THE JOURNAL OF PHYSICAL CHEMISTRY B

ARTICLE

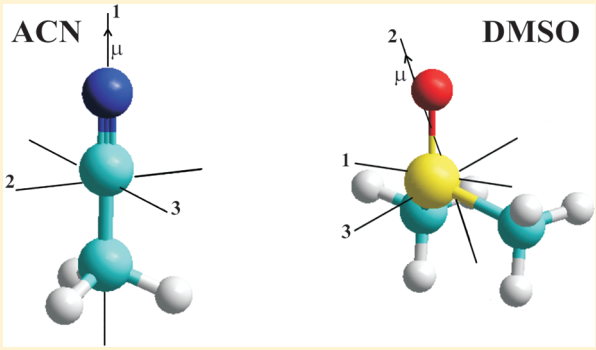
pubs.acs.org/JPCB

On Intermolecular Dipolar Coupling in Two Strongly Polar Liquids: Dimethyl Sulfoxide and Acetonitrile

Jan Jadżyn and Jolanta Świergiel*

Institute of Molecular Physics, Polish Academy of Sciences, M. Smoluchowskiego 17, 60-179 Poznań, Poland

ABSTRACT: The paper presents the results of studies of the electric and dielectric properties of dimethyl sulfoxide (DMSO) and acetonitrile (ACN), two strongly polar liquids composed of the molecules of the same dipole moment value ($\mu \approx 4$ D) but of a quite different static dielectric permittivity ($\varepsilon_S^{DMSO} \gg \varepsilon_S^{ACN}$). It was shown that the activation energies for both the dc ionic conductivity (σ_{DC}) and the viscosity (η) are two times higher for DMSO than for ACN; however, for both of the liquids, the temperature dependence of the product $\sigma_{DC}\eta$ is quite close to the prediction of the Stokes−Einstein relation. The dielectric results are interpreted in terms of the intermolecular dipole−dipole coupling. An exceptional behavior of DMSO most certainly results from its "monomolecularity", i.e., from the lack of the dipolar coupling in that strongly polar liquid. The effect is a consequence of a very specific structure of the DMSO molecule where its rotational dynamics makes the intermolecular dipole−dipole coupling very unfavorable, in contrast to the ACN molecules.



1. INTRODUCTION

Dimethyl sulfoxide (DMSO) and acetonitrile (ACN) belong to the organic solvents which are widely used in chemistry, biochemistry, pharmacy, and many branches of industry.[1−3] These highly polar aprotic liquids of convenient temperature range are miscible with many other liquids, including water and electrolytes. As liquids of high polarity, DMSO and ACN exhibit a relatively high electric conductivity even in a "pure" state, i.e., without any special ionic admixture dissolved. The "natural" background of the electric conductivity of liquids[4] certainly results from residual, thermally activated ionic impurities which can dissociate not only in a spontaneous way but also with an assistance of some external forces, like the electric fields or the cosmic rays.[5,6]

However, DMSO and ACN, two compounds composed of molecules with the same dipole moment value (about 4 D), show many striking differences in their physical properties. Although ACN is referred by many authors as the "leading dipolar system" where strong dipole−dipole coupling determines the most of its physical properties,[7,8] at the same time, DMSO exhibits really exceptional and unexpected properties. First of all, it concerns the solutions of DMSO in water which show a strong nonideal behavior of many physical properties. The most striking example concerns the freezing point (T_f): the mixture of DMSO ($T_f \approx 19$ °C) and water ($T_f \approx 0$ °C) containing the mole fraction $x \approx 0.3$ of DMSO exhibits the depression of that point up to about $T_f \approx -140$ °C.[9] So, the mixtures DMSO + water are used, among others, as a crioprotectant agent in biomedical practice. Besides, DMSO is used as a protein-dissolving solvent or as a coadjuvant drug carrier, where an unexpectedly high permeability of DMSO molecules across biomembranes is exploited.[2] Also ACN plays a significant role in numerous biochemical practices; for example, it is the dominant solvent used in the manufacture of DNA oligonucleotides from monomers. Industrially, ACN is used, among others, as a solvent for the manufacture of pharmaceuticals and photographic films. No wonder that both compounds are the subject of numerous studies both experimentally[10−13] and theoretically.[14−18]

From the electric properties point of view, the solvents being a subject of our studies are diluted electrolytes. So, the dc conductivity can represent the translational self-diffusion process in liquid; that is, the ions play a role of diffusion tracers, provided the strength of external perturbation (probing electric field) is small enough for the linear response of the system. This paper presents the results on the electric and dielectric behavior of DMSO and ACN obtained with the linear impedance spectroscopy in a wide temperature range. The static electric conductivity (representing the translational mass transport) is interpreted together with the liquid viscosity (the momentum transport) in the frame of the Stokes−Einstein model.

2. EXPERIMENTAL SECTION

Dimethyl sulfoxide $(CH_3)_2S{=}O$ (Sigma-Aldrich) and acetonitrile $CH_3C{\equiv}N$ (Baker), both of a purity better than 99.9%, were stored over the molecular sieves 4 Å before investigation.

Received: February 10, 2011
Revised: April 18, 2011
Published: April 29, 2011

ACS Publications © 2011 American Chemical Society

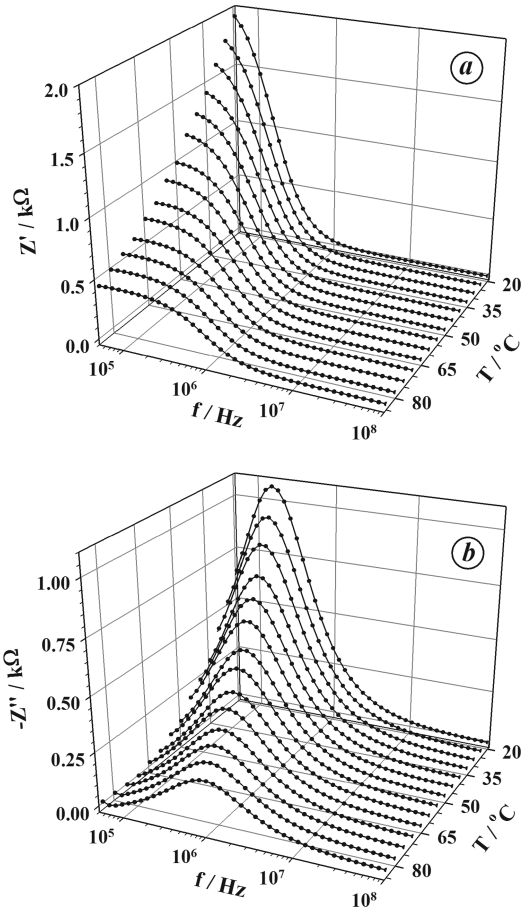


Figure 1. Impedance spectra of DMSO, the real (a) and imaginary (b) parts, recorded in the temperature range of 20−85 °C.

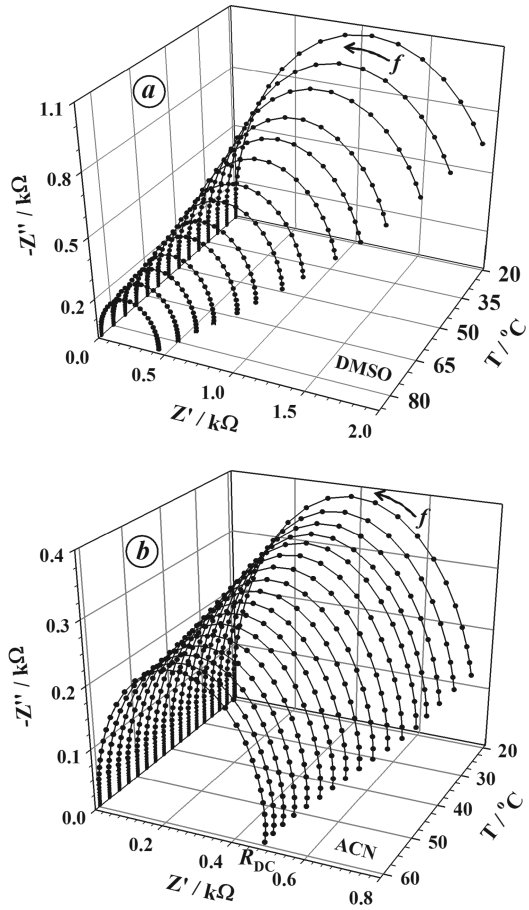


Figure 2. Impedance spectra of DMSO (a) and ACN (b) in the complex plane, at various temperatures.

The impedance spectra of the compounds were recorded with the use of an HP 4194A impedance/gain phase analyzer in the frequency range from 50 kHz to 100 MHz and in the temperature range from 20 to 85 °C for DMSO and from 20 to 60 °C for ACN. The frequency range used corresponds to the static dielectric regime of both liquids under investigation. A measuring capacitor consisted of three plane electrodes (the surface of about 1 cm^2): one central and two grounded on each side, with a distance between them of about 0.2 mm. The shape of the capacitor electrodes is rectangular, and they are made with a gold-plated copper. The capacity of the empty cell used (C_0) was equal to 9.68 pF. The probing electric field intensity E was equal to about 1 V/mm. The electrical heating of high performance with the use of a "Scientific Instruments" temperature controller, model 9700, assured very good temperature stabilization (at milikelvin level). Such equipment allows one to determine the impedance with an uncertainty less than 1%.

3. RESULTS AND DISCUSSION

Figure 1 presents the spectra of the real $Z'(a)$ and imaginary $Z''(b)$ parts of the complex impedance $Z^*(\omega) = Z'(\omega) + jZ''(\omega) = R(\omega) + 1/(j\omega C)$, $(j \equiv (-1)^{1/2})$, recorded for the cell filled with DMSO and excited by the electric stimulus of the angular frequency $\omega = 2\pi f$, f is the linear frequency. R and C denote respectively the resistance and capacitance of the system measured. The impedance spectra of ACN resemble those presented in Figure 1. In Figure 2 the impedance spectra of the both studied compounds are presented in the complex plane $-Z''$ vs Z'. An essentially different sensibility of the impedance spectra of DMSO and ACN to the temperature change is clearly seen in the picture.

The impedance spectra, as presented in Figure 2, are very useful for precise determination of the dc electric conductivity (σ_{DC}) of liquids. The situation is the simplest when in the complex plane, $-Z''$ vs Z', the spectra present the semicircles with the centers placed on the real axes of the impedance. Then, the experimental spectra can be analyzed with the Debye-type equation[19−21]

$$Z^*(\omega, T) = R_\infty(T) + \frac{R_{DC}(T) - R_\infty(T)}{1 + j\omega\tau_\sigma(T)} \quad (1)$$

where R_{DC} and R_∞ denote the dc and the high frequency resistance of the sample. The quantity τ_σ is called the conductivity relaxation time,[22] and in the case of the Debye-type impedance spectra, it corresponds to the maximum of the impedance relaxation band. Such simple impedance spectra were recorded in our experiment for both studied liquids, and an example of the best fit of eq 1 to the experimental spectrum is depicted in Figure 3. The fitting procedure gave for R_∞ the insignificant values, less than 0.1 Ω, both for DMSO and ACN, at all temperatures of the measurements. Here, the most important is the parameter R_{DC} which can be expressed as the dc electric conductivity $\sigma_{DC} = d/(SR_{DC})$, where d and S are the distance between the electrodes

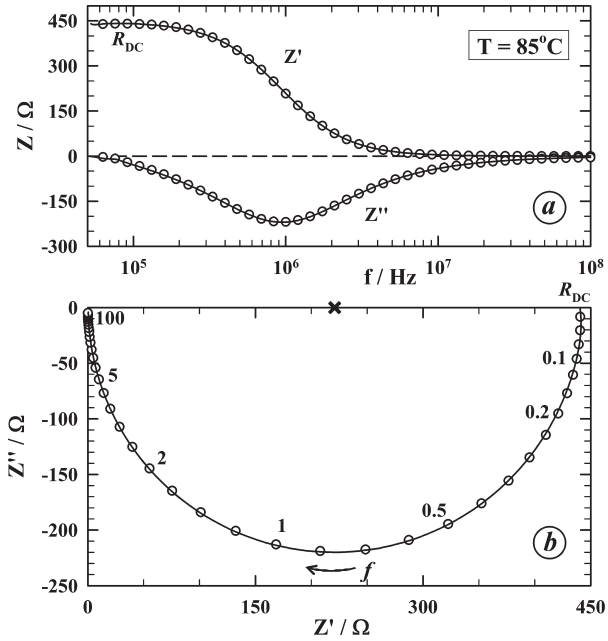


Figure 3. Frequency dependence of real Z' and imaginary Z'' parts of the impedance (a) and corresponding diagram in the complex plane (b), for DMSO, at 85 °C. The solid lines represent the best fit of eq 1 with to the experimental data (points).The parameter in (b) is the frequency of the probing electric field (in MHz).

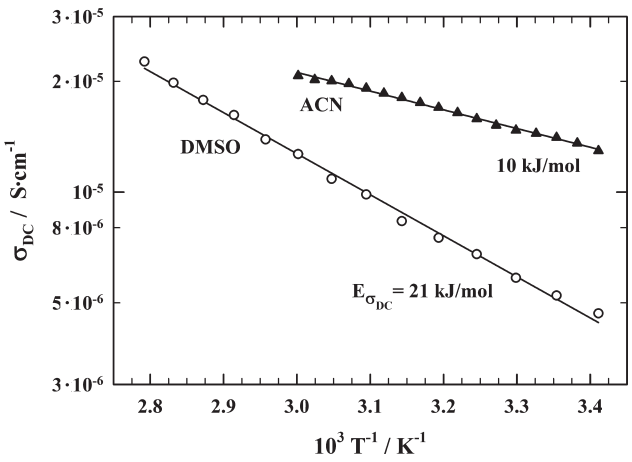


Figure 4. Arrhenius plots for the dc electric conductivity (σ_{DC}) of dimethyl sulfoxide and acetonitrile. The conductivity activation energy values are shown in the picture.

of the measuring cell and the surface of the electrode, respectively. The temperature dependences of σ_{DC} obtained for DMSO and ACN are presented in Figure 4 in the form of the Arrhenius plot. The mentioned above qualitative conclusion on the different temperature behavior of the impedance spectra of DMSO and ACN (Figure 2), now reveals itself quantitatively as significantly different activation energy for the dc ionic conductivity in these two liquids ($E_{\sigma_{DC}}^{DMSO} \approx 2E_{\sigma_{DC}}^{ACN}$).

The ionic diffusion in a liquid, which can be represented by σ_{DC}, reflects the molecular self-diffusion process in the liquid, provided the both objects, ions and molecules, are of similar dimensions. The condition seems to be fulfilled in the liquids studied, as it would be difficult to expect here the ionic

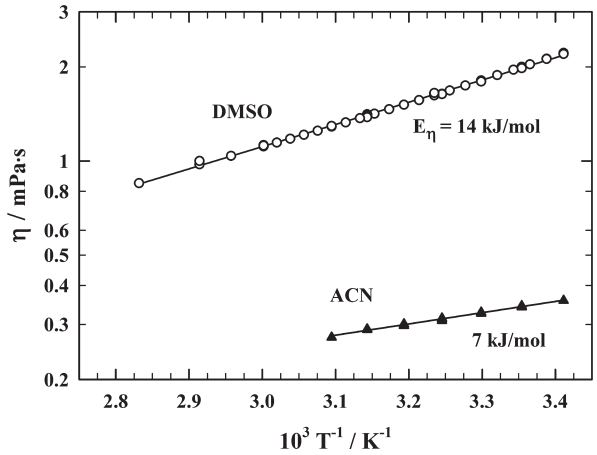


Figure 5. Arrhenius plots for the shear viscosity (η) of dimethyl sulfoxide[25,26] and acetonitrile.[26−29] The viscosity activation energy values are shown in the picture.

admixtures of dimensions significantly different than those of the molecules, and what is quite possible in conducting polymeric liquids, for example. So, if the translational dynamics of ions reflects that of the molecules of the liquid, the static electric conductivity of DMSO and ACN, can be related to the diffusion coefficient D (in an assumption of the same diffusion coefficient for all ions participated in the conductivity process) by the Nernst−Einstein equation[23]

$$D = \frac{\sigma_{DC} kT}{nq^2} \tag{2}$$

where n is the number of ions in the unit volume, q is the charge of the ions, k is the Boltzmann constant and T is the absolute temperature. On the other side, the hydrodynamic Stokes−Einstein model[23,24] relates the self-diffusion coefficient to the viscosity (η) of liquid. If the ions/molecules can be represented by the spheres of radius r (more strictly it is the effective Stokes radius), then according to the Stokes−Einstein model

$$D = \frac{kT}{6\pi\eta r} \tag{3}$$

Combination of eqs 2 and 3 yields a simple relation between the dc conductivity and the shear viscosity of liquid:

$$\sigma_{DC} \cdot \eta = \frac{nq^2}{6\pi r} \tag{4}$$

According to eq 4, the product of the dc electric conductivity and the viscosity of the liquid is expected to be constant, independently on the measuring temperature. Irrespective of the physical assumptions on which the above models are based, the constancy of the $\sigma_{DC}\eta$ product requires the invariability of n, what means the temperature independence of the degree of ionic dissociation in the liquid. Of course, the condition is fulfilled only when the full ionic dissociation occurs in the lowest temperature used, already.

The temperature dependences of the share viscosity, taken from the literature for DMSO[25,26] and ACN,[26−29] are presented in Figure 5. The viscosities of the liquids studied, like their dc conductivities, fulfill the Arrhenius dependence very well, and the viscosity activation energies of DMSO and ACN show quite

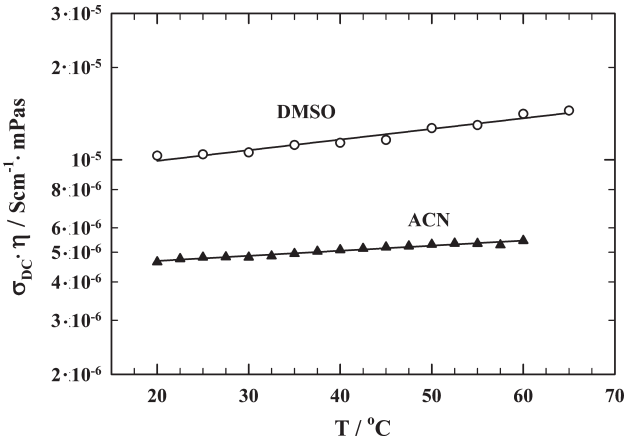


Figure 6. Verification of the Stokes−Einstein model ($\sigma_{DC}\eta$ = const) for DMSO and ACN.

similar relation to each other ($E_\eta^{DMSO} \approx 2E_\eta^{ACN}$) as the activation energies for the conductivity ($E_{\sigma_{DC}}{}^{DMSO} \approx 2E_{\sigma_{DC}}{}^{ACN}$). This fact seems to be a good prognostic for a positive verification of eq 4. However, as depicted in Figure 6, the temperature behavior of the $\sigma_{DC}\eta$ product for the liquids studied shows some deviation from the Stokes−Einstein model prediction, and an increase of the product with increasing temperature is observed: for DMSO the slope of $\sigma_{DC}\eta$ is equal about 0.35% and for ACN about 0.16%. That rather small deviation from the Stokes−Einstein model may results, for example, from a weak temperature dependence of the ions concentration in the liquids. Independently on the reason of the deviation from the $\sigma_{DC}\eta$ product constancy, the results presented in this paper show that the dc conductivity of ions represents quite well the molecular translational diffusion in liquid DMSO and ACN with a reasonably consistency to the hydrodynamic model of the molecular diffusional motions.

The dielectric properties of DMSO and ACN can be discussed on the basis of their dielectric permittivity dependence on the frequency and the temperature what can be gained by transformation of the impedance spectra into dielectric relaxation spectra. The real (ε') and imaginary (ε'') parts of the complex permittivity (ε^*) are related to the impedance as follows:[21,22] $\varepsilon^* \equiv \varepsilon' - j\varepsilon'' = (j\omega Z^* C_0)^{-1}$, where C_0 denotes the capacity of the empty measuring cell. Hence one obtains, at a given temperature T, the frequency dependences of the real and imaginary parts of the dielectric permittivity

$$\varepsilon'(f,T) = -\frac{Z''(f,T)}{Z^2(f,T)\omega C_0} \qquad \varepsilon''(f,T) = \frac{Z'(f,T)}{Z^2(f,T)\omega C_0} \tag{5}$$

Figure 7 presents the real (a) and imaginary (b) parts of the dielectric relaxation spectra of DMSO and ACN. It is clearly seen in Figure 7a that the frequency range used in our experiment corresponds to the static values of the dielectric permittivity of the liquids. As it results from the literature data,[30,31] the maximum of the dielectric absorption band of DMSO and ACN can be found at the frequencies as high as about 8 and 40 GHz, respectively. Figure 7b shows that the dielectric losses are, as expected, due to the electric conductivity only, so, the $\varepsilon''(f)$ dependences have (in the log−log scale) a form of the

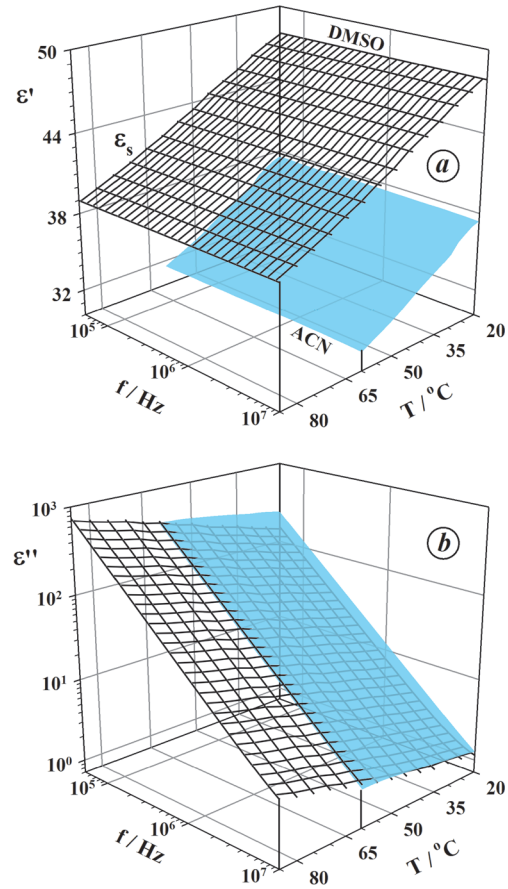


Figure 7. Dielectric relaxation spectra, the real (a) and imaginary (b) parts, resulting from transformation (eqs 5) of the impedance spectra of DMSO and ACN.

straight lines of the slope equal to −1.00 (±0.02), at all temperatures of the measurements of DMSO and ACN.

In Figure 8 are depicted the temperature dependences of the static dielectric permittivity (ε_s) of DMSO and ACN, representing the results from Figure 7a (the results are in a very good agreement with the numerous published data).[30−37] The most striking is the difference in the static permittivity values of the both liquids, for example at 20 °C: $\varepsilon_s^{DMSO} \approx 48$ and $\varepsilon_s^{ACN} \approx 37.5$. If one takes into account that the both liquids are composed of the molecules of the same dipole moment value $\mu \approx 4$ D[38,39] and that the unit volume of liquid ACN contains about 25% more dipoles than DMSO (the molar volumes ratio V_m^{ACN}/V_m^{DMSO}0.75, at 20 °C), one should expect rather higher permittivity value for ACN than for DMSO. The reason for that unexpected difference in the static permittivity ($\varepsilon_s^{DMSO} \approx 1.3\varepsilon_s^{ACN}$) must results from an essential difference in the molecular dipole−dipole coupling abilities occurring in liquid DMSO and ACN. The conclusion is strongly supported by the Kirkwood correlation factor (g_K) measurements which gave for DMSO the following results: g_K^{DMSO} = 1.01,[13,18] 0.99,[40] 1.13,[41] 1.00,[42,43] 0.95,[44] and 1.04[45] what quite clearly points out for the lack of the dipolar coupling in that liquid, whereas for ACN, the values are g_K^{ACN} = 0.74,[41] 0.75,[46] and 0.82,[47] as expected for the liquid with molecular antiparallel dipole−dipole coupling.

Figure 9 presents the structure of the DMSO and ACN molecules together with the three principal axes of the moments of inertia (I) around of which the molecule executes its thermally

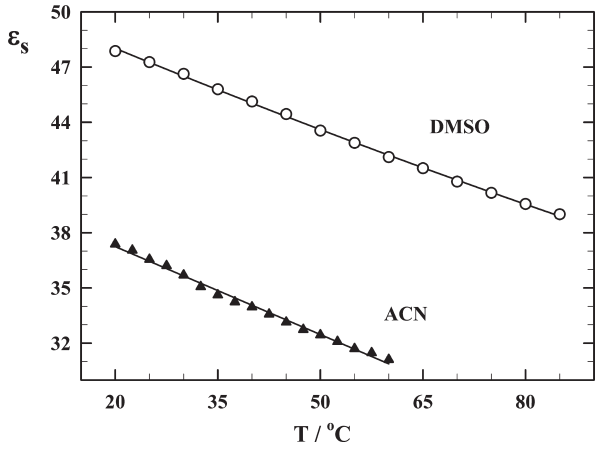


Figure 8. Temperature dependence of the static dielectric permittivity of dimethyl sulfoxide and acetonitrile.

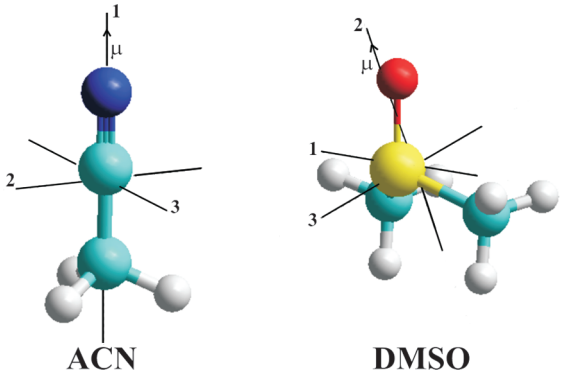


Figure 9. Molecular structure of dimethyl sulfoxide and acetonitrile molecules with the axis of their principal moments of inertia I (the axes 1 corresponds to I_{min} and the axes 3 − to I_{max}). The arrow indicates the direction of the dipole moment vector (μ) of the molecule.

activated rotations (the axis 1 corresponds to I_{min} and the axis 3 − I_{max}). Essentially different pictures of the DMSO and ACN molecules rotations and quite different possibilities of the dipolar coupling are clearly seen in the figure. The coupling can be realized in the case of ACN molecule only, where the rotation around the axis 1 (I_{min} is simultaneously the axis of the dipole moment vector of the molecule) does not hinder the dipolar antiparallel association. This coupling leads to the ACN dielectric permittivity decrease. On the other hand, it is also clearly seen in Figure 9 that a very peculiar structure of DMSO molecule does not allow for the intermolecular dipolar coupling of these molecules. So, it seems that the two compounds studied can represent two extremely different types of the intermolecular structures in liquid state: strongly self-associated by the dipolar coupling acetonitrile and practically nonassociated (monomolecular) dimethyl sulfoxide.

4. CONCLUSIONS

The main problem discussed in this paper concerns the relation between the molecular symmetry and the electric and dielectric properties of liquids composed of these molecules. The difference in the symmetry leads to the different rotational dynamics of the molecules and hence to the different abilities for intermolecular self-association of strongly polar molecules. Dimethyl sulfoxide and acetonitrile illustrate the problem very well. The symmetry of ACN molecules allows them for the antiparallel dipolar self-association, whereas in the case of DMSO molecules, such association is practically impossible. The antiparallel dipolar coupling in liquid ACN leads directly not only to the reduction of the macroscopic polarity of the liquid ACN but also to the lowering of the activation energies for the transport processes based on the translational displacement: the charge transport (electric conductivity) and the momentum transport (viscosity).

An exceptional usefulness of dimethyl sulfoxide as the liquid of high impact in biochemistry and pharmacy, with its spectacular biomembranes permeability, is the most probably connected with an exceptional molecular organization in liquid DMSO. As a matter of fact, it means rather a lack of the self-organization in that strongly polar liquid.

AUTHOR INFORMATION

Corresponding Author
*E-mail: swiergiel@ifmpan.poznan.pl.

REFERENCES

(1) Hanthal, D. M. *Dimethyl Sulfoxide*; Wiley: New York, 1975.
(2) Jacob, S. W., Herschler, R., Eds.; *Biological Actions of Dimethyl Sulfoxide*; New York Academy of Sciences: New York, 1975.
(3) Sazonov, V. P.; Shaw, D. G. *J. Phys. Chem. Ref. Data* **2002**, *31*, 989–1131and references therein.
(4) Scaife, W. G. *J. Phys. D: Appl. Phys.* **1974**, *7*, 647–652.
(5) Funke, K.; Banhatti, R. D.; Laughman, D. M.; Badr, L. G.; Mutke, M.; Šantić, A.; Wrobel, W.; Fellberg, E. M.; Biermann, C. *Z. Phys. Chem.* **2010**, *224*, 1891–1950.
(6) Park, J. K.; Ryu, J. C.; Kim, W. K.; Kang, K. H. *J. Phys. Chem. B* **2009**, *113*, 12271–12276.
(7) Mata, R. A.; Costa Cabral, B. J. *J. Mol. Struct. (Theochem)* **2004**, *673*, 155–164.
(8) Fries, P. H.; Kunz, W.; Calmettes, P.; Turq, P. *J. Mol. Struct. (Theochem)* **1995**, *330*, 287–300.
(9) Lei, Y.; Li, H.; Han, S. *Chem. Phys. Lett.* **2003**, *380*, 542–548.
(10) Safford, G. J.; Schaffer, P. C.; Leung, P. S.; Doebbler, G. F.; Brady, G. W.; Lyden, E. F. X. *J. Chem. Phys.* **1969**, *50*, 2140–2159.
(11) Gordalla, B. C.; Zeidler, M. D. *Mol. Phys.* **1991**, *74*, 975–984.
(12) Tokuhiro, T.; Menafra, L.; Szmant, H. H. *J. Chem. Phys.* **1974**, *61*, 2275–2282.
(13) Kaatze, U.; Pottel, R.; Schaefer, M. *J. Phys. Chem.* **1989**, *93*, 5623–5627.
(14) Mancera, R. L.; Chalaris, M.; Refson, K.; Samios, J. *Phys. Chem. Chem. Phys.* **2004**, *6*, 94–102.
(15) Lei, Y.; Li, H.; Han, S. *Chem. Phys. Lett.* **2003**, *380*, 542–548.
(16) Smondyrev, A. M.; Berkowitz, M. L. *Biophys. J.* **1999**, *76*, 2472–2478.
(17) Danilov, V. I.; Slyusarchuk, O. N.; Poltev, V. I.; Alderfer, J. L. *J. Biomol. Struct. Dyn.* **1997**, *15*, 347–355.
(18) Vechi, S, M.; Skaf, M. S. *J. Braz. Chem. Soc.* **2002**, *13*, 583–591.
(19) Debye, P. *Polar Molecules*; Chemical Catalog Co.: New York, 1929.
(20) Barsoukov, E.; Macdonald, J. R. *Impedance Spectroscopy: Theory Experiment & Applications*, 2nd ed.; John Wiley & Sons: London, 2005.
(21) Świergiel, J.; Jadżyn, J. *J. Phys. Chem. B* **2009**, *113*, 14225–14228.
(22) Świergiel, J.; Jadżyn, J. *Phys. Chem. Chem. Phys.* **2011**, *13*, 3911–3916.
(23) Stickel, F.; Fischer, E. W.; Richter, R. *J. Chem. Phys.* **1996**, *104*, 2043–2055.

(24) Einstein, A. *Investigations on the Theory of the Brownian Motion*; Dover: New York, 1956.
(25) Chalaris, M; Marinakis, S.; Dellis, D. *Fluid Phase Equilib.* **2008**, *267*, 47–60and references therein.
(26) Grande, M. C.; Garcia, M.; Marschoff, C. M. *J. Chem. Eng. Data* **2009**, *54*, 652–658.
(27) Hickey, K.; Waghorne, W. E. *J. Chem. Eng. Data* **2001**, *46*, 851–857.
(28) Moumouzlas, G.; Panopoulos, D. K.; Ritzoulls, G. *J. Chem. Eng. Data* **1991**, *36*, 20–23.
(29) Paez, S.; Confreras, M. *J. Chem. Eng. Data* **1989**, *34*, 455–459.
(30) Chaudhari, A.; Chaudhari, H. C.; Mehrotra, S. C. *Bull. Korean Chem. Soc.* **2004**, *25*, 1403–1407.
(31) Barthel, J.; Kleebauer, M.; Buchner, R. *J. Sol. Chem.* **1995**, *24*, 1–17.
(32) Casteel, J. F.; Sears, P. G. *J. Chem. Eng. Data* **1974**, *19*, 196–200.
(33) Gregory, A. P.; R. Clarke, R. N. *Meas. Sci. Technol.* **2005**, *16*, 1506–1516.
(34) Chimenko, M. T.; Grizenko, N. N.; Aleksandrov, V. V. *Zh. Fiz. Khim.* **1975**, *49*, 2400.
(35) Khirade, P. W.; Chaudhari, A.; Shinde, J. B.; Helambe, S. N.; Mehrotra, S. C. *J. Chem. Eng. Data* **1999**, *44*, 879–881.
(36) Usacheva, T. M.; Lifanova, N. V.; Zhuravlev, V. I.; Novozhilov, A. A.; Matveev, V. K. *Zh. Fiz. Khim.* **2000**, *74*, 1962.
(37) Kinart, C. M.; Kinart, W. J.; Ćwiklińska, A.; Chęcińska, D.; Dzikowski, T. *Phys. Chem. Liq.* **2003**, *41*, 197–210.
(38) Glasel, J. A. *J. Am. Chem. Soc.* **1970**, *92*, 372–375.
(39) Steiner, P. A.; Gordy, W. *J. Mol. Spectrosc.* **1966**, *21*, 291–301.
(40) Sengwa, R. J.; Sankhla, S.; Khatri, V. *J. Mol. Liq.* **2010**, *151*, 17–22.
(41) Bakshi, M. S.; Singh, J.; Kaur, H.; Ahmad, S. T.; Kaur, G. *J. Chem. Eng. Data* **1996**, *41*, 1459–1461.
(42) Prestbo, E. W.; McHale, J. L. *J. Chem. Eng. Data* **1984**, *29*, 387–389.
(43) Ritzoulis, G. *Can. J. Chem.* **1989**, *67*, 1105–1108.
(44) Amey, R. L. *J. Phys. Chem.* **1968**, *72*, 3358–3359.
(45) Hunger, J.; Buchner, R.; Kandil, M. E.; May, E. F.; Marsh, K. N. *J. Chem. Eng. Data* **2010**, *55*, 2055–2065.
(46) Jellema, R.; Bulthuis, J.; van der Zwan, G. *J. Mol. Liq.* **1997**, *73*−*74*, 179–193.
(47) Srinivasan, K. R.; Kay, R. L. *J. Solution Chem.* **1977**, *6*, 357–367.