.2	54.7	0.78
	0.5	31.9	4.3	45.2	0.79
	0.6	33.0	4.5	40.8	0.80
	0.7	35.0	4.3	36.0	0.79
	0.8	38.0	4.5	30.8	0.85
	0.9	46.6	5.3	28.6	0.78
DMSO-2-propanol	0.0	19.1	3.0	398.0	0.99
	0.1	19.9	3.6	230.2	0.79
	0.2	20.4	4.8	118.5	0.74
	0.3	21.0	4.4	87.4	0.69
	0.4	22.0	4.2	69.3	0.63
	0.5	26.0	4.5	49.5	0.61
	0.6	30.0	4.2	41.5	0.58
	0.7	33.6	4.6	38.3	0.58
	0.8	37.8	5.3	31.7	0.59
	0.9	46.2	4.5	25.2	0.64
DMSO-1-butanol	0.0	17.8	3.2	439.9	0.95
	0.1	18.2	3.0	192.3	0.89
	0.2	22.9	3.7	92.4	0.92
	0.3	22.7	3.9	91.0	0.92
	0.4	25.9	4.3	72.5	0.91
	0.5	29.8	4.1	62.0	0.88
	0.6	34.1	4.3	51.5	0.84
	0.7	37.8	4.2	43.4	0.84
	0.8	41.8	4.2	34.7	0.86
	0.9	44.1	4.4	30.8	0.89
DMSO-2-butanol	0.0	17.6	2.6	641.8	0.99
	0.1	19.1	3.3	346.2	0.99
	0.2	20.3	3.7	263.4	0.99
	0.3	24.5	4.1	199.3	0.91
	0.4	26.7	4.1	174.4	0.84
	0.5	29.5	4.3	154.5	0.78
	0.6	34.7	4.0	129.7	0.72
	0.7	34.7	4.3	103.0	0.67
	0.8	38.9	4.2	88.7	0.66
	0.9	44.6	4.3	59.7	0.66

<sup>a</sup> The whole measuring system was placed in room temperature at  $T = 298 \pm 0.5$  K, and pressure at  $P = 94.77 \pm 1$  kPa.

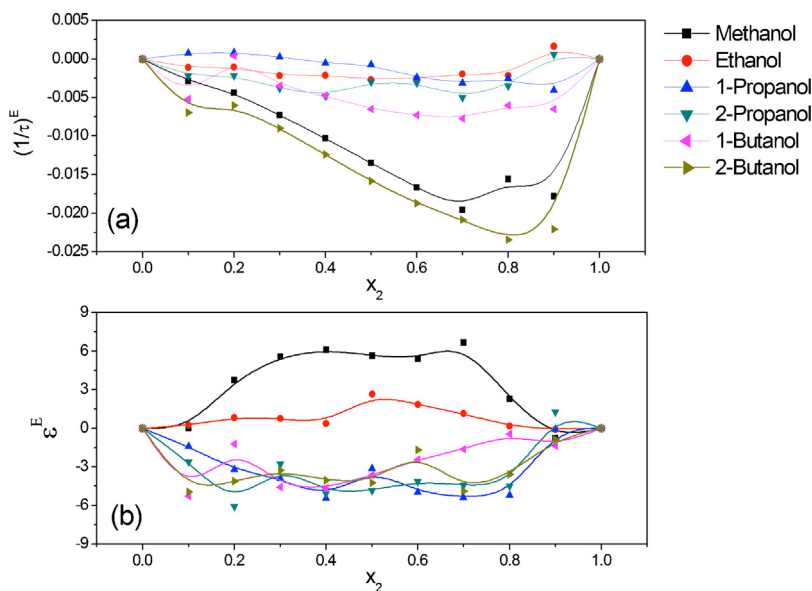
<sup>b</sup> The uncertainty for mole fraction is 2%.

<sup>c</sup> The standard uncertainty of  $\epsilon_0$  and  $\epsilon_\infty$  is  $\epsilon_0 \pm 5.3\%$ ,  $\epsilon_\infty \pm 5.3\%$ .

<sup>d</sup> The standard uncertainty of  $\tau$  is  $\tau \pm 10\%$ .

<sup>e</sup> The standard uncertainty of  $\beta$  is  $\beta \pm 7\%$ .





**Fig. 4.** (a), (b) Excess inverse relaxation time  $(1/\tau)^E$  and excess dielectric constant  $(\epsilon_0)^E$  as a function of mole fraction of DMSO for DMSO-monohydric alcohol mixtures at 298 K.

in polar liquids. The correlation factors  $g_1$  and  $g_2$  are computed using the Luzar model by considering only the hydrogen-bond contribution to the dipole-dipole correlation and are described by the relation as follow:

$$g_1 = 1 + Z_{11} \cos \phi_{11} + Z_{12} \cos \phi_{12} (\mu_2/\mu_1) \quad (5)$$

$$g_2 = 1 + Z_{21} \cos \phi_{21} (\mu_1/\mu_2) \quad (6)$$

where  $x_2$  is the mole fraction of DMSO.  $Z_{11} = 2 \langle n_{HB}^{11} \rangle$ ,  $Z_{12} = 2 \langle n_{HB}^{12} \rangle$ , and  $Z_{21} = \langle n_{HB}^{21} \rangle (1 - x_2)/x_2$  are the average number of particles forming the hydrogen bond with alcohol-alcohol and alcohol-DMSO pairs, respectively.  $\phi_{11}$  and  $\phi_{12}$  are the angles between neighboring dipoles of alcohol-alcohol and DMSO-DMSO pairs, respectively, and  $\cos \phi_{ij}$  is taken to be  $1/3$ . The values of  $g_1$  and  $g_2$  depend on the concentration of DMSO in DMSO-monohydric alcohol mixtures.

The average number of hydrogen bonds  $\langle n_{HB}^{11} \rangle$ ,  $\langle n_{HB}^{12} \rangle$ , and  $\langle n_{HB}^{21} \rangle$  per alcohol molecule for 1*i* pairs ( $i = 1, 2$ ) is determined according to the following relation

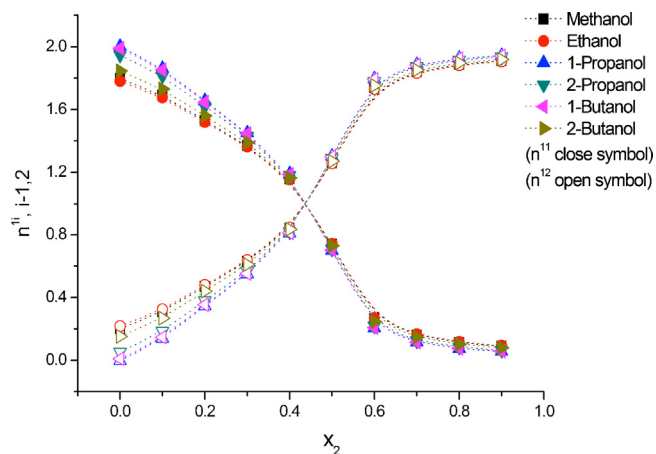
$$\langle n_{HB}^{1i} \rangle = n_{1i} \omega_{1i} / n_1 \quad (7)$$

Where  $\omega^{1i} = 1 / (1 + \alpha^{1i} e^{-\beta E^{1i}})$  is the probability of bond formation between alcohol and DMSO. The value of  $\beta = 1/kT$  and  $\alpha^{1i}$  is the ratio of the two sub volume of the phase space, related to the non-hydrogen-bonded and hydrogen-bonded pairs. These hydrogen-bonded pairs have only two energy levels,  $E^{11}$  and  $E^{12}$ , for alcohol-alcohol and alcohol-DMSO pair formed bonds, respectively.  $n_1$  is the number density of DMSO molecules. The values of  $\langle n_{HB}^{11} \rangle$  and  $\langle n_{HB}^{12} \rangle$  depend on the densities of the hydrogen-bonding pairs between DMSO-monohydric alcohol  $n^{12}$  and those between alcohol-alcohol molecule, i.e.,  $n^{11} = 2n_1 - n^{12}$ . This can be calculated when alcohol-alcohol (pair 1) and DMSO-alcohol (pair 2) are formed.

Fig. 5 shows plots of the average number of hydrogen bonds of alcohol-alcohol molecules (11 pairs) and DMSO-alcohol (12 pairs) against  $x_2$  for mixtures.  $\langle n_{HB}^{11} \rangle$  and  $\langle n_{HB}^{12} \rangle$  depend on the concentration of DMSO in DMSO-monohydric alcohol mixtures.  $n^{11}$  decreases and  $n^{12}$  increases with increasing  $x_2$ . The value of  $n^{11}$ , as well as that of  $n^{12}$  is 1 at  $x_2 = 0.45$ , it suggests that one alcohol molecule interacts with 1 surrounding DMSO molecules by hydrogen bonding in

half DMSO mixture. This result shows that DMSO plays a “breaker” in the formation of alcohol structure. The dynamical structure of a cooperative domain (CD) is defined as a domain in which the reorientation of molecules cooperatively occurs with dipole correlations. We discuss the mole fraction dependence of the population of two kinds of CDs for these mixtures. According to the cooperative domain model, the pure alcohol must contain only  $CD_1$ , because no DMSO molecules are added. At  $0 < x_2 < 0.45$ , DMSO molecule interact with surrounding alcohol molecules by hydrogen bonding, and these molecules form  $CD_{12}$ . The fraction of  $CD_{12}$  increase, and that of  $CD_1$  decrease with increasing  $x_2$ . At around  $x_2 = 0.45$ , the average size of  $CD_{12}$  and the average number of hydrogen bonds between alcohol and DMSO molecules are maximum. For  $x_2 > 0.45$ , the decrease in the number of alcohol molecules with increasing  $x_2$  leads to a decrease in the average number of hydrogen bonds between alcohol and DMSO molecules, which reflected in the decrease in the fraction of  $CD_{12}$ .

The values of  $g_1$  and  $g_2$  for different mole fraction of DMSO-monohydric alcohol mixtures are computed by using the parameters given in Table 4 and are shown in Fig. 6.



**Fig. 5.** Mole fraction dependency for average molar number of hydrogen bond of DMSO and alcohol molecules per unit volume for DMSO-monohydric alcohol mixture.

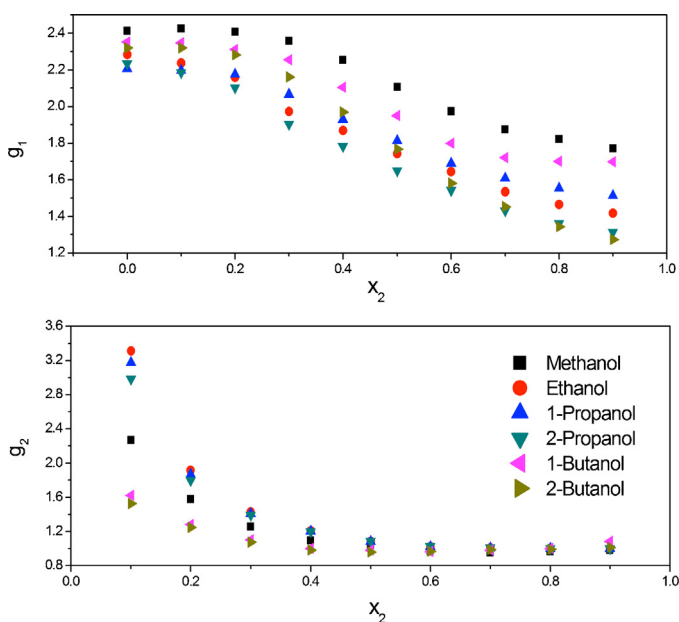
**Table 4**  
Molecular parameters used in computation of the static dielectric constants.

Molecular parameter	Methanol	Ethanol	1-Propanol	2-Propanol	1-Butanol	2-Butanol
$u_1^a$	.69D	.73D	1.68D	1.66D	1.66D	1.69D
$u_2^b$	3.96D	3.96D	3.96D	3.96D	3.96D	3.96D
$\alpha^{11c}$	40.96	41.02	40.57	38.35	38.84	36.79
$\alpha^{12d}$	29.27	29.84	28.79	28.15	28.05	28.89
$E_{11}^e$	14.86	-14.00	-13.86	-13.83	-12.73	-12.03
$E_{12}^f$	-17.48	-17.07	-16.82	-16.17	-15.17	-15.61

<sup>a,b</sup>  $\mu_1, \mu_2$  is the dipole moment for monohydric alcohol and DMSO respectively.

<sup>c,d</sup>  $\alpha^{11}, \alpha^{12}$  is the ratio of the two sub volume of the phase space.

<sup>e,f</sup>  $E_{11}, E_{12}$  is the binding energy for alcohol-alcohol and alcohol-DMSO pair, respectively.



**Fig. 6.** Kirkwood correlation factor ( $g_1, g_2$ ) as a function of mole fraction of DMSO for the DMSO-monohydric alcohol mixtures at 298 K.

Fig. 6 indicates that  $g_1$  and  $g_2$  decreases with increasing  $x_2$ . In  $0 < x_2 < 0.5$ ,  $g_2$  decreases sharply, and above 0.5,  $g_2$  nearly keeps steady.

The binding energy for alcohol-alcohol ( $E_{11}$ ) and DMSO-alcohol ( $E_{12}$ ) are showed in Table 4.

The hydrogen bonding in the DMSO-monohydric alcohol mixtures is associated with the carbon atoms of the alcohol molecules.  $E_{11}, E_{12}$  decreases with increasing number of carbon atom. According to the maximum measurement error of the static permittivity  $\epsilon_0$  and permittivity at high frequency  $\epsilon_\infty$  is  $\pm 3\%$ ; we estimate  $E_{11}$  and  $E_{12}$  in 0.50.

## 5. Conclusions

Dielectric relaxation behavior at microwave frequencies of DMSO-monohydric alcohol mixtures were investigated over the whole composition range. Analyzed from the relaxation time, these DMSO-monohydric alcohols exhibit different relaxation dynamics in different mole fraction range. The mole fraction dependent imaginary part of the dielectric constant reveals a peak which shifts toward higher frequency with increase of DMSO in the mixtures. Two types of hydrogen bonds, one is alcohol-alcohol pair, the other

is DMSO-alcohol pair revealed by Luzar model, and it indicates that the average number of hydrogen bond depends not only solution composition but also the number of carbons. The bonding energy is sorted in numeric order as follow:

$E_{11}$ :Methanol > Ethanol > 1-Propanol > 2-Propanol > 1-Butanol > 2-Butanol

$E_{12}$ :Methanol > Ethanol > 1-Propanol > 2-Propanol > 2-Butanol > 1-Butanol

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## References

- [1] A. Antonio de la Hoz, A. Diaz-Ortiz, Moreno. Chem. Soc. Rev 34 (2005) 164–178.
- [2] J.A. Riddick, W.B. Bunger, T.K. Sakano, Organic Solvents: Physical Properties and Methods of Purification, John Wiley & Son, New York, 1986, pp. 1–3.
- [3] R.J. Sengwa, V. Khatri, S. Sankhla, J. Solution. Chem. 38 (2009) 763–769.
- [4] P.P. Wiewior, H. Shirota, E.W. Castner Jr., J. Chem. Phys. 116 (2002) 4643.
- [5] I.A. Borin, M.S. Skaf, J. Chem. Phys. 110 (1999) 6412.
- [6] A. Vishnyakov, A.P. Lyubartsev, A. Laaksonen, J. Phys. Chem. A 105 (2001) 1702–1710.
- [7] Lu. Zijie, E. Manias, D.D. Macdonald, M. Lanagan, J. Phys. Chem. A 113 (2009) 12207–12214.
- [8] A. Luzar, J. Stefan, J. Mol. Liq. 46 (1990) 221–238.
- [9] K. Ramachandran, P. Sivagurunathan, K. Dharmalingam, S.C. Mehrotra, Acta. Phys. Chim. Sin. 23 (2007) 1508–1515.
- [10] S.D. Shingire, R.B. Talware, S.S. Kadam, A.C. Kumbharkhane, J. Mol. Liq. 169 (2012) 33–36.
- [11] L. Glasser, J. Crossley, C.P. Smyth, J. Chem. Phys. 57 (1972) 3977.
- [12] S.N. Helambe, A. Chaudhari, S.C. Mehrotra, J. Mol. Liq. 84 (2000) 235–244.
- [13] A.D. Vyas, V.A. Rana, Indian J. Pure Appl. Phys. 40 (2002) 69–71.
- [14] A. Chaudhari, P. Khirade, R. Singh, S.N. Helambe, N.K. Narain, S.C. Mehrotra, J. Mol. Liq. 82 (1999) 245–253.
- [15] A.C. Kumbharkhane, S.M. Puranik, S.C. Mehrotra, J. Mol. Liq. 51 (1992) 307–319.
- [16] J.A. Dale, D.J. Dull, Org. Chem. 34 (1969) 2543.
- [17] R. Ricciardi, F. Auremma, C. De Rosa, F. Lauprêtre, Macromolecules 37 (2004) 1921–1927.
- [18] T.W. Nee, R. Zwanzig, J. Chem. Phys. 52 (1970) 6353.
- [19] Y. Miyauchi, S. Chiashi, Y. Murakami, Y. Hayashida, S. Maruyama, Chem. Phys. Lett. 387 (2004) 198–203.
- [20] N. Guchhait, T. Ebata, N. Mikami, J. Chem. Phys. 111 (1999) 8438.
- [21] G. Onori, A. Santucci, J. Mol. Liq. 69 (1996) 161–181.
- [22] R. Noto, V. Martorana, A. Emanuele, S.L. Fornili, J. Chem. Soc. Faraday Trans. 91 (1995) 3803–3808.
- [23] C. Trandum, P. Westh, C.A. Haynes, Y. Koga, J. Phys. Chem. B 102 (1998) 5182–5195.
- [24] B. Kirchner, J. Hutter, J. Chem. Phys. 121 (2004) 5133.
- [25] A.K. Das, B. Tembe, J. Chem. Phys. 111 (1999) 7526.
- [26] M.S. Skaf, S.M. Vecchi, J. Chem. Phys. 119 (2003) 2181.
- [27] S. Havriliak, S.A. Negami, Polymer 8 (1967) 161–210.
- [28] E.P. Georgios, I.Z. Ioannis, Chem. Eng. Data 37 (1992) 172–187.
- [29] L. Saiz, E. Guardia, J.A. Padró, J. Chem. Phys. 113 (2000) 2814.
- [30] T. Sato, A. Chiba, R. Nozaki, J. Chem. Phys. 113 (2000) 9748.
- [31] C-M. Dorota, B. Adam, J.S. Ram, J. Mol. Liq. 179 (2013) 72–77.