



Contents lists available at SciVerse ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq



Q51 Correlation of molecular structure and polarity of ionic liquids

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ARTICLE INFO

12
13 Article history:
14 Received 28 March 2013
15 Accepted 30 June 2013
16 Available online xxxxx

17
18
19
20 Keywords:
21 Solvatochromism
22 Ionic liquids
23 Kamlet–Taft parameters
24 Imidazolium
25 Polarity

ABSTRACT

The empirical Kamlet–Taft solvent parameters for hydrogen bond donating (HBD) ability (α), hydrogen bond 26 accepting (HBA) ability (β), and dipolarity/polarisability (π^*) have been determined for 102 ionic liquids 27 (ILs). α , β , and π^* have been measured by means of the solvatochromic methods utilizing three specific 28 dyes Fe(phen)₂(CN)₂ (**Fe**), 3-(4-amino-3-methyl-phenyl)-7-phenyl-benzo-[1,2-*b*:4,5-*b'*]-difuran-2,6-dione 29 (**ABF**) and 4-*tert*-butyl-2-(dicyanomethylene)-5-[4-(diethylamino)benzylidene]- Δ^3 -thiazoline (**Th**) each solely 30 sensitive to one of the Kamlet–Taft parameter. 31
Different types of ILs with various cation structure such as 1,3-dialkyl imidazolium and 2- and 4-,5-methyl 32 substituted derivatives, pyridinium, tetraalkylammonium, trialkylsulphonium, and tetraalkylphosphonium 33 were used. In conjunction to the [C₄mim] cation, more than 20 various established anions, such as halides, 34 tetrafluoroborate, dicyanamide, were considered in this study. The frontiers of HBA ability strength of the an- 35 ions are marked by the specific anions chloride (N₃⁻) (large β) and azide PF₃(C₂F₅)₃⁻ (lowest β). 36
The linear intercorrelation between α and β is clearly evidenced, which shows that anion and cation interact 37 with each other, for each type of IL used. Also correlation of molecular structure of the cation and the HBD 38 ability can be recognized and supported by results from NMR spectroscopy. The interpretation of π^* is still 39 not satisfied because dipolarity and polarisability of each IL obviously contribute in different proportions to 40 the value. 41

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Q647 1. Introduction

48 Ionic liquids (ILs), although known for a long time, have awakened 49 the interest of many scientists in recent years as reaction media for 50 “green chemistry”. Therefore the use of solvatochromic dyes for the 51 determination of empirical polarity parameters of these liquids has 52 attracted the attention of physical organic chemists. Firstly, the state 53 of the art regarding this problem has been presented by C. Reichardt 54 in a very clear review article [1]. C. Chiappe and D. Pieraccini collected 55 the first set of solvatochromic polarity parameters of more ionic liq- 56 uids, in order to compare them to the chemical reactivities [2].

57 In the last decades, as well as Reichardt's E_T(30) solvent parameter 58 [1,3–6], Kamlet–Taft solvent parameters have been established for 59 liquids as well as ILs, which allow a differentiated polarity assignment 60 to be made [3–13].

61 The Kamlet–Taft equation, in its simple form, is:

$$(XYZ) = (XYZ)_0 + a\alpha + b\beta + s(\pi^* + d\delta). \quad (1)$$

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63 XYZ is the result of a solvent-dependent process; (XYZ)₀ is a reference 64 system, for example the gas phase or a non-polar solvent. α describes the 65 hydrogen bond acidity, β represents the hydrogen bond basicity and π^* 66

the dipolarity/polarisability of the solvent. The solvent-independent 67 correlation coefficients a, b, s, and d reflect the influence of the respec- 68 tive parameters on the result (XYZ) (Eq. (1)) of the chemical process. 69 For solvatochromic data (XYZ) corresponds to $\tilde{\nu}_{\max, \text{probe}}$. The param- 70 eter δ is a polarisability correction factor, which is set at 0.5 for halogenat- 71 ed solvents, and at 1.0 for aromatic solvents [7]. This is a problem, as it 72 does not permit a differentiated separation of the polarisabilities of 73 solvents. A solution of this problem would be the availability of 74 polarisability-sensitive solvatochromic probes with respect to the 75 Catalán scale of polarisability (SP), which is still not established for ILs 76 [14–21]. See later the resume in Conclusion and outlook (Section 4). 77

Furthermore, S. Lee has presented an expanded LSE basis set for 78 ILs, where the solute parameter of the dissolved substance is taken 79 into account in the LSE relationship [22]. 80

The parameter sets of polarity parameters for ILs, which have been 81 presented in the literature up to 1995, showed that singular linear 82 relationships between different solvatochromic dyes (Reichardt's 83 dye, 1-pyrenealdehyde, Nile red, dansyl amide) can deliver, according to 84 Eq. (2), different values for polarity parameters within the framework of 85 the E_T(30) scale for a defined IL, such as 1-butyl-3-methylimidazolium 86 hexafluorophosphate [C₄mim-PF₆] as an example [23–28]. The dif- 87 ferences were explained using “additional effects” such as viscosity, 88 polarisability or specific hydrogen bonds. The last of these should, 89 however, actually be already integrated in singular LSE determina- 90 tions, as the E_T(30) parameter is preferentially a function of α and 91 π^* (see Eq. (2)) [29]. 92

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$$E_T(30) = 31.2 + 15.2 \cdot a + 11.5 \cdot \pi^* \quad (2)$$

$$n = 166, r^2 = 0.96$$

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How far the influence of the β -term on the $E_T(30)$ parameter must be taken into account, is discussed in our own preliminary work for the LiCl/*N,N*-dimethylacetamide (DMAc)-solvent system [30]. The strong HBA ability of the chloride anion in LiCl/DMAc ($\beta = 2.01$) has a significant influence on the decrease of electron affinity of the pyridinium moiety of the dye and thus $E_T(30)$ apparently increases. This feature is non-proportional with respect to polarity according to Eq. (2). Thus, another indicator for HBD ability is required for ILs.

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The deciding scientific question still remains, namely can the empirical polarity parameters of the Kamlet–Taft equation be determined for ILs really independently of the probe molecule used?

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One of the problems to be solved in this connection is how the polarity term π^* allows itself to be decoupled from those of the basicity (β) or the acidity (α), as both of these are strongly associated with each other for ILs as a starting point. There are interesting discussions on this problem, which show, particularly for coumarins, that a (influence of α) and s (influence of π^*) are strongly associated with each other [31]. The problem is, that established probe molecules for π^* reflect proportions of contributions of dipolarity and polarisability differently for protic and non-protic solvents [32]. Thus a specific dye is required which shows a linear function of the UV/vis absorption energy from π^* for all classes of solvents including protic and non-protic ones. This problem could be overcome by applying a thiazoline dye [33] which has been used for ILs in this work.

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The important point is whether a parameter α , β , or π^* , respectively, is a reasonable function of the molecular structure of the IL. Initially, Huddleston et al. discussed the fact that the α -value decreases with an increase in the β -value for 1,3-dialkylimidazolium [23].

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β -Values of ILs are moderate; they are above all determined from the basicity of the counter-ion. β -Values of most ILs are in the range of 0.2 to 0.8, that is, in the region of moderately strongly HBA-solvents, such as acetonitrile ($\beta = 0.38$) [1,2,32]. The very weak coordination of the anion to the cation is also actually one reason why these compounds are liquid at room temperature. The largest known β -value for an anion is actually for the naked fluoride ion at $\beta = 2.95$ [34]. So far, HBA-properties have been determined UV/vis spectroscopically by using NH-active *p*-nitroanilines or Cu(tmen)(acac)⁺ [7,30,35–38].

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In the recent years we have shown that a set of three independent solvatochromic probes (Scheme 1) are suitable to determine the Kamlet–Taft parameters α , β , and π^* of imidazolium based ILs independent of each other by linear solvation energy (LSE) relationships [33,35–38].

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The three solvatochromic probes Fe(phen)₂(CN)₂ (**Fe**), 3-(4-amino-3-methyl-phenyl)-7-phenyl-benzo-[1,2-*b*:4,5-*b'*]-difuran-2,6-dione (**ABF**) and 4-*tert*-butyl-2-(dicyanomethylene)-5-[4-(diethylamino)benzylidene]- Δ^3 -thiazoline (**Th**), respectively, have been carefully

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investigated using various organic solvents. The original Kamlet–Taft solvent parameters serve as the reference systems for the ILs.

It must be noted, that pure Fe(phen)₂(CN)₂ crystals are insoluble in most of the ILs considered. For this purpose, the closely related complex [Fe(phen)₂(CN)₂]⁺ ClO₄[−] (**Fe**⁺) has been found suitable as an apparent probe. The Fe(III)-complex undergoes immediately reduction to Fe(II) during the dissolving process in ILs [36]. Therefore, Fe(phen)₂(CN)₂ is the actual solvatochromic probe and therefore mentioned in Scheme 1. For experimental details see Refs. [35–38].

The methodology of polarity measurements of ILs has been explained and outlined in several specific publications [35–40]. The aim of this work is to show that this methodology is not only useful for imidazolium ILs but also for a wide variety of other types of ILs which differ significantly in their molecular structure.

Are there structural polarity correlations observable? To answer this question a systematic solvatochromic study of the probes in various ILs has been performed.

The following question stands in focus of this review work:

Which influence of the following moiety of the molecular structure of the ILs has an effect on each of the Kamlet–Taft parameter α , β , and π^* ?

- the Anion X[−]
- molecular composition of the cation (imidazolium, tetraalkylammonium, tetraalkylphosphonium, trialkylsulphonium, picolinium, pyridinium, pyrrolidinium)
- the length of *n*-alkyl chains R [Rmim]X ILs (R = *n*-Butyl, *n*-Hexyl, *n*-Octyl, *n*-Decyl)
- the HBD hydrogen atoms in the 2, 4, and 5 position, respectively, of 1,3-dialkylimidazolium ILs

The molecular structures of the cations and corresponding abbreviations used are shown in Scheme 2.

2. Methodology

The LSE correlations have been calculated using well behaved regular organic solvents as the reference system. For α only HBD solvents (protic solvents) were used for the correlation analyses [35–38,41].

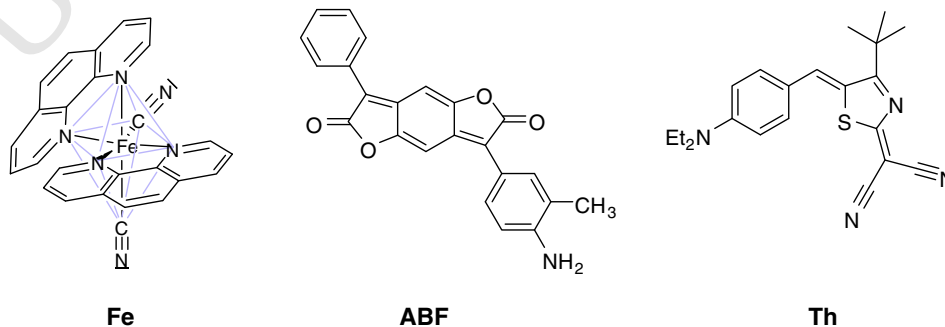
$$\alpha = -7.26 + 0.45 \tilde{\nu}_{\max, \text{Fe}} \left[10^3 \text{ cm}^{-1} \right] \quad (3)$$

$$n = 19; r^2 = 0.90; \text{sd} = 0.18, F < 0.0001$$

For β , the one parameter approach is used despite the fact, that the correlation coefficient is rather wrong. However, the significance is excellent [37].

$$\beta = -3.84 + 0.20 \tilde{\nu}_{\max, \text{ABF}} \left[10^3 \text{ cm}^{-1} \right] \quad (4)$$

$$n = 35; r^2 = 0.76; \text{sd} = 0.15, F < 0.0001$$



Scheme 1. Solvatochromic dyes Fe(phen)₂(CN)₂ (**Fe**), 3-(4-amino-3-methyl-phenyl)-7-phenyl-benzo-[1,2-*b*:4,5-*b'*]-difuran-2,6-dione (**ABF**) and 4-*tert*-butyl-2-(dicyanomethylene)-5-[4-(diethylamino)benzylidene]- Δ^3 -thiazoline (**Th**) used in this work for the determination of Kamlet–Taft parameters of ILs.

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