Solvatochromic probes within ionic liquids

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Abstract. Spectroscopic studies on a set of ionic liquids were performed using different solvatochromic probe molecules. Different probes were found to characterize ionic liquids as solvents differently. Mixtures of ionic liquids with organic solvents exhibit nonlinear behaviour of polarity with composition as measured by Reichardt's dyes.

Key words: ionic liquids, binary mixtures, solvatochromic shift, Reichardt's dyes, Nile Red.

INTRODUCTION

The IUPAC recommendation for the definition of solvent polarity specifies that the polarity is the sum of all possible, nonspecific and specific, intermolecular interactions between the solute ions or molecules and solvent molecules, excluding any interactions leading to permanent chemical alteration of the ions or molecules of the solute [1]. The microenvironment sensed by solute in a solvent depends upon interactions between solute and solvent molecules (e.g., directional interactions between dipoles; inductive, dispersive, hydrogen-bonding, and charge-transfer forces, etc.), which cannot always be related to bulk properties of the solvent. Empirical scales of solvent polarity have been developed to compare different solvents according to measurable parameters for characterizing the solvent and solute interactions. The most widely used way to assess solvent polarity is by spectroscopic studies using solvatochromic dyes as probes. These are compounds for which the absorption or emission band maximum shifts according to the polarity of the solvent in which they are dissolved. The best known empirical scale of solvent polarities of this kind is the $E_T(30)$ scale based on the following expression:

$$E_T(30) = \frac{28591}{\lambda_{max}^{abs}},$$

where $E_T(30)$ is in kcal/mol, and λ_{max}^{abs} (nm) is the wavelength of the maximum of the longest wavelength of intramolecular charge-transfer (CT) π-π* absorption band. In our case the compound is the Zwitterionic 2,6-diphenyl-4-(2,4,6-triphenyl-N-pyridino)phenolate molecule [2]. This compound, known as Reichardt's betaine dye, exhibits one of the largest observed solvatochromic effects of known organic molecules. Besides this most widely used dye there are other dyes that exhibit different chemical properties needed for some solvents. Nile Red is uniquely stable in extremely acidic media and is not susceptible to a loss of molar absorptivity in the presence of acids unlike Reichardt's dye [3]. There are neutral fluorescent probe molecules that can have some additional advantages [4].

Properties like undetectable vapour pressure and ease of recovery and reuse make room temperature ionic liquids (RTILs) a "greener" alternative to volatile, toxic organic solvents [5]. Air and water stable RTILs have begun to be used as an alternative to conventional organic solvents. The most fascinating property is the "tunability" of RTILs – the possibility of influencing various physical and chemical properties by varying the RTIL structure. While the use of ionic liquids as solvents is of current commercial interest, the polarity of RTILs is still a research topic with only few data available.

RTILs are very complex liquids with an extended three-dimensional liquid structure of ionic liquids, with a supramolecular structure influenced by hydrogen bonds. Therefore it is not surprising that there are not yet definitive answers on the question of their polarity, especially by description of single macroscopic physical parameters. Carmichael & Seddon [6] made a series of measurements on solvatochromic shifts of the dye Nile Red in 1-alkyl-3-methylimidazolium ionic liquids and they concluded that ionic liquids are in the same polarity range as lower alcohols. A similar result was found by Fletcher et al. [7] using Reichardt's dye, whose calculated $E_T(30)$ values indicate the polarity of 1-butyl-3-methylimidazolium hexafluorophosphate ($C_4MIm\,PF_6$) to be similar to that of ethanol. In addition, Nile Red showed that the polarity of the solvent in the immediate vicinity of the probe is similar to 90 wt% glycerol in water (a solvent with viscosity similar to $C_4MIm\,PF_6$).

Baker et al. [8] took the multi-parameter approach showing $C_4MIm\,PF_6$ to be a remarkable solvent with no peer among the traditional organic solvents. 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 lie between those of water and acetonitrile. Most solvents possessing such low nucleophilicities are generally regarded as non-polar. However, the dipolarity/polarizability of $C_4MIm\,PF_6$ under ambient conditions is 55–95% higher than in the case of lower chain alcohols and only 10–15% below that of water or dimethyl sulphoxide, decreasing linearly with increasing temperature. There are other results confirming the complexity of the problem. Pyrene is one of the most widely used neutral fluorescence probes. Contrary to the results obtained from probe studies with Reichardt's dye, the exited state of pyrene clearly indicates a completely different microenvironment [7].

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The spectroscopic behaviour of solutes in organic solvent mixtures with ionic liquids could be of great importance. In solvent mixtures involving polar solvents, the effects of preferential solvation are anticipated at the molecular solute level [2]. The information about solvatochromism of different indicators in solvent mixtures with ionic liquids is very limited.

The polarity study reported here was undertaken with emphasis on structural features such as the effect of anion and cation choice. It is part of a larger project aimed at improving the understanding of the properties of ionic liquids. The results give direction and insight into the fine-tuning of the properties of the solvent medium which, in turn, could assist in better selection of ionic liquids (IL) with specific properties for different applications.

EXPERIMENTAL

In this study different 1-alkyl-3-methylimidazolium salts were used.
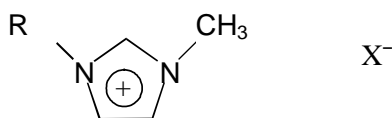
The cations were with R = C_4, C_6, C_8, and C_{10} alkyl chain lengths [C_nMIm]. The anions (X^-) were in a wide selection including the most often used hexafluorophosphate [PF_6]$^-$ and tetrafluoroborate [BF_4]$^-$ but also less common anions triflate [TfO] $CF_3SO_2^-$, nonaflate [NfO] $CF_3(CF_2)_3SO_2^-$, bis(triflyl)amide [Tf_2N] $(CF_3SO_2)_2$N$^-$, bis(pentaflyl)amide [Pf_2N] $(CF_3CF_2SO_2)_2$N$^-$, trifluoroacetate [FAc] CF_3COO^-, acetate [Ac] CH3COO$^-$, and heptafluorobutanoate [HFBc] $CF_3(CF_2)_3COO^-$. Ionic liquids under study were prepared in laboratory following the procedure published elsewhere [9]. Before experiments the RTILs were dried by vacuum, and measurements were performed immediately after each sample was removed from the vacuum. Absorption spectra were recorded on a UV–Vis diode-array spectrometer HP8453 (Waldbronn, Germany) at room temperature on wavelengths between 190 and 1100 nm. Dyes (Reichardt's dye, Sudan Black, Janus Green, Brilliant Cresyl Blue) were used as obtained from Merck (Darmstadt, Germany). Solvents were obtained from Sigma-Aldrich (Steinheim, Germany) in the form for spectroscopic use, and were used without further purification.

RESULTS AND DISCUSSION

In this study of spectroscopic properties the UV–Vis absorption spectra of other probes besides Reichardt's dyes were measured. Results are presented in Table 1. All these dyes have absorption bands in the visible light region. The absorption band shifts when moving from one solvent to another.

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Table 1. Absorption maxima (λ_{max}, nm) in solvents obtained with different dyes

Solvent	Sudan Black	Janus Green (Cl salt)	Brillant Cresyl Blue (Cl salt)	Reichardt's dye	Reichardt's dichloro-substituted dye	Nile Red
Acetonitrile	592	651	629	622	521	535
Acetone	600	645	640	653	546	532
Propylene carbonate	605	655	635	619	517	543
Water	635	615	636	453	408	
Benzene	576	579	607	812	680	
Methanol	592	653	630	515	441	553
C_4MIm PF_6	594	641	634	540	441	548

Table 1 presents absorption band wavelengths for different dyes (approximately 2 mM solution of dye) in solvents at ambient temperature ($20 \pm 1\,°C$). All they show very different band location in solvents and are hardly correlated between each other except a good correlation between Reichardt's dyes. The difference of RTILs (in this case the most popular C_4MIm PF_6 from other common organic solvents is seen already here. The results indicate different behaviour of RTILs depending on the nature of tested compounds.

Sometimes it was not possible to follow the lowest absorption maximum of Reichardt's dye 30, because the colour was bleached out. This result is consistent with protonation at the phenolic oxygen in Reichardt's dye 30 because of impurities in RTIL [8]. The dye must remain deprotonated to function as a solvatochromic indicator, in this study it was opted to use a less basic version of Reichardt's dye, the dichloro-substituted betaine dye (2,6-dichloro-4-(2,4,6-triphenyl-1-pyridinio)phenolate (Reichardt's dye 33), whose CT absorption band position has an established correlation with Reichardt's dye 30. Results of measurements for a set of RTILs are presented in Table 2. Based on these data one can say that the correlation between two different Reichardt's dyes can be followed also in the case of ionic liquids.

To these results are added measured UV–Vis cutoff wavelengths for ionic liquids, which are tabulated in Table 2 as well. Hardly any correlation can be seen between anions structure and UV absorbance cutoff wavelengths, which are in the range 230–270 nm. The trend towards the shortening of the cutoff wavelength with increasing alkyl chain length could be mentioned; however, if an experimental error for wavelength measurements of ± 1 nm is taken into consideration, the trend will become uncertain.

Information on the properties of mixtures of ionic liquids with organic solvents would be valuable. Results may suggest a possibility of changing the solvent power (solvency) of ionic liquids for organic solutes by the addition of co-solvents. Interesting results for polarity were obtained for mixtures of an ionic liquid (C_4MIm PF_6) with organic solvents. Dependence of Reichardt's dye 33 CT absorption band position on the mixture composition is illustrated by Figs. 1–3.

Table 2. Data obtained for Reichardt's dye (RD) and dichloro-substituted Reichardt's dye (RDCl) absorption wavelengths of charge transfer absorption band for different ionic liquids

| Ionic liquid	λ_{cutoff}, nm	RDCl, λ_{max}, nm	$E_T(33)$	RD, λ_{max}, nm	$E_T(30)$
C10 Pf$_2$N	231	435	65.7	540	52.9
C4 Pf$_2$N	233	454	63.0	580	49.3
C10 Tf$_2$N	232	464	61.6	nd	nd
C4 Tf$_2$N	234	454	63.0	nd	nd
C8 PF$_6$	232	442	64.7	560	51.1
C6 PF$_6$	234	437	65.4	nd	nd
C4 PF$_6$	243	441	64.8	540	52.9
C4 FAc	237	444	64.4	570	50.2
C4 Ac	258	480	59.6	nd	nd
C4 HFBc	236	480	59.6	nd	nd
C4 TfO	235	426	67.1	540	52.9
C4 NfO	234	442	64.7	nd	nd
C4 BF$_4$	248	457	62.6	nd	nd

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nd – not determined.

This non-linear behaviour points to 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 measured solvatochromic shift is the indicator solvation microsphere, which can differ considerably from that of the bulk. On the other hand, it makes clear that the solvatochromic shift of probe molecules does not provide an unambiguous measurement of the "polarity" of a solvent mixture, and one must consider the wider definition of polarity mentioned at the beginning. Already small amounts of added ionic liquids cause a substantial shift on the CT adsorption maximum towards smaller wavelengths, and the minimum is reached at ionic liquid concentration 0.05–0.06 mol%.
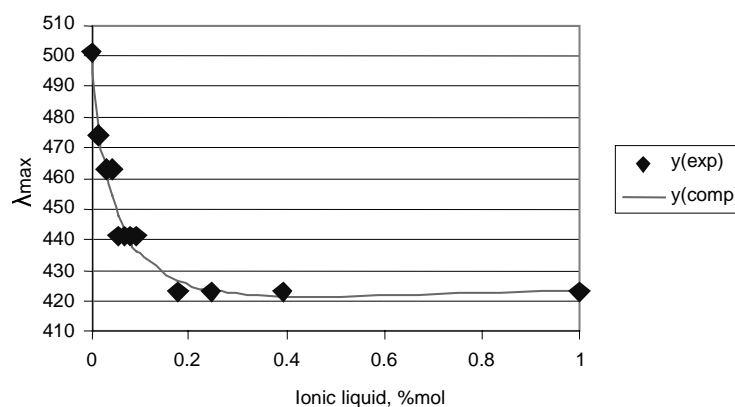
Fig. 1. Change of solvatochromic shift of Reichardt's chloro dye in a mixture of C$_8$MIm PF$_6$ and acetonitrile.
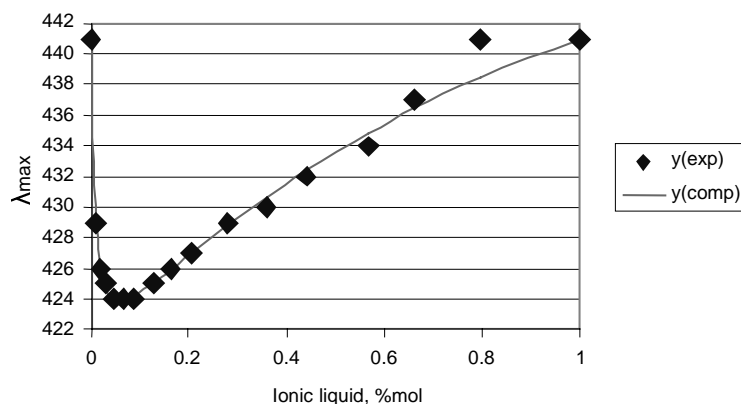
Fig. 2. Change of solvatochromic shift of Reichardt's chloro dye in a mixture of C_4MIm PF$_6$ and methanol.
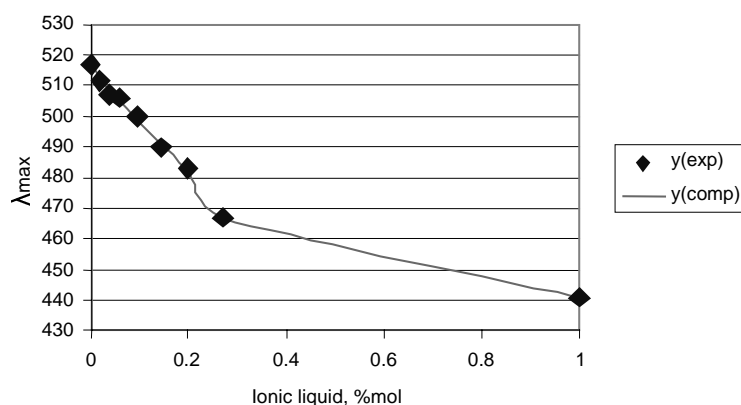
Fig. 3. Change of solvatochromic shift of Reichardt's chloro dye in a mixture of C_4MIm PF$_6$ and polypropylene carbonate.

Various approaches have been proposed to deal with solvatochromism of indicators in binary solvent mixtures. One possible model for the preferential solvation based on the two-step solvent exchange equilibrium proposed by Skwierczynski & Connors [10] is used for interpretation.

The E_T of the mixed solvent is calculated as an average of the E_T values of two pure solvents S1 and S2 and the solvent formed by the interaction of solvents 1 and 2, S12 in the sphere of the solvation of the indicator:

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

where x_1^S, x_2^S, x_{12}^S are mole fractions of solvents S1, S2, and S12, respectively, in the sphere of solvation.

In this model the general equation that relates the E_T of a binary mixture to the E_T of two pure solvents, the preferential solvation parameters, and the solvent composition can be derived as follows:

$$y = \frac{y_1(1-x)^2 + y_2 A x^2 + BC(1-x)x}{(1-x)^2 + A x^2 + B(1-x)x},$$

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

Two parameters describe the two-step solvent exchange equilibrium in this Skwierczynski and Connors model, the preferential solvation parameters $f_{2/1}$ and $f_{12/1}$ measure the tendency of the solute to be solvated by solvents S2 and S12 with reference to solvent S1 solvation. The third unknown parameter is E_{T12} – band maxima of the formed solvent. The unknown parameters that minimize the squared residuals of E_T values of each binary solvent system studied were calculated by nonlinear regression. Calculations were done in MS Excel with the function Solver, which uses Generalized Reduced Gradient (GRG2) nonlinear optimization code developed by Frontline Systems, USA.

Results are given in Table 3. Parameters show the tendency of ionic liquids to solvate the dye in a greater extent than the organic solvent and according to the model the solvent formed by the interaction of an ionic liquid and an organic solvent is very polar. Propylene carbonate is an exception. The relatively small error of regression shows that formally the preferential solvation model can be applied to describe the experimental results of binary mixtures of ionic liquids and organic solvents.

For comparison the mixture of an ionic liquid ($C_4MIm\ PF_6$) with methanol but using Nile Red dye was studied. In this case also the nonlinearity, although in the other direction, can be followed (Fig. 4). Small amounts of added ionic liquid cause a substantial shift on the CT adsorption maximum towards higher wavelengths, and the maximum is reached at ionic liquid concentration 0.14 mol%.

Table 3. Parameters of solvation model derived experimental data (SD – standard deviation of regression, n – number of data points)

Solvent system	$y_1 = E_{T1}$	$y_2 = E_{T2}$	$A = f_{2/1}$	$B = f_{12/1}$	$C = E_{T12}$	SD	n
$C_8MIm\ PF_6$ and acetonitrile	501	423	48.4	25.5	414	1.1	12
$C_4MIm\ PF_6$ and methanol	441	441	249	133	420	0.2	17
$C_4MIm\ PF_6$ and poly-propylene carbonate	517	441	0.1	1.2	360	0.5	9
$C_4MIm\ PF_6$ and methanol*	553	547	42.7	14.8	569	0.1	17

* Nile Red was used as solvatochromic dye.
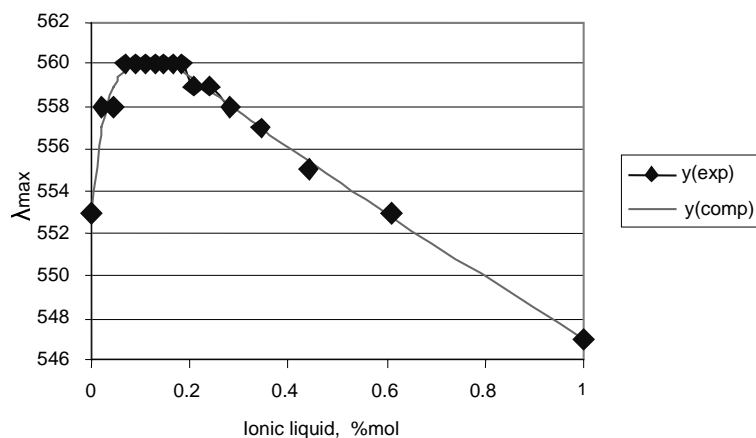
Fig. 4. Change of solvatochromic shift of Nile Red dye in a mixture of $C_4MIm\ PF_6$ and methanol.

CONCLUSIONS

These studies confirmed that measurements of single macroscopic physical parameters or functions thereof cannot adequately describe solvent polarity. Solvatochromism is an especially complex phenomenon in mixed binary solvents when one component is ionic liquid.

ACKNOWLEDGEMENTS

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Solvatokroomsed indikaatorid ioonsetes vedelikes

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On uuritud erinevate solvatokroomsete indikaatorite käitumist ioonsetes vedelikes. On leitud, et erinevad indikaatorid kirjeldavad ioonseid vedelikke väga erinevalt. Ioonsete vedelike segudes orgaaniliste lahustitega, kus indikaatoriteks on Reichardti värvid ja niiluse punane, muutub lahuse polaarsus koostise muutumisel mittelineaarselt.