1904 *J. Chem. Eng. Data* **2010,** *55,* 1904–1907

Dielectric Study of the Solvent Effect on Molecular Interaction in Nitrobenzene, Pentan-3-one, and Octan-1-ol[†]

Maria Dutkiewicz,[‡] Edward Dutkiewicz,[§] Magdalena Kosmowska,[||] and Kazimierz Orzechowski*[,||]

Faculty of Physics, A. Mickiewicz University, Umultowska 85, 61-614 Poznań, Poland, Faculty of Chemistry,
A. Mickiewicz University, Grunwaldzka 6, 60-780 Poznań, Poland, and Faculty of Chemistry, University of Wroclaw,
Joliot-Curie 14, 50-383 Wrocław, Poland

The nonlinear dielectric effect (NDE) increment has been determined experimentally for binary mixtures of polar and nonpolar components with nitrobenzene, pentan-3-one, and octan-1-ol as dipolar components and benzene, cyclohexane, and cyclohexylbenzene as nonpolar ones. The data provide information about solute−solute and solute−solvent interactions.

Introduction

The nonlinear dielectric effect (NDE)[1,2] method has been applied for many years in studies of molecular effects in liquids, as it provides valuable information about inter- and intramolecular interactions leading to hydrogen bonding,[3,4] charge transfer,[3] dipolar association,[5–9] and conformational equilibria.[2,3,10–13] The NDE method is also very useful in the investigation of critical and precritical phenomena in liquids,[1,2,14–16] liquid crystals,[2,17] electrolyte solutions,[18,19] and solids.[20]

The NDE phenomenon refers to a nonlinear dependence of the electric polarization P on the electric field strength E:[2,21]

$$\partial P/\partial E = \varepsilon_o(\varepsilon - 1) \qquad (1)$$

where ε_o is vacuum permittivity and ε relative permittivity. The NDE studies involve measurements of changes in the permittivity $\Delta\varepsilon$ caused by a strong electric field E:

$$\Delta\varepsilon = \varepsilon_E - \varepsilon_{E\to 0} \qquad (2)$$

where ε_E and $\varepsilon_{E\to 0}$ are the permittivities obtained at strong and at weak electric field strengths, respectively. The magnitude of NDE is expressed in terms of the increment $\Delta\varepsilon/E^2$. For molecular liquids $\Delta\varepsilon$ is a linear function of E^2. The ratio $\Delta\varepsilon/E^2$ can take negative or positive values. The negative NDE is associated with the so-called orientational Debye−Langevine effect resulting from the interaction of the electric field with the total electric dipole moment.[21] The positive NDE results from the influence of a strong external electric field which perturbs the equilibrium between the molecular structures favoring those with larger dipole moments. Also other molecular mechanisms as fluctuations related to density, polarizability, or precritical phenomena bring positive contributions to NDE.[2] The net result of $\Delta\varepsilon/E^2$ is a sum of many effects.

The aim of the present study is to show the effect of the structure and molecular properties of nonpolar solvents on the molecular interaction in nitrobenzene (strongly dipolar), pentan-3-one (weakly dipolar), and octan-1-ol (hydrogen bonded). The nonpolar component molecules which differ in their molecular structure and properties (double bonds, aromaticity, and others) influence significantly the dipolar interaction and hence the measured $\Delta\varepsilon/E^2$ increment. The nonpolar components used were benzene, cyclohexylbenzene, and cyclohexane. It is interesting to observe a change in the solvent properties from aromatic to aliphatic.

Experimental Section

Chemicals. Nitrobenzene with a mass fraction purity ≥ 0.99 was twice recrystallized and dried over molecular sieves type 4A. The pentan-3-one supplied by Fluka with a mass fraction purity of ≥ 0.99, octan-1-ol obtained from Riedel de Haën with a stated mass fraction purity of 0.995, the benzene with a mass fraction purity of 0.997, cyclohexane with a mass fraction purity of 0.995, and cyclohexylbenzene obtained from Fluka with a mass fraction purity of ≥ 0.97 were all also dried over molecular sieves.

Measurements. Changes in the permittivity $\Delta\varepsilon$ were measured in the direct response system. The duration of the strong field pulse was 0.8 ms, and the measurements were performed at 2000 V. The measurements were made in a capacitor with the plane-parallel plates of the diameter of 13 mm distanced at 0.25 mm. Details of the experimental setup have been described previously.[18] The measurements were made at $T = 293$ K.

The measurements were made at first for one of the components and then subsequently for the solutions of target concentrations obtained by adding the second component through a buret. After mixing, the solution of a desired concentration was infused into the capacitor by a syringe. Mixtures were prepared at $T = (293 \pm 1)$ K.

NDE increment $\Delta\varepsilon/E^2$ was determined for the systems studied as a function of concentration of the polar compound expressed in mole fraction. Density ρ of pure components, required for calculation of mole fraction, was assumed to be equal to the literature values:[23] ρ(nitrobenzene) = 1203.7 kg·m^{-3}, ρ(pentan-3-one) = 813.8 kg·m^{-3}, ρ(octan-1-ol) = 827.0 kg·m^{-3}, ρ(benzene) = 876.5 kg·m^{-3}, ρ(cyclohexane) = 778.5 kg·m^{-3}, and ρ(cyclohexylbenzene) = 950.2 kg·m^{-3}. For the sake of

---

[†] Part of the "Josef M. G. Barthel Festschrift".

* Corresponding author. E-mail: orzech@wchuwr.pl. Fax: +48(71)328 23 48.

[‡] A. Mickiewicz University, Umultowska. E-mail: maridu@amu.edu.pl.

[§] A. Mickiewicz University, Grunwaldzka. E-mail: edutkiew@amu.edu.pl.

[||] University of Wroclaw. E-mail: kosmo@eto.wchuwr.pl (M.K.).

10.1021/je900908u © 2010 American Chemical Society
Published on Web 04/02/2010

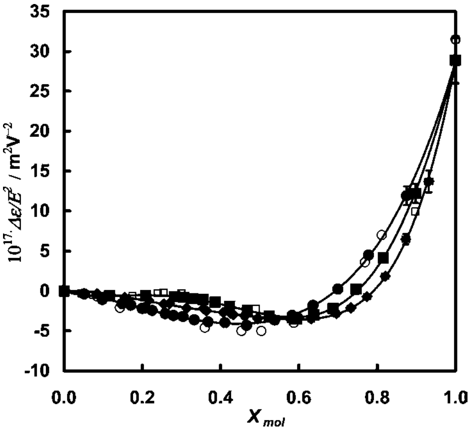

Figure 1. Measured nonlinear dielectric increment as a function of the mole fraction of nitrobenzene. ●, (nitrobenzene + benzene); ■, (nitrobenzene + cyclohexane); ◆, (nitrobenzene + cyclohexylbenzene); ○, (nitrobenzene + benzene) from ref 22; and □, nitrobenzene + cyclohexane from ref 22.

Table 1. Comparison of $(\Delta\varepsilon/E^2)_{\rm id}$ Calculated According to Equation 3 with the Experimental Values $(\Delta\varepsilon/E^2)_{\rm expt}$ Obtained for Nitrobenzene, Pantan-3-one and Octan-1-ol at 293 K[a]

compound	ε	n	ρ kg·m^{-3}	μ_s C·m	$(\Delta\varepsilon/E^2)_{\rm id}$ m^2·V^{-2}	$(\Delta\varepsilon/E^2)_{\rm expt}$ m^2·V^{-2}
nitrobenzene	35.95	1.5524	1203.2	$13.4\cdot10^{-30}$	$-31\cdot10^{-17}$	$29\cdot10^{-17}$
pentan-3-one	17.0	1.3924	813.8	$9.07\cdot10^{-30}$	$-3.9\cdot10^{-17}$	$-15\cdot10^{-17}$
octan-1-ol	10.3	1.4295	827.0	$5.74\cdot10^{-30}$	$-0.42\cdot10^{-17}$	$-5.5\cdot10^{-17}$

[a] Permittivity (ε), refractive index (n), density (ρ), and dipole moment values of isolated molecules (μ_s) are taken from the literature.[23]

comparison the NDE measurements were also determined for (nitrobenzene + benzene) and (nitrobenzene + cyclohexane). These systems had been studied earlier,[2,22] but to get a reliable comparison of the data (obtained in the same series) the measurements were repeated. Comparisons between the results obtained in this work and those reported in the literature[22] are shown in the Figure 1.

Measurement Error. The error of the NDE measurement is relatively large because of the geometry of the capacitor in which the marginal capacities bring significant contribution to the total capacity. The relative error was estimated as ± 15 %. The scatter of results on repeating the measurements was of an order of ± 10 %.

Concentrations (expressed in mole fraction) of the mixtures investigated were calculated from the mass of the first component and the volume and density of the second one. The relative error of concentration was < ± 1 %.

Results and Discussion

Figure 1 presents the effect of solvents under investigation on $\Delta\varepsilon/E^2$ of nitrobenzene. All of the curves intersect at the point corresponding to a concentration of nitrobenzene close to 0.6 mole fraction at which the arrangement of the curves changes. This point separates the two ranges of nitrobenzene concentrations below and above 0.6 mole fraction, corresponding to different characters of the curves. To understand the effect of solvent on intermolecular interactions, it is useful to calculate the NDE effect of nitrobenzene (as well as pentan-3-one and octan-1-ol) when intermolecular interactions do not exist. Table 1 presents values of $(\Delta\varepsilon/E^2)_{\rm id}$ obtained assuming that the dipole moment is equal to that of isolated molecule. In the calculations we used the Onsager local field. The $(\Delta\varepsilon/E^2)_{\rm id}$ was calculated according to equation:[2]

$$\left(\frac{\Delta\varepsilon}{E^2}\right)_{\rm id} = -\frac{[\varepsilon(n^2+2)]^4}{(2\varepsilon^2+n^4)(2\varepsilon+n^2)^2}\frac{\rho}{M}\frac{{\mu_s}^4 N_{\rm A}}{45\varepsilon_o k^3 T^3} \qquad (3)$$

where ε is permittivity, n the refractive index, ρ the density, μ_s the dipole moment of isolated molecule, N_A Avogadro's constant, M the molar mass, k the Boltzmann constant, and T temperature.

According to Table 1, the NDE increment in nitrobenzene calculated assuming that intermolecular interactions do not influence local arrangement should be negative and relatively large. However, the experimental value of the increment is positive. The large, positive value of NDE increment in nitrobenzene was explained by Piekara.[5] Nitrobenzene molecules are planar and strongly dipolar. In the absence of external electric field an antiparallel arrangement of neighboring molecules is preferred. Strong electric field favors parallel arrangement, which results in an increase in the net dipole moment and hence in positive $\Delta\varepsilon/E^2$. The nonpolar solvent disturbs the interaction of neighboring molecules, and $\Delta\varepsilon/E^2$ strongly decreases as a result of dissolving of nitrobenzene. From the point of view of the molecular structure, it can be suspected that the molecules of benzene can more easily interact with the molecules of nitrobenzene (weak charge-transfer interaction between benzene and nitrobenzene molecules has been found).[24] However, Figure 1 demonstrates that cyclohexylbenzene disturbs nitrobenzene interaction more effectively than cyclohexane or benzene. In cyclohexylbenzene the interaction of the phenyl substituent (corresponding to benzene molecules) with nitrobenzene molecules is hindered because cyclohexylbenzene occurs in solution in the form of the chair-equatorial conformer, which is energetically most favorable. Such a conformer would determine the molecular dynamics and the interaction with nitrobenzene molecules. In the solvent effect of cyclohexylbenzene on NDE of nitrobenzene a considerable contribution comes from the nonaromatic cyclohexyl fragment which dominates over that of the phenyl fragment. The weaker solvent effect of benzene we explain as a result of an ability to conserve molecular complexes existing in concentrated solutions of nitrobenzene.

At mole fractions in the range 0 to 0.6 of nitrobenzene, for mixtures containing cyclohexane, the NDE increment approaches "zero line", whereas for benzene it attains more negative values when compared to the cyclohexylbenzene and cyclohexane. This type of dependence observed for (nitrobenzene + cyclohexane) solution is related to the fact that at 0.3 mole fraction of nitrobenzene we deal with the far precritical[2] behavior, similar to that observed in (nitrobenzene + decahydronaphthalene).[25,26]

For the nitrobenzene concentrations below 0.6 mole fraction the dependence of the NDE increment in cyclohexylbenzene runs between the curves obtained for cyclohexane and benzene. It suggests a kind of competition between the effects of the phenyl fragment and the cyclohexyl fragment bonded in one molecule of cyclohexylbenzene. The cyclohexyl fragment tends to behave like cyclohexane, while the phenyl fragment tends to behave like benzene, which leads to the behavior intermediate between those of the latter two compounds. To get more detailed information on the contribution of the aromatic (phenyl-) and nonaromatic (cyclohexyl-) components, the measurements of $\Delta\varepsilon/E^2$ were made for the solutions of nitrobenzene (at a constant 0.3 mole fraction of nitrobenzene) in a mixed solvent (cyclohexane + benzene). The reason why we chose the concentration of 0.3 mole fraction was that at this point the differences in the

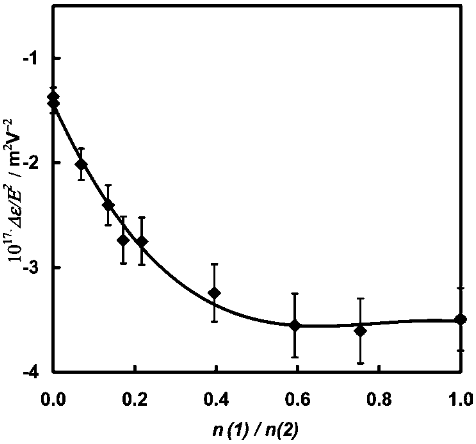

Figure 2. Nonlinear dielectric increment for (nitrobenzene + benzene + cyclohexane) as a function of the ratio of the mole number of benzene (1) to the mole number of cyclohexane (2). The nitrobenzene mole fraction is constant and equal to 0.3.

NDE increment for particular solvents are the most pronounced. The results are presented in Figure 2.

It is worth noting that the value of $\Delta\varepsilon/E^2 = -2\cdot10^{-17}$ m$^2\cdot$V^{-2} obtained for the binary mixture of 0.3 mole fraction of nitrobenzene in cyclohexylbenzene shown in Figure 1 is much larger than that obtained in the ternary mixture of 0.3 mole fraction of nitrobenzene in an equimolar mixture of benzene and cyclohexane ($\Delta\varepsilon/E^2 = -3.5\cdot10^{-17}$ m$^2\cdot$V^{-2}, shown in Figure 2). The difference between these two “semi-aromatic” solvents is remarkable and seems to indicate that the more aromatic solvent (more similar to benzene in its NDE behavior) is the equimolar mixture of benzene and cyclohexane (although a “half” of this solution is nonaromatic), while cyclohexylbenzene seems to resemble more the behavior of cyclohexane which means that it is less aromatic (although a half of its molecule is aromatic).

Our consideration concerning the influence of the molecular structure of solvents on the NDE increment could be supported by theoretical and X-ray diffraction works on the structure of cyclohexylbenzene[27,28] and on (benzene + cyclohexane).[29] Theoretical analysis (all-atom molecular dynamics simulation) concerning (cyclohexane + benzene)[29] leads to conclusions that the most relevant configuration for the benzene−benzene dimers in pure liquid and in a mixture with cyclohexane is the T-shape; for cyclohexane dimers the nonshifted sandwich structure is more stable. In the mixture of benzene−cyclohexane the nonshifted sandwich arrangements of unlike dimers are the most relevant configuration. In general, we can say that all of these structural properties of particular solvents influence clearly the NDE behavior of the polar component (nitrobenzene).

The next system under investigation, representing weak molecular interaction, was pentan-3-one with the solvents considered as shown in Figure 3. The most remarkable difference in the solvent effect on the NDE increment of pentan-3-one is seen in the range (0.6 to 1) mole fraction of pentan-3-one. The NDE increment is negative for the whole range of pentan-3-one concentration, similarly as it has been observed for propan-2-one.[30] It means that in the case of weak molecular interaction (taking place in ketones) the Debye−Langevine effect plays the dominant role. The more negative values of the NDE increment are obtained for benzene and cyclohexane solutions, while the less negative ones for cyclohexylbenzene. According to Table 1, the $\Delta\varepsilon/E^2$ value calculated for pure pentan-3-one on the assumption that the dipole moment is equal

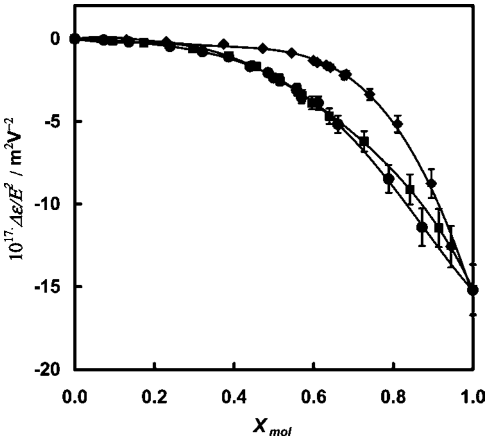

Figure 3. Nonlinear dielectric increment as a function of mole fraction of pentan-3-one. ●, (pentan-3-one + benzene); ■, (pentan-3-one + cyclohexane); and ◆, (pentan-3-one + cyclohexylbenzene).

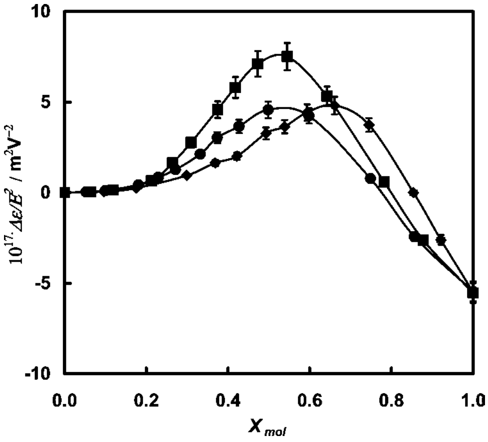

Figure 4. Nonlinear dielectric increment as a function of mole fraction of octan-1-ol. ●, (octan-1-ol + benzene); ■, (octan-1-ol + cyclohexane); and ◆, (octan-1-ol + cyclohexylbenzene).

to that in the gas phase is equal to $-3.9\cdot10^{-17}$ m$^2\cdot$V^{-2}, whereas the experimental value was found to be $-15\cdot10^{-17}$ m$^2\cdot$V^{-2}. It means that in pure pentan-3-one, and probably in concentrated solutions, a parallel configuration of neighboring molecules is preferred. Cyclohexylbenzene disturbs this rearrangement more effectively than benzene. This observation is similar to that mentioned for concentrated solutions of nitrobenzene.

Figure 4 illustrates the solvent effect on the NDE increment of octan-1-ol which is the polar component for which hydrogen bond interaction is the most important. In all solvents the NDE dependence on the concentration is typical of (*n*-alcohols + hydrocarbon), where a characteristic maximum of $\Delta\varepsilon/E^2$ is observed.[2,3] This type of dependence is due to the presence of various associates of alcohols. Strong electric field shifts equilibriums toward complexes of large dipole moment what results in positive NDE effect. The NDE effect measured in pure octan-1-ol is much larger than that expected when alcohol molecules do not mutually interact as listed in Table 1. It means that in pure alcohol the parallel conformation of associates is favored. Analyzing the concentration dependence of the NDE increment close to the pure alcohol it is evident that cyclohexylbenzene disturbs association more effectively than benzene or cyclohexane. This observation is similar to that obtained in mixtures containing nitrobenzene and pentan-3-one.

Conclusions

In concentrated solutions of nitrobenzene, pentan-3-one, and octan-1-ol dissolved in nonpolar solvents the intermolecular interactions are the most effectively disturbed by cyclohexylbenzene, whereas benzene seems to conserve molecular complexes existing in polar liquids. This is an astonishing observation, because we expected much stronger competition between the solute and the solvent when the solvent is aromatic, when the weak charge-transfer interactions are expected. Evidently the shape and volume of the solvent molecule play a predominant role in solute−solvent interactions in mixtures rich in the polar component.

For the mixtures containing nitrobenzene we observed that, in the mixtures with dominating nonpolar components, the solvent ability follows the expected one: benzene, cyclohexylbenzene, and cyclohexane. It is linked with the structure of liquid benzene and charge-transfer interactions between benzene and nitrobenzene rings. Equimolar mixtures of benzene and cyclohexane have solvent properties similar to benzene, while cyclohexylbenzene seems to resemble the behavior of cyclohexane.

Literature Cited

(1) Rzoska, J. S.; Zhelezny, V. P., Eds. In *Nonlinear Dielectric Phenomena in Complex Liquids*, NATO Science Series, II Mathematics, Physics and Chemistry, *Vol. 157*; Kluwer Academic Publishers: Dordrecht, 2004.

(2) Chełkowski, A. *Dielectric Physics*; Elsevier: Amsterdam, 1980.

(3) Małecki, J. In *Molecular Interactions*; Ratajczak, H., Orville-Thomas, W. J., Eds.; Wiley: New York, 1982; *Vol. 3*.

(4) Małecki, J.; Nowak, J.; Liszi, J.; Varga-Puchony, Z. Dielectric studies of association of alcohols with steric hindrances. *Pol. J. Chem.* **1991**, *65*, 1773–1783.

(5) Piekara, A. The phenomena of molecular orientation in polar liquids and their solutions. *Acta Phys. Pol.* **1950**, *10*, 37–68 (Part I) and 107−140 (Part II).

(6) Dutkiewicz, M. Non-linear dielectric study of dipolar association of nitrocyclohexane in cyclohexane. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1301–1308.

(7) Dutkiewicz, M. Dipolar association as a function of molecular structure studied by nonlinear dielectric effect. *J. Mol. Liq.* **1984**, *28*, 147–157.

(8) Dutkiewicz, M. Non-linear dielectric effect study of molecular association: Extension to aprotic dipolar solvents. *Chem. Phys. Lett.* **1985**, *121*, 73–76.

(9) Dutkiewicz, M. Dielectric study of dipolar association in dihalogenobenzenes. *Acta Phys. Pol., A* **1992**, *82*, 443–447.

(10) Małecki, J. Non-linear dielectric behavior and chemical equilibria in liquids. *Electrochim. Acta* **1988**, *33*, 1235–1241.

(11) Dutkiewicz, M.; Koput, J. Conformational equilibrium in 1,2-dimethoxybenzene studied by the non-linear dielectric effect method. *J. Mol. Struct.* **1995**, *354*, 153–159.

(12) Dutkiewicz, M. Conformational equilibrium in 1,3-dimethoxybenzene studied using the non-linear dielectric effect method. *J. Mol. Struct.* **1996**, *382*, 147–154.

(13) Dutkiewicz, M.; Małecki, J. Nonlinear dielectric effect (NDE) and molecular orbital study of the conformational equilibrium in 1,4-dimethoxybenzene in benzene solution. *J. Mol. Struct.* **1997**, *416*, 105–111.

(14) Małecki, J.; Zioło, J. Nonlinear dielectric study of pretransitional effects in liquids above the phase transition temperature. *Chem. Phys.* **1978**, *35*, 187–192.

(15) Rzoska, S. J.; Zioło, J. Experimental studies on the temperature behavior of the nonlinear dielectric effect in a critical binary solution. *Phys. Rev. E* **1993**, *47*, 1445–1447.

(16) Orzechowski, K. Electric field effect on the upper critical solution temperature. *Chem. Phys.* **1999**, *240*, 275–281.

(17) Drozd - Rzoska, A.; Rzoska, S. J.; Zioło, J. Critical behavior of dielectric permittivity in the isotropic phase of nematogens. *Phys. Rev. E* **1996**, *54*, 6452–6456.

(18) Orzechowski, K.; Kosmowska, M. Apparent non-linear dielectric effect in liquids containing ions. *Chem. Phys. Lett.* **2004**, *393*, 290–294.

(19) Orzechowski, K. Non-linear dielectric effect in an ethanol + dodecane critical mixture with minor amounts of ions. *J. Phys.: Condens. Matter* **2006**, *18*, 6225–6236.

(20) Orzechowski, K.; Bator, G.; Jakubas, R. Comparison studies of the influence of an electric field on permittivity close to ferroelectric-paraelectric phase transition in TGS, DMACA and DMABA crystals. *Ferroelectrics* **1995**, *166*, 139–148.

(21) Böttcher, C. J. F.; Bordewijk, P. *Theory of Electric Polarisation*; Elsevier: Amsterdam, 1978.

(22) Dutkiewicz, M.; Chełkowski, E. Dielectric saturation of nitrobenzene in some dipolar and nondipolar solvents. *Acta Phys. Pol.* **1969**, *35*, 651–654.

(23) *Handbook of Chemistry and Physics*, 72th and 85th ed.; CRC: Boca Raton, FL, 1991 and 2004.

(24) Goldman, S. The Calculation of Effective Pair Potentials in Solution from Activity Coefficient Data: Nitrobenzene in Benzene. *Can. J. Chem.* **1975**, *53*, 2608–2618.

(25) Dutkiewicz, M.; Dutkiewicz, E. Molecular interactions in binary mixture of nitrobenzene/decahydronaphthalene studied by dielectric methods. *Pol. J. Chem.* **2004**, *78*, 1765–1775.

(26) Dutkiewicz, M.; Dutkiewicz, E. Study of microheterogeneous structure of non-aqueous mixed solvents by non-linear dielectric and viscometric methods. *Electrochim. Acta* **2006**, *51*, 2346–2350.

(27) Wiberg, K. B.; Castejon, H.; Bailey, W. F.; Ochterski, J. Conformational Studies in the Cyclohexane Series. 2. Phenylcyclohexane and 1-Methyl-1-phenylcyclohexane. *J. Org. Chem.* **2000**, *65*, 1181–1187.

(28) Bochyñski, Z.; Drozdowski, H. X-ray diffraction studies of molecular correlations in liquid phenylcyclohexane. *J. Mol. Liq.* **1999**, *80*, 53–63.

(29) Milano, G.; Müller-Plathe, F. Cyclohexane-Benzene Mixtures: Thermodynamics and Structure from Atomistic Simulations. *J. Phys. Chem. B* **2004**, *108*, 7415–7423.

(30) Dutkiewicz, M. Non-linear dielectric effect in the acetone-benzene and acetophenone-benzene systems. *Chem. Phys. Lett.* **1984**, *112*, 177–181.

Received for review October 28, 2009. Accepted March 18, 2010.

JE900908U