

**DIELECTRIC RELAXATION STUDY  
OF DIPROPYLSULFOXIDE/ CCl<sub>4</sub> SOLUTIONS**

**L. S. GABRIELIAN and S. A. MARKARIAN\***

Yerevan State University  
1, A. Manoukyan Str., 0025, Yerevan, Armenia  
Fax: (37410) 576421; E-mail: shmarkar@ysu.am

The complex permittivity of pure dipropylsulfoxide (DPSO) and binary mixtures of DPSO/CCl<sub>4</sub> in the whole concentration range has been measured as a function of frequency between 100 MHz and 20 GHz at 298.15 K. Different relaxation spectral functions have been fitted to the measured frequency-dependent permittivity data. It was found that the Cole-Davidson spectral function, which presumes an unsymmetrical relaxation time distribution, "properly" applies for the measured spectra of DPSO and DPSO/CCl<sub>4</sub> mixtures. The results have been compared with those reported recently for the lower homologues dimethyl- and diethylsulfoxides.

Fig. 6, table 1, references 11.

**Introduction**

The interest in the study of dialkylsulfoxides and their solutions comes from both physicochemical peculiarities and biomedical significance of these systems [1-6]. Intriguing molecular characteristics of dimethyl sulfoxide (DMSO) and its homologues are the ability for self-association. This association reflects a complex interplay of hydrophilic and hydrophobic patches of the molecular structure. Variation of the non-polar alkyl chains in dialkylsulfoxides should therefore shed light on important facets of this interplay. Dielectric relaxation spectroscopy is one of the efficient techniques for studying dynamical processes in liquids. Dielectric relaxation spectrometry has proven a powerful tool, suitable to gain insights into the mechanisms of association and into reorientational dynamics of dipolar liquids [7, 8]. Detailed DRS studies of pure DMSO and diethyl sulfoxide (DESO) and the binary systems DMSO/CCl<sub>4</sub> and DESO/CCl<sub>4</sub> have been presented recently [5, 6]. In this paper, we present results of a dielectric relaxation study of pure dipropylsulfoxide (DPSO) and its solutions in non-polar solvent carbon tetrachloride. The results will be compared with those reported recently for the lower homologues.

## Experimental

DPSO was synthesized and purified according to reference [9]. All solutions were made up by weight from dry  $\text{CCl}_4$  of the highest purity available (Sigma-Aldrich, 99.9%).

We have determined the  $\varepsilon^*(\nu)$  spectra of DPSO/ $\text{CCl}_4$  mixtures over the entire composition range ( $0.1 \leq X_{\text{DPSO}} \leq 1$ ). Dielectric spectra were recorded by a coaxial reflection technique based on a microwave network analyzer (Hewlett-Packard HP 8720C) [10]. The probe (HP 85070B) was fixed in a glass cell thermostatted with an accuracy of  $\pm 0.02$  K. Reflected waves were sampled at  $0.1 < \nu < 20$  GHz and were converted to dielectric spectra using software based on the Nicolson-Ross method. The method requires 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.

Properties such as density,  $d$ , and refractive index,  $n_D$ , of the mixtures were measured in addition (the densities of the mixtures were measured using a vibrating tube densimeter, type Anton Paar DMA 4500, which is capable to yield an accuracy to  $\pm 5 \cdot 10^{-5}$  g·cm<sup>-3</sup>, a standard refractometer with an accuracy of  $\pm 5 \cdot 10^{-4}$  was used to measure the refractive index  $n_D$  of the samples at the wave length of the sodium D line).

## Results and Discussion

Typical examples of the real part  $\varepsilon'(\nu)$  and imaginary part  $\varepsilon''(\nu)$  of the complex permittivity  $\varepsilon^*(\nu) = \varepsilon'(\nu) - i\varepsilon''(\nu)$  of the DPSO/ $\text{CCl}_4$  mixtures in the whole concentration range ( $0.1 \leq X_{\text{DPSO}} \leq 1$ ) at 298.15 K temperature are shown in fig. 1. The spectra comprise about 1000 data triples  $\{\nu, \varepsilon'(\nu), \varepsilon''(\nu)\}$  in the range  $100 \text{ MHz} \leq \nu \leq 20 \text{ GHz}$ .

In fig. 2 are presented for comparison dielectric loss spectra ( $\varepsilon''$ ) for DMSO, DESO and DPSO at 298.15 K. Along the homologous series of dialkylsulfoxides the dielectric constant (which is proportional to the value of  $\varepsilon''$  amplitude) decreases slightly in going from DMSO to DESO, followed by a more substantial decrease in DPSO. Thus, on the macroscopic level the solvent becomes less polar. It can be seen from fig.2 that the position of the peak in the plot of the imaginary part of permittivity vs frequency shifts toward low frequency in going from DMSO to DESO and DPSO. It shows that the relaxation time largely increase in the series  $\text{DMSO} < \text{DESO} < \text{DPSO}$  [5].

In the analysis of the complex permittivity  $\varepsilon^*(\nu)$  various models based on a sum of  $n$  Havriliak-Negami (HN) equations

$$\varepsilon^*(\nu) = \varepsilon_\infty + \sum_{j=1}^n \frac{\Delta\varepsilon_j}{[1 + (i2\pi\nu\tau_j)^\alpha]^\beta} \quad (1)$$

or its variants the Debye (D), the Cole-Davidson (CD) or Cole-Cole (CC) equations with adjustable  $\alpha$  and  $\beta$  have been tested using a nonlinear least-squares fitting procedure [7, 8].

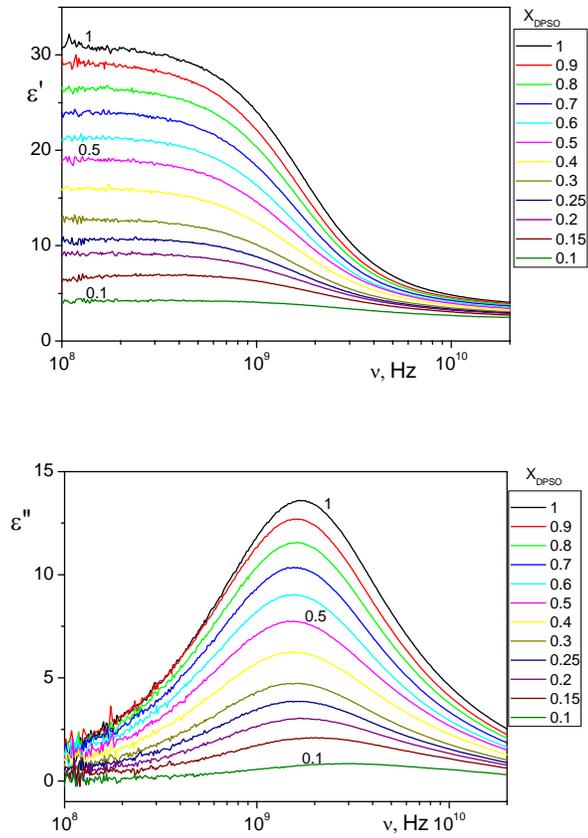


Fig. 1. Dielectric permittivity,  $\epsilon'(\nu)$ , and loss  $\epsilon''(\nu)$ , spectra of DPSO/ $\text{CCl}_4$  mixtures at 298.15 K in concentration range  $0.1 \leq X_{DPSO} \leq 1$ .

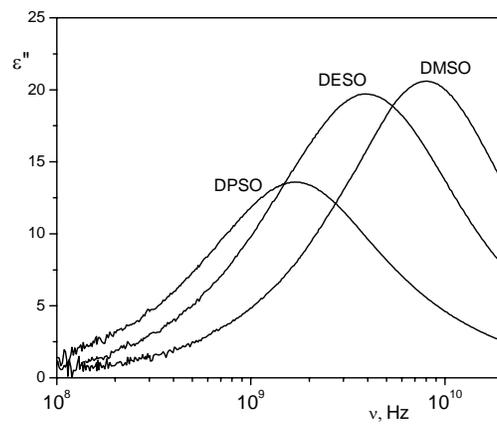


Fig. 2. Dielectric loss spectrum ( $\epsilon''$ ) against frequency ( $\nu$ ) for DMSO, DESO and DPSO at 298.15 K.

It was found that the Cole-Davidson spectral function, which presumes an unsymmetrical relaxation time distribution, "properly" applies for the measured spectra of DPSO and DPSO/CCl<sub>4</sub> mixtures.

$$\varepsilon_{CD}^*(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{(1 + i\omega\tau_{CD})^{\beta}} \quad (2)$$

The parameters  $\beta$  ( $0 < \beta \leq 1$ ) describes an asymmetric broadening of the relaxation function for frequencies  $\omega > 1/\tau_{CD}$ , where  $\tau_{CD}$  is the Cole-Davidson relaxation time. For  $\beta = 1$  the Debye function is recovered again.

The dielectric parameters, static dielectric constant ( $\varepsilon_S$ ), relaxation time ( $\tau$ ), relaxation strength ( $\Delta\varepsilon$ ), the CD parameter ( $\beta$ ), the high frequency limiting dielectric constant ( $\varepsilon_{\infty}$ , approximated by Maxwell as  $\approx 1.1n_D^2$ ) and the mean relaxation time  $\langle\tau_{CD}\rangle$  of the CD distribution ( $\langle\tau_{CD}\rangle = \beta\tau_{CD}$ ) obtained from the dielectric relaxation spectra of DPSO/CCl<sub>4</sub> are summarized in table 1.

Table

**Parameterization of dielectric spectra for the binary mixture  
DPSO/CCl<sub>4</sub> at 298.15 K.**

X <sub>DPSO</sub>	$\varepsilon_S$	$\Delta\varepsilon$	$\tau_{CD}$ , ps	$\beta$	$\langle\tau_{CD}\rangle$	$\varepsilon_{\infty} = 1.1n_D^2$	d, g cm <sup>-3</sup>	$g_K$
0.1	4.25	2.06	71.33	0.727	51.86	2.34	1.5026	0.834
0.15	6.97	4.47	101.44	0.731	74.15	2.35	1.4634	1.261
0.20	9.24	6.64	110.51	0.782	86.42	2.36	1.4256	1.381
0.25	10.73	7.88	115.67	0.814	94.16	2.36	1.3892	1.348
0.30	12.82	9.94	114.81	0.851	97.70	2.36	1.3541	1.407
0.40	16.08	13.08	116.57	0.859	100.13	2.37	1.2873	1.412
0.50	19.14	15.90	114.13	0.890	101.58	2.37	1.2244	1.410
0.60	21.48	17.97	108.95	0.939	102.30	2.37	1.1650	1.379
0.70	24.11	20.42	106.48	0.952	101.37	2.37	1.1088	1.385
0.80	26.66	22.88	103.57	0.959	99.32	2.37	1.0556	1.396
0.90	29.29	25.49	102.06	0.969	98.90	2.37	1.0053	1.418
1.00	31.10	26.98	103.80	0.900	93.42	2.36	0.9580	1.405

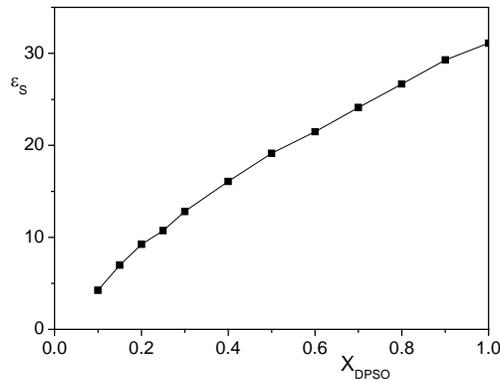


Fig. 3. The static dielectric constant  $\epsilon_s$  for DPSO/ $\text{CCl}_4$  mixture against mole fraction of DPSO at 298.15 K.

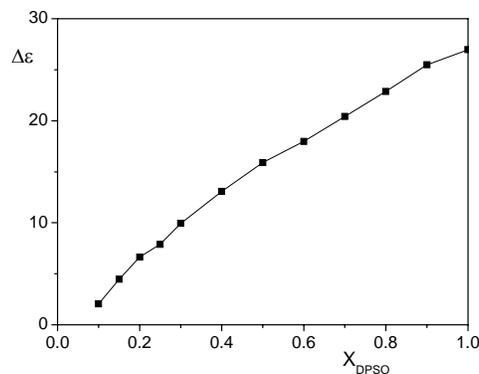


Fig. 4. The dielectric strength  $\Delta\epsilon$  for DPSO/ $\text{CCl}_4$  mixture against mole fraction of DPSO at 298.15 K.

The concentration dependent static dielectric constant ( $\epsilon_s$ ), relaxation strength ( $\Delta\epsilon$ ) and the mean relaxation time ( $\langle\tau_{CD}\rangle$ ) for DPSO/ $\text{CCl}_4$  binary mixtures have been presented in fig. 3-5. Since tetrachloromethane is a non-polar molecule, the observed relaxation component can essentially be ascribed to the highly polar sulfoxide molecule. As shown in fig. 3 and 4 the relaxation contribution becomes more intense with increasing concentration of DPSO in the mixture.

An interesting feature is the dependence of the mean relaxation time ( $\langle\tau_{CD}\rangle = \beta\tau_{CD}$ ) on the mole fraction of DPSO, fig. 5. It is important to notice that in case of DPSO/ $\text{CCl}_4$  mixtures the dependence of the relaxation time on the mole fraction of DPSO considerably differs from DMSO/ $\text{CCl}_4$  and DESO/ $\text{CCl}_4$  mixtures [4]. In this case the position of the plateau of  $\tau$  corresponds to a DPSO mole fraction 0.5-0.7. Early, on the basis of dielectric relaxation measurements on the DMSO/ $\text{CCl}_4$  and DESO/ $\text{CCl}_4$  systems a complex formation (with 1:1 stoichiometry) between dialkyl sulfoxide and tetrachloromethane was suggested [4].

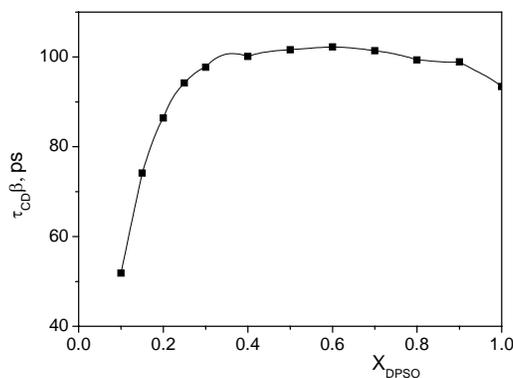


Fig. 5. Plot of the mean relaxation time ( $\tau_{CD}^*\beta$ ) from fitted Davidson-Cole functions versus the DPSO mole fraction for DPSO/ $\text{CCl}_4$  mixture against molar ratio of DPSO at 298.15 K.

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.

Kirkwood factors were calculated from  $\epsilon_S$  by the standard relation of Kirkwood–Fröhlich theory. For a pure liquid, the relevant expression is

$$g_K \mu^2 = \frac{(\epsilon_S - \epsilon_\infty)(2\epsilon_S + \epsilon_\infty)9\epsilon_0 kT}{\epsilon_S(\epsilon_\infty + 2)^2 N_A \mu^2 c} \quad (3)$$

where  $\epsilon_\infty$  is the high-frequency limit due to optical and vibrational processes, approximated by Maxwell as  $\approx 1.1n_D^2$ ,  $k$  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),  $\epsilon_S$  is the dielectric constant,  $\epsilon_0$  is the permittivity of the vacuum,  $\mu$  is the dipole moment in a gas phase (for DPSO  $\sim 3.9$  D).

In mixtures of apolar solvents such as  $\text{CCl}_4$ , Eq. (2) is, however, more easily generalized, because apolar solvents do only contribute to the nuclear and electronic polarization, but not to orientational polarization. Dielectric theory of mixtures then yields for a system comprising a of a polar component 1 at mole fraction  $x_1$  and non-polar component 2 at mole fraction  $x_2$

$$g_K \mu^2 = \frac{9k_B T \epsilon_0}{N_A x_1} \frac{(2\epsilon_S + \epsilon_\infty)^2}{(2\epsilon_S + 1)(\epsilon_\infty + 2)^2} \times \left[ \frac{\varphi(\epsilon_S - 1)}{\epsilon_S} - \frac{3x_2 M_2 (\epsilon_{S,2} - 1)}{(2\epsilon_S + \epsilon_{S,2})d_2} - \frac{3x_1 M_1 (\epsilon_\infty - 1)}{(2\epsilon_S + \epsilon_\infty)d_1} \right], \quad (4)$$

where  $\varphi$  is the molar volume of the mixture and the  $M_i$ ,  $\epsilon_{S,i}$ , and  $d_i$  ( $i=1,2$ ) are the molar masses, dielectric constants, and densities of the pure components, respectively [7,11].

The calculated Kirkwood correlation factor for DPSO is sufficiently above unity ( $g = 1.4$ ). The observed Kirkwood factors indicate a moderate extent of parallel dipole correlations in DPSO, as also observed in DESO and DMSO [6]. Upon dilution of DPSO

in  $\text{CCl}_4$ , the dipolar correlations gradually vanish, and at infinite dilution  $g_K$  approaches unity, as expected for an isolated dipole (fig. 6).

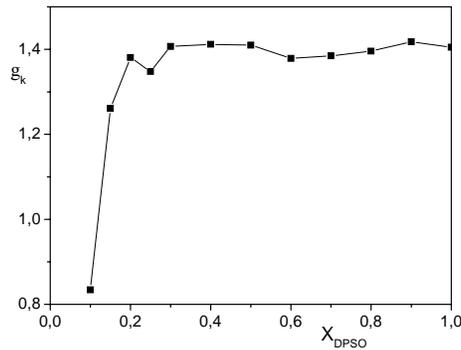


Fig. 6. Kirkwood correlation factor  $g_K$  as a function of mole fraction of DPO for DPO/ $\text{CCl}_4$  mixture at 298.15 K.

### Acknowledgement

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### ԴՊՈՒՊԻԼՍՈՒԼՖՕՔՍԻԴ/CCl<sub>4</sub> ԼՈՒԾՈՒՅԹՆԵՐԻ ԴԻԷԼԵԿՏՐԻԿ ՌԵԼԱՔՍԱՑԻԱՅԻ ՈՒՍՈՒՄՆԱՍԻՐՈՒԹՅՈՒՆԸ

Լ. Ս. ԳԱԲՐԻԵԼՅԱՆ և Շ. Ա. ՄԱՐԳԱՐՅԱՆ

Ուսումնասիրվել է մաքուր դիպոլայիլսուլֆօքսիդի (ԴՊՍՕ) և ԴՊՍՕ/ $\text{CCl}_4$  բինար խառնուրդի կոմպլեքս դիէլեկտրիկ թափանցելիությունը լայն կոնցենտրացիոն մարզում 100 ՄՀց-ից մինչև 20 ԳՀց հաճախության տիրույթում 298.15 Կ ջերմաստիճանում: Դիէլեկտրիկ թափանցելիության հաճախությունից կախվածության փորձնական տվյալների մշակման համար օգտագործվել են տարբեր ռելաքսացիոն ֆունկցիաներ: Ցույց է տրվել, որ Կոուլ-Դեվիդսոնի ֆունկցիան, որը ներկայացնում է ռելաքսացիայի ժամանակի ոչ սիմետրիկ բաշխումը, ամենաճշգրիտ է նկարագրում ԴՊՍՕ և ԴՊՍՕ/ $\text{CCl}_4$  դիէլեկտրիկ սպեկտրները: Ստացված արդյունքները համեմատվել են այլ հոմոլոգների՝ դիմեթիլ- և դիէթիլսուլֆօքսիդների տվյալների հետ:

## ИЗУЧЕНИЕ ДИЭЛЕКТРИЧЕСКОЙ РЕЛАКСАЦИИ РАСТВОРОВ ДИПРОПИЛСУЛЬФОКСИД/ССl<sub>4</sub>

Л. С. ГАБРИЕЛЯН и Ш. А. МАРКАРЯН

Ереванский государственный университет  
Армения, 0025, Ереван, ул. А. Манукяна 1  
Факс: (37410) 576421; E-mail: shmarkar@ysu.am

Измерены комплексные диэлектрические проницаемости чистого дипропилсульфоксида (ДПСО) и бинарной системы ДПСО/ССl<sub>4</sub> в широком концентрационном интервале в частотной области от 100 МГц до 20 ГГц при 298.15 К. Различные релаксационные функции были использованы для обработки частотно-зависимой диэлектрической проницаемости. Выявлено, что спектральная функция Коула-Дэвидсона, которая предполагает несимметричное распределение времени релаксации, наиболее точно описывает измеренные спектры ДПСО и системы ДПСО/ССl<sub>4</sub>. Полученные результаты сопоставлены с ранее описанными данными для низших гомологов: диметил- и диэтилсульфоксидов.

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