

# Study of microheterogeneous structure of non-aqueous mixed solvents by non-linear dielectric and viscometric methods

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

## Abstract

The paper presents a comparative analysis of the non-linear dielectric and viscometric studies of the liquid systems: acetone/cyclohexane, acetone/decahydronaphthalene, nitrobenzene/cyclohexane and nitrobenzene/decahydronaphthalene. All these systems reveal precritical-like behaviour (in specific ranges of temperatures and concentrations) manifested by a characteristic maximum on the curve of the concentration dependence of the non-linear dielectric effect parameter ( $\Delta\epsilon/E^2$ ). The concentrations corresponding to the maxima of  $\Delta\epsilon/E^2$ ,  $x \cong 0.35$  for acetone in cyclohexane,  $x \cong 0.55$  for acetone in decahydronaphthalene,  $x \cong 0.3$  for nitrobenzene in cyclohexane and  $x \cong 0.42$  for nitrobenzene in decahydronaphthalene, which seems to indicate a significant steric effect (not only) of the solvent molecules. For the solutions of nitrobenzene in cyclohexane and in decahydronaphthalene and for acetone in cyclohexane, the curve of the activation energies of viscosity as a function of concentration also reveals maxima close to the concentrations of the maxima of  $\Delta\epsilon/E^2$ .

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## 1. Introduction

Various chemical, physical and biological processes take place in liquid phase. In many cases, a selection of a proper solvent or mixed solvent with special parameters is decisive for a given process. It is well known that an appropriate choice of solvent can accelerate or inhibit chemical reaction, and/or change their kinetics and mechanism.

Solvent properties are usually expressed in terms of the “solvent polarity” which, although very common, is often not precisely defined. According to Reichardt [1], “solvent polarity” can be defined as “the overall solvation capability (or solvation power) for reactants and activated complexes as well as for molecules in the ground and excited states which

in turn depends on the action of all possible, specific and non-specific intermolecular interaction forces between solvent and solute molecules, including Coulomb interactions between ions, directional interactions between dipoles and inductive, dispersion, hydrogen-bonding and charge-transfer forces, as well as solvophobic interactions”. Some physical properties such as permittivity, dipole moment, free volume, viscosity, etc., are frequently used for determination of “solvent polarity”. Various empirical parameters have been proposed, based on the response of a particular system towards a change of solvent. Spectroscopic parameters of solvent polarity derived from solvent-sensitive solvatochromic dyes allowed the introduction of solvent polarity scales based upon changes in the position of the longest wavelength absorption bands of such solvatochromic dyes [1,2 and references cited therein]. Another approach is to describe the solvent polarity on the basis of a statistical compilation of different physicochemical properties of the solvent [3–6]. Various

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empirical parameters have also been proposed, based on the response of a particular system to 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 (see [7] for review). There was also an attempt [8] to describe solvent polarity in terms of dielectric parameter  $\beta$  (proportional to  $\mu^2/V$ , where  $\mu$  is the electric dipole moment and  $V$  is the molar volume). Empirical solvent polarity parameters as well as statistical methods (chemometrics) [1] describe the solvent polarity and solvent effects as results of many different types of interactions between the molecules. We have also found [9] a correlation between the solvent polarity expressed in terms of Dimroth–Reichardt spectroscopic parameter  $E_T^N$  and the non-linear dielectric effect (NDE) expressed in terms of the parameter  $\Delta\varepsilon/E^2$ , where  $\Delta\varepsilon$  is a change in the electric permittivity  $\varepsilon$  of a solvent in an external strong electric field  $E$ . Both  $\Delta\varepsilon/E^2$  and  $E_T^N$  are extremely sensitive to the dielectric properties of a solvent depending on molecular interactions and they are determined in quite different ways. Spectroscopic parameter  $E_T^N$  describes the interaction between the “probe” molecule (pyridinium-*N*-phenoxide betaine dye) and the solvent, while the NDE parameter  $\Delta\varepsilon/E^2$  is related to the behaviour of dipolar molecules in an electric field, to intra- and intermolecular interactions and to density (and concentration) fluctuations. Although it is difficult to strictly link the NDE parameter with the solvent polarity parameter, nevertheless such a correlation has been shown for two groups of solvents, namely alcohols and halogenobenzenes.

Molecular interactions are much more complicated in a mixed solvent, where one has to take into account intermolecular interactions not only between solute–solute but also solute–solvent and solvent–solvent molecules. In particular, in a binary system of solvent molecules of much different chemical structure and physical properties (e.g. density, permittivity and refractive index), molecular interactions of the polar species lead to formation of clusters, fluctuating in the solution and in an extreme case (critical solution—specific temperature and concentration) cause a separation of the solution into two phases. In the vicinity of the critical dissolution point, the fluctuations in concentrations are significantly strong and the solution has a microheterogeneous structure due to dipolar molecular cluster formation. Critical liquids have been a subject of many experimental and theoretical works [10–15 and references cited therein]. A precritical state of systems being in homogeneous phase can show anomalies of various physicochemical properties [15] (e.g. permittivity, conductivity, non-linear dielectric behaviour and others). A method particularly useful in investigation of properties of critical liquids is the non-linear dielectric effect [15,16] which has been applied for many years in studies of molecular effects in liquids, providing valuable information about inter- and intramolecular interactions resulting in hydrogen bonding [17,18], charge transfer [17], dipolar association [19,20] and conformational equilibria [16,17,21–24] in liquids.

The NDE refers to a non-linear dependence of the electric polarisation  $P$  on the electric field strength  $E$  [25]:

$$\frac{\partial P}{\partial E} = \varepsilon_0(\varepsilon - 1) \quad (1)$$

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

$$\Delta\varepsilon = \varepsilon_E - \varepsilon \quad (2)$$

An experimental 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 also been shown [9], which indicates that the parameter  $\Delta\varepsilon/E^2$  can also be used as a solvent polarity parameter. In this paper, we apply the NDE method to study mixed solvents, investigating binary systems: acetone/cyclohexane and acetone/decahydronaphthalene referring in the discussion to our former results concerning the systems of nitrobenzene/cyclohexane [26] and nitrobenzene/decahydronaphthalene [27] in order to draw a more general conclusion. We also report the viscosity activation energies (determined from the temperature dependence of viscosity coefficients) as functions of concentration for three selected temperatures for binary systems of acetone/cyclohexane and nitrobenzene/decahydronaphthalene. The dependence of viscosity activation energy for nitrobenzene/cyclohexane was taken from our earlier work [26], for comparison.

## 2. Experimental

### 2.1. Materials

Acetone GR dried Merck was used from flask and cyclohexane and decahydronaphthalene were purified by distillation.

### 2.2. Methods

The NDE measurements were carried out with the automatically recording pulse device described in Ref. [21]. The values of  $\Delta\varepsilon/E^2$  were determined at a frequency of about 2 MHz with an accuracy of  $\pm 5\%$ . The concentration of acetone in cyclohexane and in decahydronaphthalene is expressed as mole fraction  $x$ . The viscosity of the solutions as a function of temperature was measured with an Ubbelohde viscometer. The temperature  $T$  expressed in Kelvin was measured to an accuracy of  $\pm 0.1$  K.

## 3. Results and discussion

Figs. 1 and 2 show the dependencies of the non-linear dielectric parameter  $\Delta\varepsilon/E^2$  on the mole fraction  $x$  of acetone

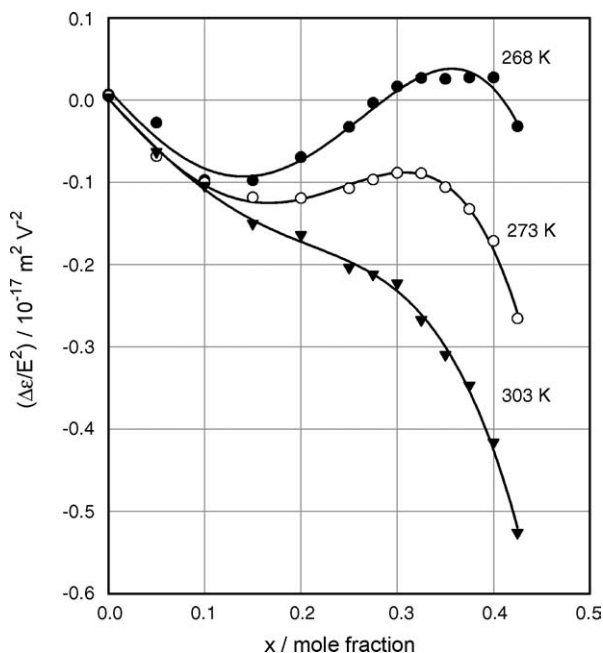


Fig. 1. NDE parameter  $\Delta\epsilon/E^2$  vs. mole fraction  $x$  of acetone in cyclohexane.

in cyclohexane (Fig. 1) and in decahydronaphthalene (Fig. 2) for three temperatures.

In both cases, a significant maximum for lower temperature is observed. Generally, such a behaviour (maximum) is typical of critical solutions [15,16] for which the critical miscibility temperature and concentration have been found.

In this study, the measurements were carried out in the temperature range over which the macroscopic criti-

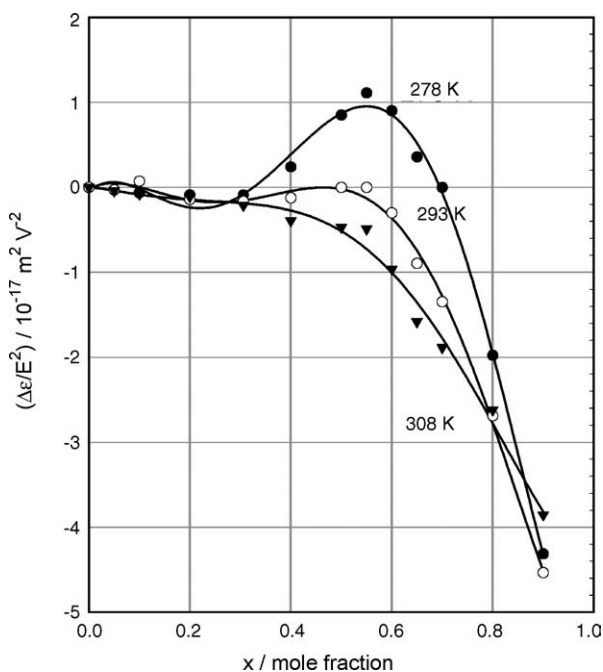


Fig. 2. NDE parameter  $\Delta\epsilon/E^2$  vs. mole fraction  $x$  of acetone in decahydronaphthalene.

cal phenomena (like opalescence, phase separation, etc.) were not observed, as in other systems [28]. It is worth to emphasise that the NDE method reveals precritical phenomena even to several dozen of degrees from the critical temperature. In the vicinity of the critical dissolution point, the fluctuation accounts for the very strong increase in  $\Delta\epsilon/E^2$ . This effect is independent of the sign of the NDE in the pure dipolar component [16]. Nitrobenzene (and many other aromatic compounds like benzonitrile, phenylisothiocyanate and nitrotoluenes) is characterised by a positive change in permittivity in a strong electric field applied ( $\Delta\epsilon/E^2 \cong 30 \times 10^{-17} \text{ m}^2 \text{ V}^{-2}$ ), whereas acetone (and many other non-aromatic compounds, e.g. nitrocyclohexane, methyl isothiocyanate and acetonitrile [20]) shows a negative NDE ( $\Delta\epsilon/E^2 \cong -4 \times 10^{-17} \text{ m}^2 \text{ V}^{-2}$ ) [29,30]. But in all critical solutions of such liquids in non-polar solvents, a strong increase of  $\Delta\epsilon/E^2$  in the vicinity of critical concentration, increasing with lowering temperature, is observed [16].

An inspection of the plots in Figs. 1 and 2 reveals a solvent effect on the non-linear behaviour of acetone. For solutions in cyclohexane, the maximum is smaller than in decahydronaphthalene and the concentrations at which these maxima appear are  $x \cong 0.35$  for acetone in cyclohexane and  $x \cong 0.55$  for acetone in decahydronaphthalene. Recently, we have published [27] a similar report on the system nitrobenzene/decahydronaphthalene. Fig. 3 shows a dependence of  $\Delta\epsilon/E^2$  on nitrobenzene concentration,  $x$ , selected from paper

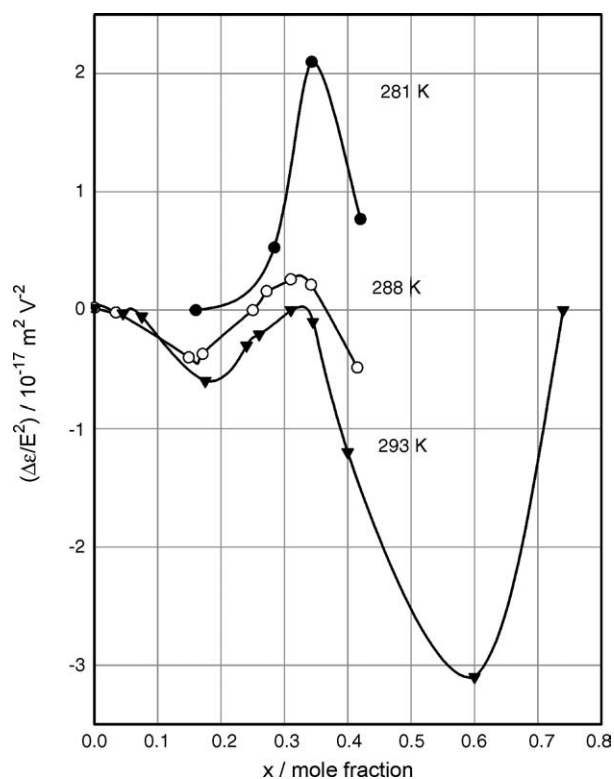


Fig. 3. NDE parameter  $\Delta\epsilon/E^2$  vs. mole fraction  $x$  of nitrobenzene in cyclohexane.

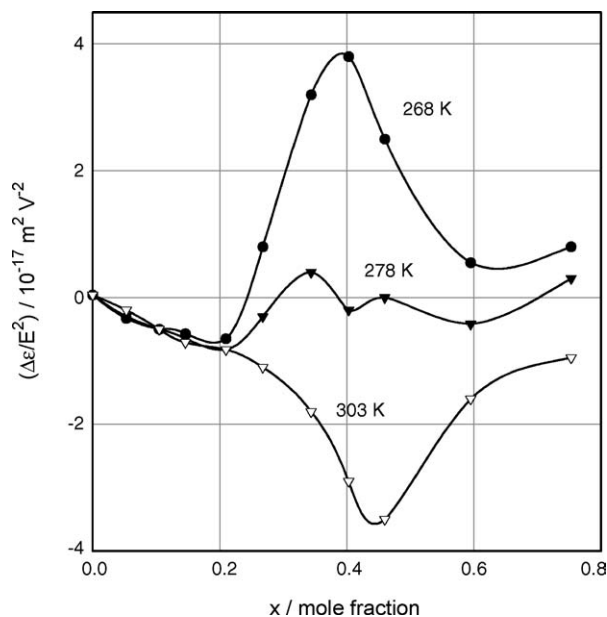


Fig. 4. NDE parameter  $\Delta\epsilon/E^2$  vs. mole fraction  $x$  of nitrobenzene in decahydronaphthalene.

[27] for three temperatures. For comparison, we also have added in Fig. 4 the plot of  $\Delta\epsilon/E^2$  versus nitrobenzene concentration in cyclohexane,  $x$ , taken from [26].

We have compared the non-linear behaviour of the following four systems: acetone/cyclohexane, acetone/decahydronaphthalene, nitrobenzene/cyclohexane and nitrobenzene/decahydronaphthalene. In the two latter systems, the concentrations corresponding to the maximum in the plot of  $\Delta\epsilon/E^2$  versus  $x$  are:  $x \cong 0.3$  for nitrobenzene in cyclohexane and  $x \cong 0.42$  for nitrobenzene in decahydronaphthalene. The solvent effect on the NDE parameter of acetone in cyclohexane and in decahydronaphthalene can be explained in a similar way as it has been done for nitrobenzene in decahydronaphthalene and in cyclohexane [27], namely the “shift” in critical concentration seems to be related mainly to differences in molar volumes of the two non-polar solvents ( $V_{\text{cycl}} = 108.2 \text{ cm}^3 \text{ mol}^{-1}$  and  $V_{\text{dec}} = 156.2 \text{ cm}^3 \text{ mol}^{-1}$ ), because only the molar volume is significantly different in the two solvents; their chemical character and their physical properties are very similar (density, permittivity and refractive index have similar values; see Tables 1–3 in [27]).

A comparison of the non-linear dielectric behaviour of the four binary systems (mixed solvents), composed of a polar and a non-polar compound, shows that for all the systems analysed in this work, there is a maximum on the concentration dependence of  $\Delta\epsilon/E^2$ , increasing with decreasing temperature, irrespective of whether the pure polar component is characterised by a negative  $\Delta\epsilon/E^2$  (acetone) or positive  $\Delta\epsilon/E^2$  (nitrobenzene). The appearance of this maximum indicates the existence of precritical behaviour related to increase in the concentration fluctuations and their deformation in a strong electric field. The precritical behaviour observed in

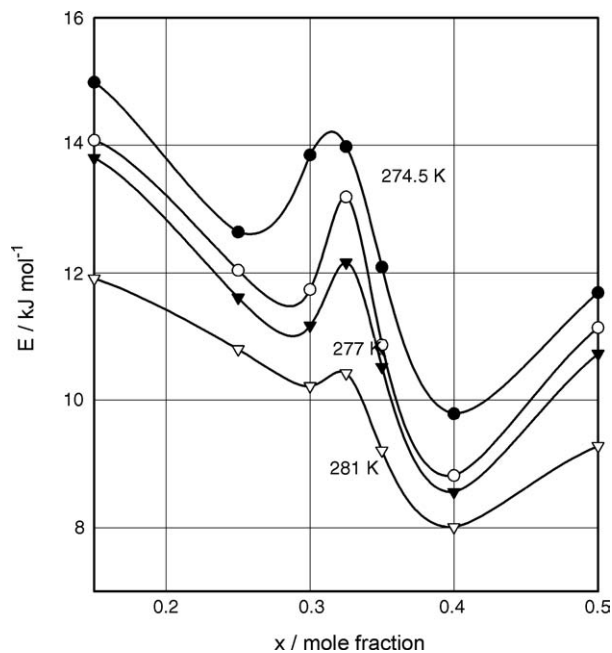


Fig. 5. Viscosity activation energy  $E$  vs. mole fraction of acetone in cyclohexane.

the four analysed systems reveals their microheterogeneity already far from the critical temperature.

The microheterogeneity of these systems can also be deduced from the viscosity measurements from which the viscosity activation energy was determined. Since the temperature dependence of the viscosity coefficient  $\eta$  ( $\ln \eta$  versus  $1/T$ ) has been found to be non-linear, the activation energy could not be determined unequivocally from the Arrhenius equation:  $\ln \eta = \ln \eta_0 + E/RT$  (where  $\eta_0$  is a constant). Hence, we applied the same procedure as in Ref. [26], similar to that of Ref. [32], taking into account the dependence of the activation energy  $E$  on temperature as determined by the method of tangents from the curve of  $\eta$  versus  $1/T$  on the basis of the following formula:

$$E = R \frac{d \ln \eta}{d(1/T)} \approx R \frac{\Delta \ln \eta}{\Delta(1/T)} = R \frac{1}{\eta} \frac{\Delta \eta}{\Delta(1/T)} \quad (3)$$

Figs. 5–7 present the dependence of viscosity activation energy  $E$  on the mole fraction  $x$  of polar component (acetone or nitrobenzene) at three selected temperatures. (Detailed data on the viscosity measurements of acetone/cyclohexane and nitrobenzene/decahydronaphthalene systems will be published in a separate paper [31].) The data for nitrobenzene/cyclohexane are taken from Ref. [26], for comparison.

The plots in Figs. 5–7 show the maxima of viscosity activation energy in the regions of concentration where the maxima of  $\Delta\epsilon/E^2$  have been found. The increase in the viscosity activation energy in these regions can also be explained in terms of the presence of the clusters (or associates) in the solution.

The results presented in this work additionally support our former conclusion [27] that the mechanism and kinetics of many physico-chemical processes in mixed solvents can be

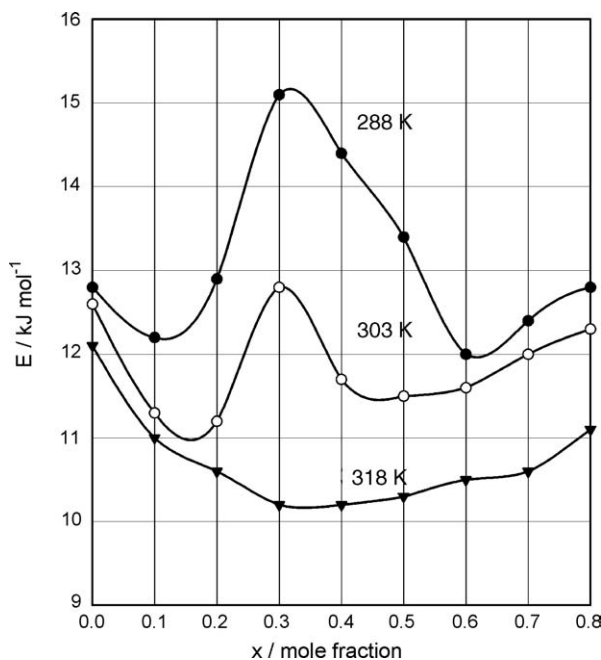


Fig. 6. Viscosity activation energy  $E$  vs. mole fraction of nitrobenzene in cyclohexane [26].

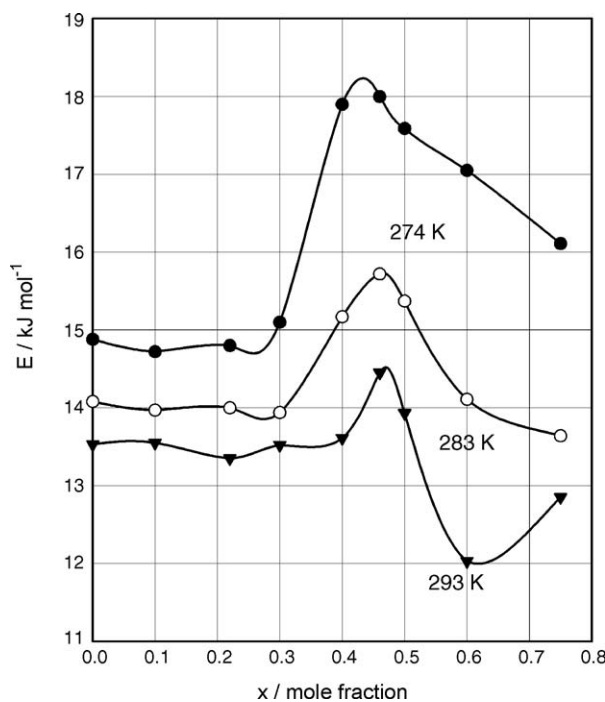


Fig. 7. Viscosity activation energy  $E$  vs. mole fraction of nitrobenzene in decahydronaphthalene.

considerably affected by the microstructural changes taking place in the solvents and undetectable on macroscopic scale. These changes, namely from the homogeneous into microheterogeneous structure, depending on the composition and

temperature can have significant effect on the results of the study and its interpretation which is also mentioned in [15].

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