Solvatochromic Study on Binary Solvent Mixtures with Ionic Liquids

Mihkel Koel

Institute of Chemistry, Tallinn University of Technology, Akadeemia tee 15, Tallinn 12618, Estonia

Reprint requests to M. K.; E-mail: vmihkel@chemnet.ee

Z. Naturforsch. **63a,** 505 – 512 (2008); received December 4, 2006

Presented at the EUCHEM Conference on Molten Salts and Ionic Liquids, Hammamet, Tunisia, September 16 – 22, 2006.

Solvent effects on 2,6-dichloro-4-(2,4,6-triphenyl-pyridinium-1-yl)phenolate [$E_T(33)$ dye] and 7-diethylamino-3,4-benzophenoxazine-2-one (Nile Red) in binary mixtures of organic solvents (acetone, acetonitrile, propylene carbonate, methanol and ethane-1,2-diol) with 1,3-dialkyl imidazolium-based ionic liquids were studied by UV-visible spectroscopy. Highly nonlinear behaviour of mixtures of alcohols and ionic liquids was found. A preferential solvation model was applied to the data obtained on solvatochromic shifts over the entire mixing range. It is fitting the data well for alcohol mixtures and for other solvent mixtures with different ionic liquids.

Key words: Binary Solvent Mixtures; Solvent Effects; Solvatochromism; Pyridinium *N*-Phenolate Betaine Dyes; Nile Red; Ionic Liquids.

1. Introduction

Ionic liquids (IL) or molten salts at room temperature presently experience significant attention in many areas of chemistry. There is competition to find a proper niche for these materials, and also more insight is needed. The most attractive property is the "tunability" of the physical and chemical properties of ILs by varying structure. There are several reviews available on different aspects of ILs [1].

Both air- and water-stable ILs have begun to be used as an alternative to conventional organic solvents. The use of ionic ILs as solvents demands information about their behaviour in the presence of other compounds including organic solvents, water (given the very hygroscopic nature of ILs) or supercritical CO_2, commonly used for product extraction. In addition, the efficiency of chemical processes (syntheses, extractions, separations) carried out in ILs can be increased in some cases, when co-solvents are added, which can affect the physical properties of ILs considerably [2]. With conventional methods it is not possible to measure the dielectric constant of ILs. Complicated indirect measurements like microwave dielectric spectroscopy must be used [3]. The few data available on dielectric relaxation in mixtures of ILs with acetonitrile show nonlinear behaviour, which can be explained by different interactions between solvent and IL depending on the concentration of the latter [4].

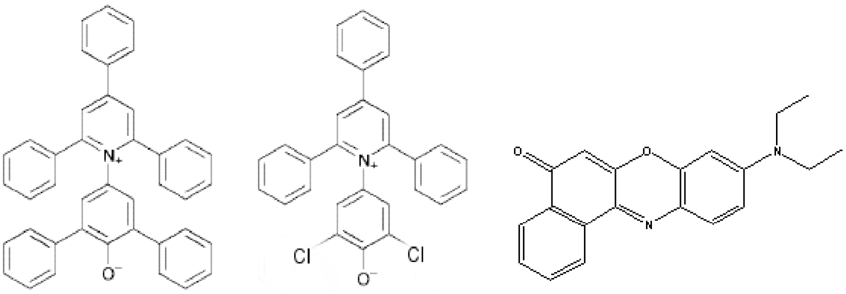
Solvatochromic dyes as a kind of molecular probes in some instances "sense" the solute environment in the solution better than it is revealed in more macroscopic parameters.

The best-known empirical scale of this kind is the $E_T(30)$ scale based on the intramolecular charge-transfer energy (CT) π-π^* absorption band of 2,6-diphenyl-4-(2,4,6-triphenyl-pyridinium-1-yl)phenolate (**1**, Fig. 1) [5]. This compound, also known as Reichardt's betaine dye, exhibits one of the largest observed solvatochromic ranges of known organic solvatochromic dyes.

In the study presented, a less basic version of betaine dye, the dichloro-substituted betaine dye 2,6-dichloro-4-(2,4,6-triphenyl-pyridinium-1-yl)phenolate [**2**, Fig. 2, $E_T(33)$ dye], was also used. The molar transition energy has been employed as a measure of interaction of the dye molecules with the solvent system. The following expression was used for the calculations:

$$E_T(X) = \frac{28591}{\lambda_{\max}^{\text{abs}}}, \tag{1}$$

where $\lambda_{\max}^{\text{abs}}$ is the wavelength of the absorption band maximum.



1 **2** **3**

Fig. 1. Chemical structures of compounds **1**–**3**.

A good linear relation between the E_T values of the betaine dyes **1** and **2** is known and this indicates very similar solute-solvent interactions [6].

Beside these two compounds, there are other dyes exhibiting relatively large solvatochromic shifts, for example Nile Red [**3**, Fig. 1, E_T(NR) dye], which belongs to the class of vinyloguous carboxylic amides and is more stable in acidic media. The relation between ET(NR) and $E_T(30)$ or $ET(33)$ scales is not linear but provides a clear picture of the relative strengths of the solvents [7].

Nile Red produces a bathochromic wavelength shift, which is a contrast to the hypsochromic shift of Reichardt's dye. Recently Nile Red was used as a fluorescence probe to monitor the properties of complicated mixed solvent systems, and changes in the organization of surfactants could be followed [8].

Room temperature molten salts are complex liquids with an extended three-dimensional liquid structure consisting only of ions, possibly influenced by interionic hydrogen bonds, and it is not surprising that there are not yet definitive answers on the question of their polarity [9, 10].

Carmichel and Seddon [11] made a series of measurements on solvatochromic shifts of Nile Red (**3**) in 1-alkyl-3-methylimidazolium ILs and they concluded that ILs are in the same polarity range as lower alcohols. A similar result was found by Fletcher et al. [12] using Reichardt's dye (**1**), whose calculated $E_T(30)$ values indicate the polarity of 1-butyl-3-methylimidazolium hexafluorophosphate ([C_4MIm][PF_6]) to be similar to ethanol. From their measurements using Nile Red (**3**), it was also concluded that the polarity of the solvent in the immediate vicinity of the Nile Red probe is similar to 90 wt% glycerol in water (a solvent with viscosity similar to [C_4MIm][PF_6]). Alteration of the anion ($[PF_6]^-$, $[BF_4]^-$, $[TfO]^-$) has very little effect on the E_T(NR) values, with the exception of [C_4MIm][Tf_2N], which seems to be less polar than [C_4MIm][PF_6].

Baker et al. [13] used a multi-parameter approach and emphasized that [C_4MIm][PF_6] is a different solvent with no peer among the traditional organic solvents. They concluded as follows: while $E_T(30)$ and Kamlet-Taft studies are suggestive of hydrogen bond donor strengths akin to the short-chain alcohols, hydrogen bond acceptor abilities of the IL lay between those of water and acetonitrile. Therefore, considering the indications arising from Reichardt' dye (**1**), 1,3-dialkylimidazolium salts seem to have a hydrogen bond donor ability similar to that of short-chain alcohols but a much lower nucleophilic character. The complexity of the problem is confirmed when using other spectroscopic probes. Pyrene is one of the most widely used neutral fluorescence probes. Contrary to the results obtained from probe studies with Reichardt's dye (**1**), the exited state of pyrene clearly indicates a completely different micro-environment [13]. Such a complexity suggests for solvent-dependent processes the use of a multi-parameter description with various solvatochromic parameters as part of them. The most up-to-date review on polarity measurements, based on solvatochromic probes measured in pure ILs, is given by Reichardt [14]. Despite the difficulties arising from the use of UV/Vis spectrophotometric probes to determine the IL polarity, these probes offer a versatile mean to investigate the local micro-environments, dynamics, and organization within ILs.

The study of the physico-chemical properties is much more complex in mixed solvent systems than in pure solvents. On the one hand, the solute can be preferentially solvated by any of the solvents present in the mixture; on the other, solvent-solvent interactions can affect the solute-solvent interactions.

The binary mixtures of ILs with molecular solvents in principle should be better considered as solutions of salts (or electrolytes) in organic solvents. Once dissolved, it makes no difference whether the salt was a liquid or a solid before dissolution. By analogy with the definition of solvatochromism, the term "negative (positive) halochromism" for such a hypsochromic (bathochromic) shift of the UV/Vis absorption band of a dissolved compound with increasing ionophore concentration could be used [5]. It is clear that this halochromism must be strongly dependent on the molecular structure of the solvatochromic probe used, because the probe molecules can interact in solvents either selectively with the cation or the anion of the added salt [15].

The polarity study reported here was undertaken with emphasis on structural features such as the effects of anion and cation choices. It is part of a larger project aimed at a better understanding of the properties of ILs and mixtures of ILs with organic solvents. The results give insight into the fine-tuning of the properties of binary IL/solvent mixtures which, in turn, could assist a better choice of ILs with specific properties for different applications by the addition of co-solvents.

2. Solvation Model

The measured solvatochromic shift is strongly influenced by the indicator solvation microsphere, which can differ considerably from that of the bulk in binary solvent mixtures. One possible model for the preferential solvation based on the two-step solvent-exchange equilibrium is that proposed by Skwierczynski and Connors [16] and further extended and generalized by Roses et al. [17]. Despite of electrolyte solutions it was expected that mixtures of organic solvents with room temperature molten salts can be treated analogously as a normal binary solvent mixture, and the non-linear behaviour results from the preferential solvation of the dye by one component of the mixture or other interactions between the components of this mixture (indicator + organic solvent + ionic liquid).

The E_T value of the binary solvent mixture is calculated as a combination of the E_T values of two pure solvents S_1 and S_2, and the solvent S_{12} formed by the interaction of solvents S_1 and S_2, in the sphere of solvation of the indicator dye, according to

$$E_T = x_1^S E_{T1} + x_2^S E_{T2} + x_{12}^S E_{T12}, \tag{2}$$

where x_1^S, x_2^S, x_{12}^S are mole fractions of the solvents S_1, S_2, and S_{12}, respectively, present in the solvation sphere of the solute.

In this model the relation of the E_T value of a binary mixture to the E_T value of two pure solvents, the preferential solvation parameters, and the solvent composition can be described as follows:

$$y = \frac{y_1(1-x)^2 + y_2Ax^2 + BC(1-x)x}{(1-x)^2 + Ax^2 + B(1-x)x}. \tag{3}$$

Here, $y = E_T$, $y_1 = E_{T1}$, $y_2 = E_{T2}$, $C = E_{T12}$, $B = f_{12/1}$, $A = f_{2/1}$.

There are two parameters describing the two-step solvent-exchange equilibrium in this solvation model: The preferential solvation parameters $f_{2/1}$ and $f_{12/1}$ measure the tendency of the solute to be solvated by solvents S_2 and S_{12} with reference to solvent S_1. S_{12} represents a solvent complex formed by specific interaction between solvent S_1 and solvent S_2. The third unknown parameter is E_{T12} – related to the absorption band maxima of the solvent S_{12} formed by interaction of S_1 with S_2.

3. Experimental

The most popular IL systems are based on 1,3-dialkylimidazolium cations with alkyl groups with different chain length. In this study different 1-alkyl-3-methylimidazolium salts were used. The cations had C_4 and C_8 alkyl chains [C_nMIm]. The anions were taken from a wide set of possibilities to be the most used hexafluorophosphate $[PF_6]^-$ and tetrafluoroborate $[BF_4]^-$; also less common anions were used as bis(trifluoromethanesulfonyl)imide $(F_3C\text{-}SO_2)_2N^-$ (Tf_2N), trifluoroacetate $F_3C\text{-}CO_2{}^-$ (FAcO), acetate $CH_3CO_2{}^-$ (AcO), or heptafluorobutanoate $F_3C\text{-}(CF_2)_3\text{-}CO_2{}^-$ (FBuO).

The ILs used in this work were prepared following the procedures published elsewhere [18]. Before use all ILs were dried in vacuo and the measurements were performed immediately after the sample was removed from the vacuum.

Absorption spectra were recorded on a UV/Vis Jasco V530 spectrometer equipped with a thermostated cell holder at (20.0 ± 0.1) °C between 190 – 1100 nm with a spectral bandwidth of 2 nm. The maximum of the absorption band $\lambda_{\max}^{\text{abs}}$ was determined by built-in software of the spectrometer, whose algorithm is based on differentiation of smoothed signals, and are accurate to ±1 nm.

	Reichardt's dye (**1**)		2,6-Dichloro substituted betaine dye **2**		Nile Red (**3**)	
	λ_{max} (nm)	$E_T(30)$ (kcal/mol)	λ_{max} (nm)	$E_T(33)$ (kcal/mol)	λ_{max} (nm)	E_T(NR) (kcal/mol)
Acetonitrile	622	46.0	521	54.9	535	53.4
Acetone	675	42.4	560	51.1	532	53.7
Propylene carbonate	619	46.2	517	55.3	543	52.7
Methanol	515	55.5	441	64.8	553	51.7
Ethane-1,2-diol	514	55.6	432	66.2	–	–
[C_4MIm][Tf_2N]	–	–	454	63.0	–	–
[C_8MIm][PF_6]	560	51.1	442	64.7	–	–
[C_4MIm][PF_6]	540	52.9	441	64.8	548	52.2
[C_4MIm]FAc	570	50.2	444	64.4	–	–
[C_4MIm]Ac	–	–	480	59.6	–	–
[C_4MIm]FBc	–	–	480	59.6	–	–
[C_4MIm][BF_4]	542	52.7	457	62.6	549	52.1

Table 1. The long-wavelength visible absorption band maxima of three solvatochromic dyes and corresponding transition energies [λ_{max} (±1 nm) and $E_T(30)$, $E_T(33)$, E_T(NR) (±0.2 kcal/mol), respectively] measured in different solvents.

The dyes [Reichardt's dye (**1**), dichloro betaine dye **2** and Nile Red (**3**)] were used as they were obtained from Merck (Darmstadt, Germany). The solvents of spectroscopic grade high-purity were obtained from Sigma-Aldrich (Steinheim, Germany) and used without further purification. Repetitive measurements showed that it is important to use freshly made mixtures from dried solvents. In some cases, it was not possible to observe the long-wavelength visible absorption maximum of **1**, because the colour was bleached out. This resulted from protonation of **1** at the phenolate oxygen atom because of acidic impurities in the IL [18]. It was possible to restore the colour of the mixture with a drop of triethylamine, but this complicated the system and these results were not used.

The unknown parameters that minimize the squared residuals of E_T values in the preferential solvation model for each binary solvent system studied were calculated by non-linear regression. The calculations were done in MS Excel with function Solver, which uses a generalized reduced gradient (GRG2) non-linear optimization code developed by Frontline Systems, USA.

4. Results and Discussion

At first the UV/Vis absorption spectra of betaine dyes were measured in different solvents and ILs. Table 1 tabulates the wavelengths λ_{max}^{abs} (in nm) of the long wavelength visible absorption bands and corresponding transition energies $E_T(X)$ (in kcal/mol) for the different dyes (with concentration approximately 2 mmol/L of dye) and some solvents. While the data on **1** are comparable with data from the literature, the data on **2** are new.

Nile Red (**3**) was used for comparison to show how dyes with different properties can behave.

The $E_T(X)$ values of the binary solvent mixtures or salt solutions as considered in this study are not related to their composition in a simple linear manner. They are non-ideal mixtures. The same conclusion concerning the aqueous tetra-*n*-butylammonium bromide solutions measured by $E_T(30)$ betaine dye and $E_T(8)$ betaine dye has been drawn by Herodes at al. [19]; they observed a sharp decrease of dye-sensed water polarity under adding of even small amounts of salt.

In Figs. 2 and 3 one can see the different influence of cations and anions of the IL on the solvatochromic shift of dye in IL mixtures with acetonitrile. In both figures it is seen that a hypsochromic shift of the CT band occurs. In case of acetonitrile this study shows a purely negative halochromism for betaine dye with increasing concentration of the alkylimidazolium salts. Already a small amount of added IL gives a substantial change, which reaches almost the value of the pure

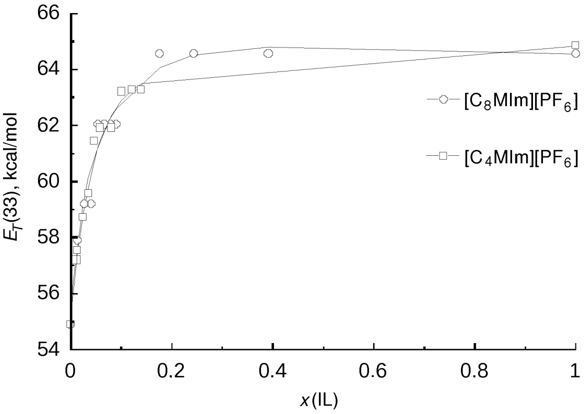


Fig. 2. Solvatochromic shift of the dichloro betaine dye **2** dissolved in mixtures of acetonitrile with ionic liquids with the same anion ($[PF_6]^-$) but with a different cation (C_4 and C_8 alkyl chains at imidazolium cation).

	Solvent system	$y_1 =$ E_{T1}	$y_2 =$ E_{T2}	$A =$ $f_{2/1}$	$B =$ $f_{12/1}$	$C =$ E_{T12}	SD[a]	n[b]
1	$[C_8MIm][PF_6]$ and acetonitrile	54.9	64.7	48.5	21.2	65.7	3.2	12
2	$[C_4MIm][PF_6]$ and acetonitrile	54.9	64.8	188	25.6	64.4	2.2	13
3	$[C_4MIm][PF_6]$ and methanol	64.8	64.8	249	133	68.1	0.7	17
4	$[C_4MIm][BF_4]$ and methanol	64.8	62.6	112	51.7	68.9	2.0	20
5	$[C_4MIm][PF_6]$ and propylene carbonate	55.3	64.8	0.1	0.8	80.7	0.6	9
6	$[C_4MIm][PF_6]$ and acetone	51.1	64.8	206	100	59.4	3.6	18
7	$[C_4MIm][PF_6]$ and ethane-1,2-diol	66.2	64.8	17.7	80,7	68.0	0.3	18
8	$[C_4MIm][PF_6]$ and methanol[c]	51.7	52.2	43.8	13.2	50.1	0.4	17

Table 2. Parameters of a solvation model derived from experimental data.

[a] SD, standard deviation of regression.

[b] n, number of data points.

[c] Nile Red was used as a solvatochromic dye.

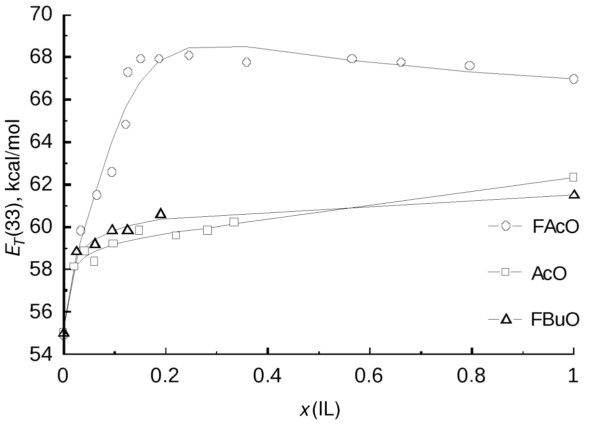


Fig. 3. Solvatochromic shift of the dichloro betaine dye **2** dissolved in mixtures of acetonitrile with $[C_4MIm]^+$ ionic liquids with different anions (FAcO, fluoroacetate; AcO, acetate; FBuO, fluorobutanoate).

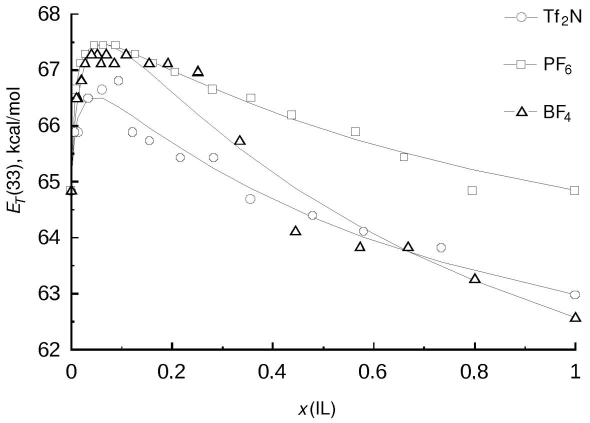


Fig. 4. Solvatochromic shift of the dichloro betaine dye **2** dissolved in mixtures of methanol with $[C_4MIm]^+$ ionic liquids with different anions ($[Tf_2N]^-$, $[PF_6]^-$ and $[BF_4]^-$).

IL at 0.2 mole fraction of the IL. The further change is small and almost linear. One cannot see by eye the differences in case of different lengths of the alkyl chain at the cation, but a difference is seen in the parameter $A = f_{2/1}$ (Fig. 1). [Lines are calculated from (3) using the parameters from Table 2.] The negative halochromism of betaine dye mainly stems from specific dye (charged oxygen atom)/cation interactions, reflecting salt-induced perturbations in the molecular-microscopic environment of the phenolate part of the betaine dye [20]. Longer chains at the cation result in weaker interaction between dye and cation. Surprisingly, the anion of the salt has a larger influence on the solvatochromic shift; such difference is also seen in case of mixtures of IL with different solvents. It confirms the complex influence of anions and cations on the halochromism of betaine dye dissolved in alkylimidazolium-based ILs.

In case of mixtures with methanol, the polarity of which is similar to the pure IL polarity as estimated with betaine dye, one observes a different picture (Fig. 4). Already the addition of small amounts of ILs causes a substantial shift of the CT absorption maximum towards higher energies; a maximum is reached at an IL content of 0.05 – 0.06 mole fractions. After that, an almost linear positive halochromic shift with increasing IL concentration takes place. Fletcher and Pandey [21] when they studied mixtures of $[C_4MIm][PF_6]$ with ethanol, explained this behaviour with the altered properties of the solution due to solvent-solvent interactions and a change of the hydrogen bond donor ability of the binary solvent mixture. This is completely different from the behaviour of mixtures of tetramethylammonium salts with alcohols, where a steady increase of the $E_T(30)$ value of the medium can be found if more salt is added to the alcohol [22].

Figure 5 summarizes the halochromic behaviour of $[C_4MIm][PF_6]$ dissolved in different solvents. The influence of the solvent's nature is clearly seen. Big differences are found between solutions of alcohol and other organic solvents. A drastic example is the mixture with ethane-1,2-diol (Fig. 6) in the range where both liquids are miscible with each other. Adding a small amount of $[C_4MIm][PF_6]$ causes a large nega-

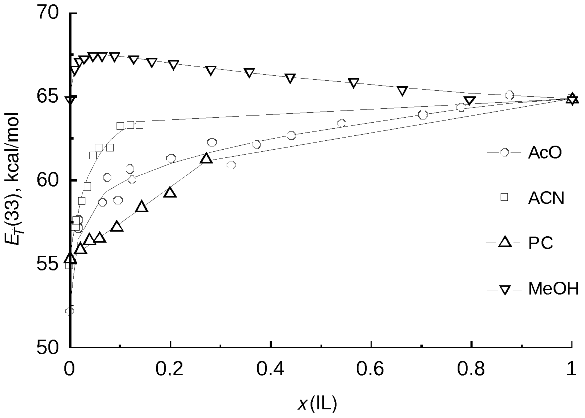


Fig. 5. Solvatochromic shift of the dichloro betaine dye **2** dissolved in mixtures of organic solvents (AcO, acetone; ACN, acetonitrile; PC, propylene carbonate; MeOH, methanol) with ionic liquid $[C_4MIm][PF_6]$.

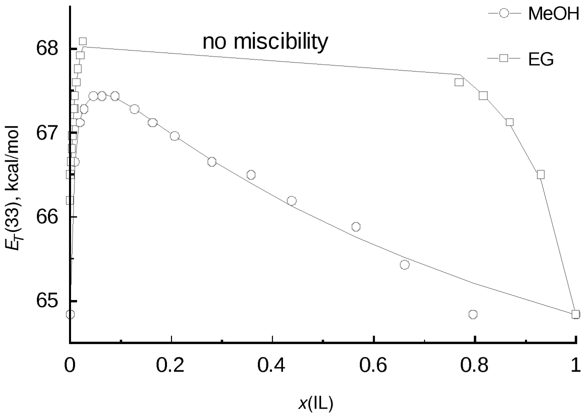


Fig. 6. Solvatochromic shift of the dichloro betaine dye **2** dissolved in mixtures of alcohols (MeOH, methanol; EG, ethane-1,2-diol) with ionic liquid $[C_4MIm][PF_6]$.

tive halochromic shift, and in the opposite case, with small amounts of ethane-1,2-diol in the IL, a positive halochromic shift is observed. A very similar behaviour of the solvatochromic shift of Reichardt's dye was obtained in case of $[C_4MIm][PF_6]$ addition to a water and ethanol mixture in the range of miscibility with the IL by Fletcher and Pandey [23]. In other work on binary IL/H_2O mixtures [24], this was explained by salt dissolution at first and then hydration of ions at higher concentrations of IL. On dissolution of ILs into H_2O at infinite dilution, IL ion pairs break away from their pure environment and settle in the water environment as hydrated ions. As the concentration of the IL increases, the IL cations and anions begin to interact with each other, either directly or in a water mediated manner (e. g. to generate solvent-separated ion pairs). Probably, in this study with the mixture of IL with methanol the situation is similar because of the hydrogen bond interactions which exist also in methanol. The effect of different anions is clearly seen; on Fig. 4 which indicates a separate influence of the ionic parts of the IL on the solvation. This separate influence is confirmed by findings of Crosthwaite et al. [25], where the liquid phase behaviour of imidazolium-based ILs with alcohols was found to be influenced very much by the length of the alkyl chain in the IL cation and the origin of the anion as well as by the alkyl chain length of the alcohol.

In case of ILs there seems to be more than just a gradual displacement of the solvent molecules by the solvated cation in the micro-environment of the active moiety of the dye. One can speak here about synergistic solvent effects, as it was proposed for binary solvent mixtures by Herodes et al. [26]. The behaviour of synergistic binary solvent systems can be explained by the formation of solvent/solvent complexes, which creates a third, new, polar solvent, or by the cooperative solvation of the dye solute by the two pure co-solvents, as the preferential solvation model proposes. This is probably more complicated in case of salts because of the different behaviour of anions and cations [27]. The dye is sensing then the changes in the solvent structure [or solvent-salt (IL) interaction] under changing the composition of mixture.

Nile Red exhibiting a positive solvatochromism (bathochromic band shift with increasing solvent polarity) was used in mixtures of the IL $[C_4MIm][PF_6]$

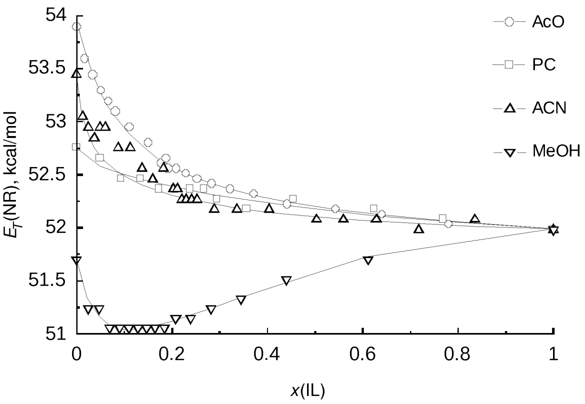


Fig. 7. Solvatochromic shift of the dye Nile Red (**3**) in mixture with $[C_4MIm][PF_6]$ in different solvents (AcO, acetone; PC, propylene carbonate; ACN, acetonitrile; MeOH, methanol).

with organic solvents. As shown in Fig. 7, one can notice a similar nonlinearity but in opposite direction as compared with betaine dyes. The addition of small amounts of ILs causes a substantial shift of the CT absorption maximum towards lower energies, and a minimum is reached at an IL content of 0.14 mole fractions. Considering the results of using modified Nile Red to monitor the aggregation behaviour and micelle formation of ILs in aqueous solution, where Miskolezy et al. [28] found that 1-butyl-3-methylimidazolium octyl sulfate can act as a surfactant above 0.031 M critical micelle concentration, indicates the possibility of aggregation of imidazolium-based molten salts in organic solvents. In Consorti et al. [29] work the ^{1}H NMR spectroscopy, conductivity, and microcalorimetry results on 1,3-dialkylimidazolium salts in acetonitrile and chloroform were interpreted very well in frame with supramolecular aggregates in solutions. In solution the supramolecular structural organization of pure molten salt is maintained to a great extent, at least in solvents of low dielectric constant, indicating that mixtures of imidazolium-based molten salts with other solvents can be considered also as nanostructured materials.

The use of the proposed solvation model gives relatively good fits in both cases, i. e., for mixtures of ILs with methanol and with other organic solvents. The fit parameters are given in Table 2. The parameters show the tendency of ILs to solvate the betaine dye to a greater extent than the organic solvents, as well as solvent/solvent complexes better than the organic solvent – parameters $f_{2/1}$ and $f_{12/1}$, respectively, in all cases are much bigger than 1. There is no difference for methanol and acetonitrile or acetone. The situation with ethane-1,2-diol (entry 7) is different because there is a miscibility cap in the graph and thus the data are not really comparable.

One exception is propylene carbonate (PC) (entry 5), when the dye is preferentially solvated by PC as compared with the IL and bound complex ($f_{2/1} < 1$ and $f_{12/1}$ is relatively small), which needs further careful study.

The relatively small error of regression shows that the preferential solvation model of Connors and Roses can be applied to describe the experimental results of binary mixtures of ILs with organic solvents, but it needs more systematic work with different ILs (different imidazolium-based cations and different anions).

5. Conclusions

Binary mixtures of ILs with molecular solvents in principle should be better considered as solutions of salts (or electrolytes) in organic solvents, and the term “negative (positive) halochromism” for such a hypsochromic (bathochromic) shift of the UV/Vis absorption band of a dissolved compound with increasing salt concentration should be used. In binary solvent systems with participation of ILs, trends of halochromism when changing the concentration of IL are complicated because the probe dyes interact selectively with the cation/anion of an added salt and the extent of which is probe-dependent. Therefore, the determination of a kind of ”absolute polarity” of binary systems by means of different solvatochromic probe dyes seems to be principally not possible. But these dyes show the strong interaction between ILs and organic solvents in their binary mixture, which is influenced very much by the origin of the solvent.

Acknowledgements

Prof. Ch. Reichardt, University of Marburg, Germany, and Prof. Ch. H. Lochmüller, Duke University, UK, are acknowledged for their valuable comments and helpful discussion. The Estonian Science Foundation is acknowledged for financial support grant No. 5610.

[1] T. Welton, Chem. Rev. **99**, 2071 (1999); H. Olivier, J. Mol. Cat. A: Chem. **146**, 85 (1999); M. J. Earle and K. R. Seddon, Pure Appl. Chem. **72**, 1391 (2000); P. Wasserscheid and W. Keim, Angew. Chem. Int. Ed. **39**, 3772 (2000); J. F. Brennecke and E. J. Maginn, AIChE J. **47**, 2384 (2001); R. A. Sheldon, R. M. Lau, M. J. Sorgedrager, F. van Rantwijk, and K. R. Seddon, Green Chem. **4**, 147 (2002); H. Olivier-Bourbigou and L. Magna, J. Mol. Cat. A: Chem. **182 – 183**, 419 (2002); J. Dupont, R. F. de Souza, and P. A. Z. Suarez, Chem. Rev. **102**, 3667 (2002); F. van Rantwijk, R. M. Lau, and R. A. Sheldon, Trends Biotechnol. **21**, 131 (2003); J. S. Wilkes, J. Mol. Cat. A: Chem. **214**, 11 (2004); K. N. Marsh, J. A. Boxall, and R. Lichtenthaler, Fluid Phase Equil. **219**, 93 (2004).

[2] A. Wolfson, I. F. J. Vankelecom, and P. A. Jacobs, J. Organomet. Chem. **690**, 3558 (2005).

[3] C. Wakai, A. Oleinikova, M. Ott, and H. Weingärtner, J. Phys. Chem. B **109**, 17028 (2005).

[4] M. L. T. Asaki, A. Redondo, T. A. Zawodzinski, and A. J. Taylor, J. Chem. Phys. **116**, 10377 (2002).

[5] C. Reichardt, Solvents and Solvent Effects in Organic Chemistry, 3rd ed., Wiley-VCH, Weinheim 2003.

[6] M. A. Kessler and O. S. Wolfbeis, Chem. Phys. Lipids **50**, 51 (1989).

[7] J. F. Deye, T. A. Berger, and A. G. Anderson, Anal. Chem. **62**, 615 (1990).

[8] M. C. Stuart, J. C. van de Pas, and J. B. F. N. Engberts, J. Phys. Org. Chem. **18**, 929 (2005).

[9] L. Crowhurst, P.R. Mawdsley, J. M. Perez-Arlandis, P. A. Salter, and T. Welton, Phys. Chem. Chem. Phys. **3**, 2790 (2003).

[10] J. N. A. Canongia Lopez and A. A. H. Padua, J. Phys. Chem. B **110**, 3330 (2006), and references therein.

[11] A. J. Carmichel and K. R. Seddon, J. Phys. Org. Chem. **13**, 591 (2000).

[12] K. A. Fletcher, I. A. Storey, A. E. Hendricks, S. Pandey, and S. Pandey, Green Chem. **3**, 210 (2001).

[13] S. N. Baker, G. A. Baker, and F. V. Bright, Green Chem. **4**, 165 (2002).

[14] C. Reichardt, Green Chem. **7**, 339 (2005).

[15] I. Koppel, J. Koppel, and V. Pihl, Org. React. (Tartu) **21**, 98, 144 (1984).

[16] R. D. Skwierczynski and K. A. Connors, J. Chem. Soc. Perkin Trans. 2, 467 (1994).

[17] M. Roses, C. Rafols, J. Otrega, and E. Bosch, J. Chem. Soc. Perkin Trans. 2, 1607 (1995).

[18] P. Bonhote, A. P. Dias, N. Papageorgiou, K. Kalyanasudaram, and M. Grätzel, Inorg. Chem. **35**, 1168 (1996).

[19] K. Herodes, I. Leito, J. Koppel, C. Reichardt, and I. A. Koppel, J. Phys. Org. Chem. **18**, 1013 (2005).

[20] C. Reichardt, S. Asharin-Fard, and G. Schäfer, Chem. Ber. **126**, 143 (1993).

[21] K. A. Fletcher and S. Pandey, Appl. Spectrosc. **56**, 1498 (2002).

[22] M. C. Rezende, Tetrahedron **44**, 3513 (1988).

[23] K. A. Fletcher and S. Pandey, J. Phys. Chem. B **107**, 13532 (2003).

[24] H. Katayanagi, K. Nishikawa, H. Shimozaki, K. Miki, P. Westh, and Y. Koga, J. Phys. Chem. B **108**, 19451 (2004).

[25] J. M. Crosthwaite, S. N. V. K. Aki, E. J. Maginn, and J. F. Brennecke, Fluid Phase Equil. **228 – 229**, 303 (2005).

[26] K. Herodes, J. Koppel, C. Reichardt, and I. Koppel, J. Phys. Org. Chem. **16**, 626 (2003).

[27] M. J. Muldoon, C. M. Gordon, and I. R. Dunkin, J. Chem. Soc., Perkin Trans. 2, 433 (2001).

[28] Z. Miskolczy, K. Sebök-Nagy, L. Biczok, and S. Göktürk, Chem. Phys. Lett. **400**, 296 (2004).

[29] C. S. Consorti, P. A. Z.Suarez, R. F. de Souza, R. A. Burrow, D. H. Farrar, A. J. Lough, W. Loh, L. H. M. da Silva, and J. Dupont, J. Phys. Chem. B **109**, 4341 (2005).