Polish J. Chem., **78**, 1765–1775 (2004)

Molecular Interactions in Binary Mixture of Nitrobenzene/Decahydronaphthalene Studied by Dielectric Methods*

by M. Dutkiewicz[1] and E. Dutkiewicz[2]

[1]*Faculty of Physics, A. Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland*
[2]*Faculty of Chemistry, A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland*
E-mail: edutkiew@amu.edu.pl

(Received March 9th, 2004; revised manuscript April 27th, 2004)

Dielectric methods: relative permittivity (ε) measurements and the nonlinear dielectric effect (NDE) have been applied to study molecular interactions in a system of nitrobenzene/decahydronaphthalene. The electric permittivity (ε), density (d) and *NDE* parameter ($\Delta\varepsilon/E^2$) have been determined as a function of temperature (T) and concentration (x – mole fraction). The results obtained indicate the ”precritical behaviour” of the system under investigation for a given temperature and composition. A pronounced maximum of the *NDE* parameter for ≅ 0.4 mole fraction of nitrobenzene at lower temperatures has been observed.

Key words: nitrobenzene, decahydronaphthalene, molecular interactions, non-linear dielectric effect, permittivity

Many physical and chemical processes are carried out in solvent or in solvent mixtures (mixed solvent) and their mechanisms and rate constants strongly depend on the choice of solvent. Solvent effect is strictly connected with the term “solvent polarity”, which, although very common, has not been precisely defined yet. There have been several attempts at quantitative determination of the polarity of solvent in terms of its physical properties, such as dipole moment, permittivity, refractive index, free volume, viscosity, solubility and others (for review see [1,2]).

Various empirical parameters have also been proposed, based on the behaviour of a particular system towards a change of solvent. Many approaches have been suggested to describe the solvent effects by several parameters which take into account different sources of these effects [3, for review]. Various multiparameters equations have been introduced [3–9] in the form of a combination of existing solvent parameters, with at least four factors accounting for dipolarity, polarizability, proton donor ability and proton acceptor ability of solvent molecules. Solvatochromic parameters [8] account for dipolarity and polarizability Gutmann donor numbers, Mayer acceptor numbers [10,11] and Kamlet-Taft acidity and basicity parameters [3,8,11] account for proton donor and proton acceptor abilities. Spectroscopic parameters Z of Kosower and $E_T(30)$ of Dimroth and Reichardt [1], account for solvent dipolarity/solvent proton donor ability.

---

* Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

There was also an attempt [12] to describe solvent polarity through dielectric parameter β (proportional to μ^2/V, where μ is the electric dipole moment and V the molar volume).

Empirical solvent polarity parameters as well as statistical methods (chemometrics) [1,13] describe the solvent polarity and solvent effects as results of many kinds of interaction between the molecules.

In order to learn more about molecular interactions in a mixed solvent we studied in this work a binary mixture of nitrobenzene/decahydronaphthalene by the nonlinear dielectric effect (NDE). This method [14,15] has been used for many years, as a sensitive method in studies of molecular effects in liquids (including liquid crystals [16]) and has provided valuable information about inter- and intramolecular interactions resulting in hydrogen bonding [17,18], charge transfer [17], dipolar association [19–21] and conformational equilibria [14,17,22–24] in liquids.

The NDE refers to a nonlinear dependence of the electric polarization P on the electric field strength E [25]:

$$\partial P/\partial E = \varepsilon_0(\varepsilon - 1) \tag{1}$$

In practice, NDE studies involve measurements of changes in the permittivity $\Delta\varepsilon$ caused by a strong electric field E:

$$\Delta\varepsilon = \varepsilon_{\mathrm{E}} - \varepsilon \tag{2}$$

A measure of the NDE is the parameter $\Delta\varepsilon/E^2$. For molecular liquids $\Delta\varepsilon$ is a linear function of E^2.

A correlation between the parameter $\Delta\varepsilon/E^2$ and the Dimroth-Reichardt spectroscopic polarity parameter E_T^N [1] has been shown [26], which indicates that the parameter $\Delta\varepsilon/E^2$ may also be used as a solvent polarity parameter.

EXPERIMENTAL

Materials: Nitrobenzene was purified by distillation under reduced pressure and dried over Al_2O_3 and decahydronaphthalene were also distilled.

Methods: The NDE measurements were carried out with the automatically recording pulse device described in ref. [15]. The values of $\Delta\varepsilon/E^2$ were determined at a frequency of about 2 MHz with an accuracy of ± 5%. The permittivity ε was measured to an accuracy of ± 0.1% by the beat technique. The density d was measured pycnometrically to an accuracy of ± 0.01%, the refractive index n (for the sodium D line) to an accuracy of ± 0.01% using a Pulfrich refractometer. The concentration of nitrobenzene in decahydronaphthalene is expressed as a mole fraction x. The temperature T expressed in K was measured to an accuracy of ± 0.1 K.

RESULTS AND DISCUSSION

Tables 1, 2 and 3 present results of the measurements of density *d*, refractive index *n* and relative permittivity ε for solutions of nitrobenzene in decahydronaphthalene for different concentrations *x* and temperatures *T*. The dependencies $d = f(T)_x$, $n = f(T)_x$ and $\varepsilon = f(T)_x$ are linear and so they are not shown as plots. However, the dependencies of $d = f(x)_T$, $n = f(x)_T$ and $\varepsilon = f(x)_T$ are nonlinear. Examples of these plots are shown in Figs. 1, 2 and 3. The nonlinearity, clearly seen in Fig. 4, showing the dependence of $\Delta\varepsilon/E^2 = f(x)_T$ is much more pronounced and may indicate some molecular interaction, taking place in the solution. As mentioned above, the nonlinear dielectric effect is very sensitive to dipolar interactions, much more than the permittivity alone.

Table 1. Density *d* [kg m^{-3}] of nitrobenzene/decahydronaphthalene system as a function of nitrobenzene concentration *x* [mole fraction] and temperature *T* [K].

x	*T*	*d*	*x*	*T*	*d*
0.0000	274.5	898.5	0.5018	273.2	1023.8
	282.5	892.0		283.4	1014.9
	292.9	884.2		291.0	1008.4
	305.1	874.9		298.0	1002.1
				303.4	997.3
0.1034	273.7	919.6	0.5952	274.1	1053.0
	281.9	913.4		280.6	1047.1
	292.3	905.4		289.7	1038.6
	300.2	899.1		296.8	1032.7
	305.9	894.7		303.5	1026.9
0.2200	274.0	946.5	0.7534	273.8	1111.1
	281.7	939.8		281.8	1104.3
	290.9	932.6		291.3	1095.1
	297.7	927.2		298.0	1088.7
	304.0	923.3		304.6	1082.4
0.2985	273.9	966.4			
	281.7	959.7			
	293.6	949.9			
	304.0	941.3			

In order to explain the dependence of $\Delta\varepsilon/E^2$ on *x*, shown in Fig. 4, we should keep in mind that the net values of the NDE parameter $\Delta\varepsilon/E^2$ depend on the competition between two main effects [15]:

1) the orientational Debye-Langevin effect $(\Delta\varepsilon/E^2)_{or}$ resulting from the interaction of the electric field with the total dipole moment, and
2) the effect of the electric field on molecular equilibria (*e.g.* clusters, associates, complexes, conformational equilibria); an application of an electric field causes a shift of equilibrium towards the more polar products of the process which in turn results in increase of the permittivity of the medium; this effect is called "*chemical effect*" $(\Delta\varepsilon/E^2)_{ch}$.

Table 2. Refractive index n of nitrobenzene/decahydronaphthalene system as a function of nitrobenzene concentration x [mole fraction] and temperature T [K].

x	T	n	x	T	n
0.0000	274.0	1.48296	0.5018	273.3	1.51249
	282.3	1.47953		282.9	1.50910
	292.9	1.47529		291.2	1.50564
	305.0	1.47019		298.0	1.50257
				303.4	1.50001
0.1034	273.6	1.48744	0.5952	274.0	1.51945
	281.5	1.48417		280.3	1.51707
	292.3	1.47982		289.8	1.51317
	300.3	1.47662		296.9	1.51005
	305.8	1.47415		303.4	1.50715
0.2200	274.0	1.49336	0.7534	273.9	1.53381
	281.5	1.49008		281.6	1.53083
	291.2	1.48619		291.3	1.52659
	297.7	1.48328		297.9	1.52356
	304.0	1.48047		304.6	1.52039
0.2985	274.2	1.49853			
	281.5	1.49544			
	293.8	1.49034			
	304.0	1.48510			

Table 3. Relative permittivity ε of nitrobenzene/decahydronaphthalene system as a function of nitrobenzene concentration x [mole fraction] and temperature T [K].

x	T	ε	x	T	ε
0.0000	272.8	2.1740	0.5018	273.1	13.5550
	281.1	2.1620		277.7	13.2860
	295.5	2.1440		283.6	12.9210
	307.1	2.1310		290.3	12.5450
				298.9	12.0730
				306.0	11.6860
0.1034	273.3	3.7120	0.5952	271.6	17.2502
	279.6	3.6600		281.6	16.4769
	289.1	3.5830		287.1	15.9610
	297.6	3.5150		294.2	15.4350
	307.1	3.4330		305.3	14.6616
0.2200	273.7	5.8593	0.7534	271.6	22.7390
	280.2	5.7465		279.6	21.7610
	288.1	5.5993		286.0	21.0630
	297.5	5.4372		295.4	20.0320
	307.1	5.2825		307.2	18.8610
0.2985	272.3	7.6487			
	287.2	7.2610			
	296.1	7.0139			
	307.7	7.7220			

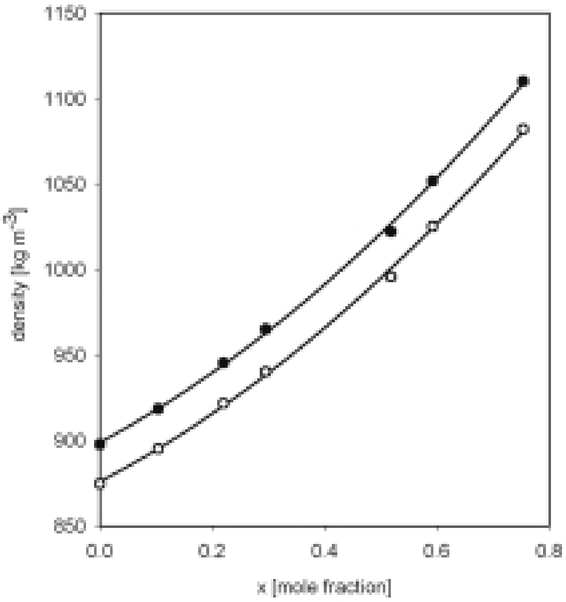

Figure 1. Density *d* vs. mole fraction *x* of nitrobenzene in decahydronaphthalene for: ● 275 K, ○ 305 K.

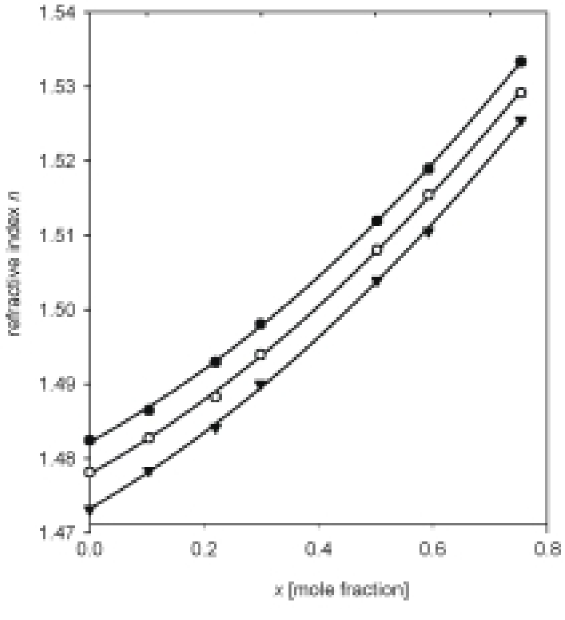

Figure 2. Refractive index *n* vs. mole fraction *x* of nitrobenzene in decahydronaphthalene for: ● 275 K, ○ 285 K, ▼ 295 K.

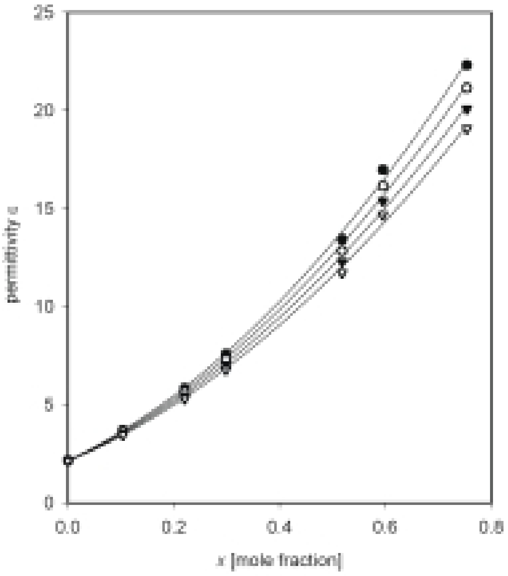

Figure 3. Permittivity ε vs. mole fraction x of nitrobenzene in decahydronaphthalene for: ● 275 K, ○ 285 K, ▼ 295 K, ▽ 305 K.

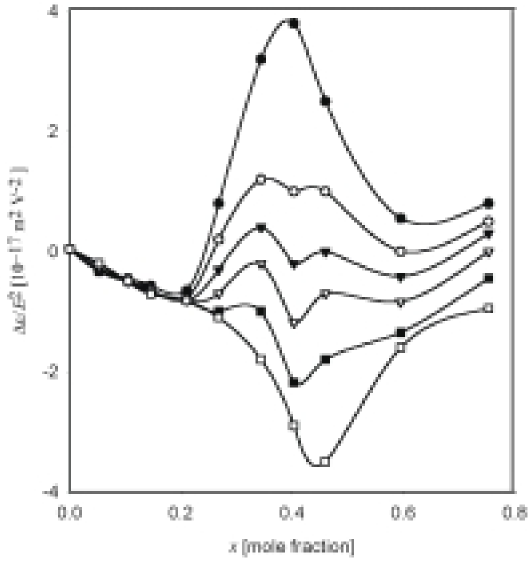

Figure 4. NDE parameter $\Delta\varepsilon/E^2$ vs. mole fraction x of nitrobenzene in decahydronaphthalene for: ● 268 K, ○ 273 K, ▼ 278 K, ▽ 283 K, ■ 293 K, □ 303 K.

The orientational effect gives rise to a decrease in the permittivity (negative NDE), while the "chemical effect" gives rise to an increase in the permittivity (positive NDE). The net result $\Delta\varepsilon/E^2$ is the sum of both effects

$$\Delta\varepsilon/E^2 = (\Delta\varepsilon/E^2)_{or} + (\Delta\varepsilon/E^2)_{ch} \tag{3}$$

and the sign of $\Delta\varepsilon/E^2$ is determined by the dominant factor.

It is clearly seen from Fig. 4 that the dependence of $\Delta\varepsilon/E^2$ on x is rather complicated; for higher temperatures, a minimum of $\Delta\varepsilon/E^2$ is observed for concentration of about 0.4 mole fraction of nitrobenzene in decahydronaphthalene and a pronounced maximum of $\Delta\varepsilon/E^2$ is observed for lower temperatures. Looking at the dependence shown in Fig. 4 we may conclude, that the orientational Debye-Langevin effect predominates for lower concentration of nitrobenzene, but for higher concentrations a decreasing temperature causes an increase in the so-called "chemical effect" contribution to the total NDE due to dipolar interaction of nitrobenzene molecules.

For higher concentration of nitrobenzene and lower temperature the dipole ⇔ dipole interaction become stronger which results in stronger statistical fluctuations in the solute concentrations. These fluctuations are significantly strong particulary in critical solutions in the vicinity of critical dissolution point. At that point, the solution has a microheterogeneous structure due to dipolar molecular clusters formation. The dipolar clusters formation can be described by reversible reaction nNb ⇔ $(Nb)_n$, (where Nb stands for a nitrobenzene molecule). Increasing the polar component concentration shifts the equlibrium toward the dipolar clusters formation and, in addition, this process is favoured by the electric field. That accounts for a very strong increase in the permittivity in the vicinity of the critical dissolution point; the NDE parameter increases and becomes positive ($\Delta\varepsilon/E^2 > 0$). In the system studied, the concentration $x \cong 0.4$ mole fraction of nitrobenzene may be assumed as the critical concentration of mixing, although in the temperature range of our investigation we have not observed macroscopically any critical phenomena like opalescence or phase separation. The opalescence has been observed in temperatures close to 263 K [27].

Similar behaviour has been observed [28] for the system nitrobenzene/cyclohexane, where for the concentration of about 0.3 mole fraction a pronounced maximum of $\Delta\varepsilon/E^2$ occurs, which increases with decreasing temperature. Generally, such type of a dependence of $\Delta\varepsilon/E^2$ on x is typical for critical solutions [29–34 and cited therein], for which the critical miscibility temperature and concentration have been found.

Recently we have also found [35] maxima in the plots of $\Delta\varepsilon/E^2$ *vs.* x for the systems acetone/cyclohexane and acetone/decahydronaphthalene in the temperature range, over which macroscopic critical phenomena were not observed, similarly as it has been found in dimethoxybenzenes [32 and cited therein]. This points to the presence of microscopic inhomogeneities due to fluctuations in density already at temperatures considerably higher than the critical one, while the solution still maintains macroscopic homogeneity in the entire range of concentrations.

For a more detailed analysis of the obtained results we have converted the direct experimental data (electric permittivity ε, refractive index n, density d and nonlinear dielectric effect parameter $\Delta\varepsilon/E^2$) into more convenient molar quantities: the mean square of the dipole moment (the molar dipolar polarizability, $<\mu^2>$) and the mean fourth power of the dipole moment (the nonlinear molar polarizability, $<\mu^4>$), which are defined in the following way [21]:

$$<\mu^2> \equiv \frac{3kT}{r}\frac{\partial<\mu>_E}{\partial F} \tag{4}$$

$$<\mu^4> \equiv -\frac{15k^3T^3}{r}\frac{\partial}{\partial(F^2)}\left(\frac{\partial<\mu>_E}{\partial F}\right) = -k^2T^2\frac{\partial<\mu^2>}{\partial(F^2)} \tag{5}$$

Where: $<\mu>_\mathrm{E}$, usually expressed with the Langevin function, denotes the average value of the dipole moment projected onto the external electric field E direction. F denotes the internal field component acting on a molecule along the field E direction and $r=\mu/\mu_0$ is the ratio of the effective dipole moment in a given medium to its value in the gas phase. T and k denote the absolute temperature and the Boltzmann constant, respectively.

Applying the Onsager local field model, the two above molar quantities $<\mu^2>$ and $<\mu^4>$ can be expressed by the data obtained directly from experiment [15]:

$$<\mu^2> = \left(\frac{9kT\varepsilon_oV}{N_A}\right)\left[\frac{(\varepsilon-n^2)(2\varepsilon+n^2)}{\varepsilon(n^2+2)^2}\right] \tag{6}$$

and

$$<\mu^4> = -\left(\frac{45k^3T^3\varepsilon_oV}{N_A}\right)\left[\frac{(2\varepsilon^2+n^4)(2\varepsilon+n^2)^2}{\varepsilon^4(n^2+2)^4}\right]\frac{\Delta\varepsilon}{E^2} \tag{7}$$

where ε_o is the permittivity of vacuum, V is the molar volume and N_A is Avogadro's number. The formulae for the exact calculation of $<\mu^2>$ and $<\mu^4>$ in solution are given in [21].

It should be emphasized that these two quantities are obtained independently and provide two separate sets of information on the molecular interactions taking place in the system studied; $<\mu^2>$ *vs.* x provides the information on the influence of the medium on the molecular equilibria (*e.g.* monomer ⇔ n-mer) under field free conditions, whereas $<\mu^4>$ *vs.* x gives the information on the electric field effect on those equilibria [15].

Figures 5 and 6 show $<\mu^2>$ and $<\mu^4>$ as functions of the concentration x of nitrobenzene in decahydronaphthalene. The concentration and temperature dependencies of $<\mu^2>$ and $<\mu^4>$ reveal considerable differences. The parameter $<\mu^4>$ is much more sensitive to molecular interactions than $<\mu^2>$, and its dependence on x and T illustrates the effect of strong electric field on dipolar interactions in the fluctuating clusters

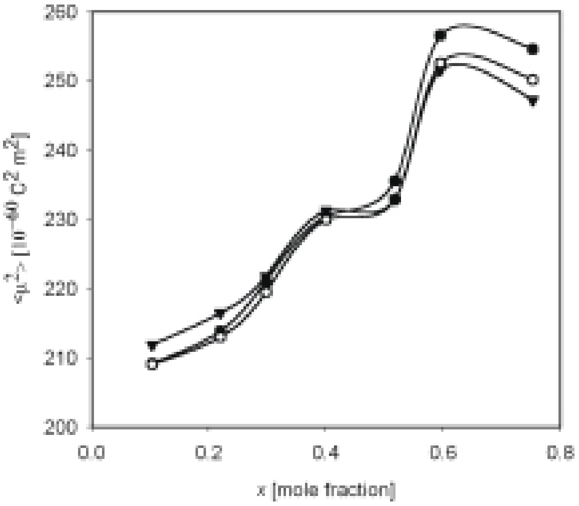

Figure 5. Dependence of molar dipolar polarizability $< \mu^2 >$ of nitrobenzene on its concentration x in decahydronaphthalene for three temperatures: ● 268 K, ○ 278 K, ▼ 303 K.

Figure 5. Dependence of molar dipolar polarizability $< \mu^2 >$ of nitrobenzene on its concentration x in decahydronaphthalene for three temperatures: ● 268 K, ○ 278 K, ▼ 303 K.

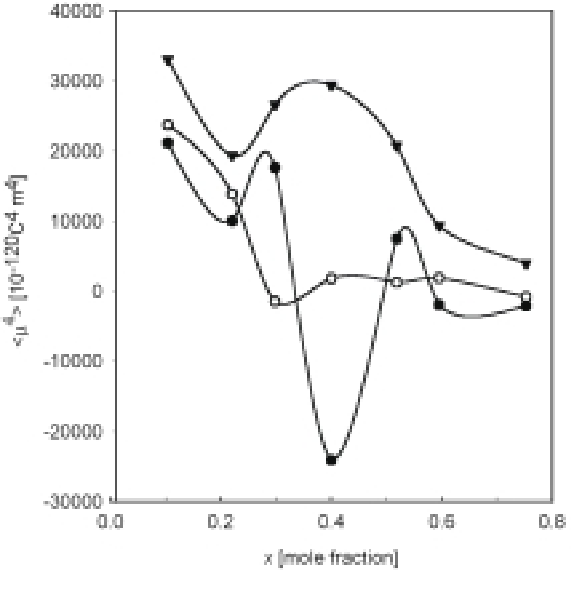

Figure 6. Dependence of nonlinear molar polarizability $< \mu^4 >$ of nitrobenzene on its concentration x in decahydronaphthalene for three temperatures: ● 268 K, ○ 278 K, ▼ 303 K.

of the polar component (nitrobenzene). Interestingly, a small maximum in $<\mu^2>$ at a concentration close to 0.4 mole fraction of nitrobenzene (Fig. 5) coincides with the minimum (for lower temperatures) and maximum (for higher temperatures) of $<\mu^4>$, shown in Fig. 6. These distinct maximum and minimum indicate that the system of nitrobenzene/decahydronaphthalene can show limited miscibility and for a certain temperature and concentrations of the components can separate into two phases, similarly as it has been observed for other systems [28–35]. This supposition is confirmed by the opalescence appearing at about 263 K, for the 0.42 mole fraction of nitrobenzene in decahydronaphthalene [27].

A comparison of the critical concentrations of the systems nitrobenzene/cyclohexane (x ~0.3) [28] and nitrobenzene/decahydronaphthalene (x ~0.4) [this work], implies that the difference can be to a significant degree explained by the different molar volumes of the two nondipolar solvents ($V_{cycl} = 108.2$ cm^{3}mol^{-1}, $V_{dec} = 156.2$ cm^{3}mol^{-1}). Only molar volume is significantly different for the molecules of decahydronaphthalene and cyclohexane as their other parameters (*d, n,* ε) have similar values (see Tables 1,2 and 3).

In conclusion, it should be emphasized that in studies of physical and chemical processes in mixed solvents one should keep in mind that depending on the composition and temperature, the mixed solvent may undergo dramatic changes in the structural and physico-chemical properties on the molecular scale (undetectable on the macroscopic scale) that can have significant effect on the results of the investigation and their interpretation.

REFERENCES

1. Reichardt C., Solvents and Solvent Effects in Organic Chemistry, 3rd, Updated and Enlarged Edition., Wiley 2003.
2. Katritzky A.R., Fara D.C., Yang H., Tamm K., Tamm T. and Karelson M., *Chem. Rev.*, **104**, 175 (2004).
3. Abboud J.L.M., Kamlet M.J. and Taft R.W., *Progr. Phys. Org. Chem.,* **13**, 485 (1981).
4. Koppel I.A. and Palm V.A., in Advances in Linear Free Energy Relationship, Chapman N.B. and Shorter J., eds., Plenum, London, 1972.
5. Taft R.W., Abboud J.L.M., Kamlet M.J. and Abraham M.H*., J. Solution Chem.*, **14**, 153 (1985).
6. Laurence C., Nicolet P., Lucon M., Dalati T. and Reichardt C., *J. Chem. Soc. Perkin Trans.*, **2,** 873 (1989).
7. Krygowski T.M. and Fawcett W.R**.,** *J. Am. Chem. Soc.***,** **97**, 2143 (1975).
8. Abraham M.H., Doherty R.M., Kamlet M.J., Harris J.M. and Taft R.W.,*J. Chem. Soc. Perkin Trans. 2,* 913 and 1097 (1987).
9. Krygowski T.M., Wrona P.K., Zielkowska U. and Reichardt C., *Tetrahedron,* **41,** 4519 (1985).
10. Gutmann V., The Donor-Acceptor Approach to Molecular Interactions (Plenum, New York and London, 1978): Mayer U., Gutmann V., Gerger W., *Monaths. Chem*., **106**, 1235 (1975); **108**, 489 (1977).
11. Marcus Y., *J. Solution Chem*., **13**, 599 (1984); **20**, 929 (1991).
12. Dutkiewicz M., *J. Chem. Soc. Faraday Trans.,* **86**, 2237 (1990).
13. Zalewski R.J., Kokocińska H. and Reichardt C.,*J. Phys. Org. Chem.*, **2**, 232 (1989).
14. Chełkowski A., Dielectric Physics, Ed. PWN – Polish Scientific Publishers,, Warszawa; Elsevier Scientific Publishing Company, Amsterdam – Oxford – New York, 1980.
15. Małecki J., *Electrochim. Acta*, **33**, 1235 (1988).

16. Rzoska S.J. and Zioło J., *Liq. Cryst.,* **17**, 629 (1994).
17. Małecki J., in Molecular Interactions, Eds. H. Ratajczak and W.J. Orville-Thomas, Vol. 3, Wiley, New York 1982.
18. Małecki J., Nowak J., Liszi J. and Varga-Puchony Z., *Polish J. Chem.,* **65**, 1773 (1991).
19. Piekara A., *Acta Phys. Polon.,* **10**, 37 and 107 (1950).
20. Dutkiewicz M.,*J. Chem. Soc. Faraday Trans. 2*, **77**, 1301 (1981); *J. Mol. Liquids*, **28**, 147 (1984); *Chem. Phys. Lett.,* **121**, 73 (1985); *Acta Phys. Polon.*, **A82**, 443 (1992).
21. Małecki J. and Dutkiewicz M., *J. Solution Chem.,* **28**, 101 (1999).
22. Dutkiewicz M. and Koput J., *J. Mol. Struct.,* **354**, 153 (1995).
23. Dutkiewicz M., *J. Mol. Struct*., **382**, 147 (1996).
24. Dutkiewicz M. and Małecki J., *J. Mol. Struct*., **416**, 105 (1997).
25. Bottcher C.J.F. and Bordewijk P., Theory of Electric Polarisation, Elsevier, Amsterdam 1978.
26. Dutkiewicz M. and Dutkiewicz E., *J. Solution Chem.,* **22**, 787 (1993).
27. Dutkiewicz M. and Dega-Dałkowska A. (to be published).
28. Dega-Dałkowska A., Dutkiewicz M. and Surma D., *Acta Phys. Polon.,* **A52**, 719 (1977).
29. Pyżuk W. and Zboiński K., *Chem. Phys. Lett.,* **52**, 577 (1977).
30. Małecki J. and Zioło J., *Chem. Phys.,* **35**, 187 (1978).
31. Rzoska, S.J. and Zioło J., *Phys. Rev. E.,* **47**, 1445 (1993).
32. Śliwińska-Bartkowiak M. and Radojewska L., *Ber. Bunsenges. Phys. Chem*., **99**, 1187 (1995).
33. Rzoska S.J., Drozd-Rzoska A., Górny A. and Zioło J., *Phys. Rev. E*., **52**, 6325 (1995).
34. Orzechowski K., *Chem. Phys.,* **204**, 275 (1999).
35. Dutkiewicz M. and Dutkiewicz E., Materiały zjazdowe, XLVI Zjazd PTCh i SITPCh, Lublin 2003 (in Polish).