Molecular solvent/ionic liquid binary mixtures: designing solvents based on the determination of their microscopic properties

P. M. Mancini[a]; G. G. Fortunato[a]; L. R. Vottero[a]

[a] Departamento de Química, Área Química Orgánica, Facultad de Ingeniería Química, Universidad Nacional del Litoral, Santiago del Estero 2829, (3000) Santa Fe, República Argentina

PLEASE SCROLL DOWN FOR ARTICLE

MOLECULAR SOLVENT/IONIC LIQUID BINARY MIXTURES: DESIGNING SOLVENTS BASED ON THE DETERMINATION OF THEIR MICROSCOPIC PROPERTIES

P.M. MANCINI*, G.G. FORTUNATO and L.R. VOTTERO

Departamento de Química, Área Química Orgánica, Facultad de Ingeniería Química, Universidad Nacional del Litoral, Santiago del Estero 2829, (3000) Santa Fe República Argentina

This work aims at analyzing the microscopic features of binary solvent systems formed by a molecular solvent (dimethylsulfoxide or acetonitrile or methanol) and an ionic liquid cosolvent (ethylammonium nitrate). The empirical solvatochromic solvent parameters $E_T(30)$, π^*, α and β were determined from the solvatochromic shifts of adequate indicators. The behavior of the solvent systems was analyzed according to their deviation from ideality. The study pays particular attention to the identification of solvent mixtures with relevant solvating properties. We have focused our attention on the most remarkable microscopic property of the explored systems, acidity, selecting three mixtures with particular hydrogen bond donating characteristics.

Keywords: Molecular solvent; Ionic liquid; Binary mixtures; Microscopic properties; Solvatochromic parameters

INTRODUCTION

Molecular solvents are the usual media where physical and chemical processes in solution take place. From the combination of pure solvents in binary mixtures, the availability and diversity of media were strongly increased [1]. In the last decade, attention has been drawn to the use of room temperature ionic liquids as solvents for different applications [2]. Moreover, some binary mixtures of molecular solvents with ionic liquids have been investigated [3].

To evaluate liquid behavior as a solvent, it is of interest to quantify its most relevant microscopic properties which determine how it will interact with potential solutes. An appropriate method to study solute–solvent interactions is the use of solvatochromic indicators which reflect the specific and nonspecific solute–solvent interactions on the UV–Vis spectral shifts. In this sense, a number of empirical solvatochromic parameters

---

*Corresponding author. Tel.: +54-0342-4571164 (2539); Fax: +54-0342-4571162; E-mail: pmancini@fiqus.unl.edu.ar

have been proposed to quantify the molecular-microscopic solvent properties. In most cases only one indicator is used to build the respective scale. Among them, $E_T(30)$ parameter was proposed by Dimroth and Reichardt to measure solvent dipolarity/polarizability, though it is also sensitive to hydrogen-bond donor capacity [1]. On the other hand, the Kamlet, Abboud and Taft multiparametric approach assigns different parameters to each particular solvent characteristics (dipolarity/polarizability π^*, hydrogen-bond donor acidity α and hydrogen-bond acceptor basicity β) [4].

At this point, the challenge is to develop a "desired solvent", with particular microscopic properties required for each application. In this sense, the discussion about the notion of "property of a mixed solvent" and whether such a property can be defined, not to say be measured, by means of chemical probes has been proposed [5,6].

The main purpose of this work is to investigate solvent systems which result from the basis of binary mixtures formed by a molecular solvent and an ionic liquid cosolvent, in order to modulate the most relevant microscopic properties which determine how a single mixture will interact with potential solutes.

So far, the aims are: (i) to quantify the microscopic solvent properties measuring a set of empirical solvatochromic parameters for molecular solvent/ionic liquid systems; (ii) to analyze the response patterns *property vs. solvent composition* focusing on the changes in the ability to develop the most relevant interactions (hydrogen-bond acidity, hydrogen-bond basicity and polarity); and (iii) to identify relevant mixtures paying particular attention to pronounced changes in the microscopic solvent features.

RESULTS AND DISCUSSION

Three kinds of binary solvent systems were selected for this analysis: (i) molecular solvent with hydrogen bond acceptor ability/ionic liquid cosolvent; (ii) molecular solvent with hydrogen bond acceptor and hydrogen bond donor ability/ionic liquid cosolvent; and (iii) molecular protic solvent/ionic liquid cosolvent. The molecular solvents included in the analysis are dimethylsulfoxide (DMSO, $E_T^N = 0.44$, $\pi^* = 1.00$, $\alpha = 0.02$, $\beta = 0.76$) as a hydrogen bond acceptor solvent, acetonitrile (AcN, $E_T^N = 0.46$, $\pi^* = 0.75$, $\alpha = 0.19$, $\beta = 0.40$) as a hydrogen bond acceptor/hydrogen bond donor solvent, and methanol (MeOH, $E_T^N = 0.76$, $\pi^* = 0.60$, $\alpha = 0.98$, $\beta = 0.66$) as a protic solvent [1,4]. Ethylammonium nitrate [EtNH$_3$][NO$_3$] (EAN, $E_T^N = 0.95$, $\pi^* = 1.12$, $\alpha = 1.10$, $\beta = 0.46$) is the ionic liquid used as the cosolvent, which is an N–H hydrogen bond donor [6]. In all the cases, the pure component part of the mixtures are able to form associated species through hydrogen-bonding interactions.

For the explored solvent mixtures, the empirical parameters E_T^N, π^*, α and β are calculated from the wavenumbers of the maximum of absorbance of the corresponding chemical probes at 25°C. The calculated microscopic properties, which were systematically determined over the full solvent composition range, are presented in Table I. In order to analyze the changes in the microscopic solvent properties of the mixtures when the ionic liquid is added to the molecular solvent, the plots of E_T^N, π^*, α and β parameters against the EAN mole fraction are presented in Figs. 1–3.

DMSO/EAN System

According to the shapes of the curves, π^* and β values vary almost ideally with changes in the cosolvent concentration (in the case of π^* the plot shows an S-shaped curve).

TABLE I   Empirical solvent parameters for molecular solvent/EAN binary mixtures, measured at 25°C

| Molecular solvent		EAN molar fraction									
		0.05	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
DMSO	E_T^N	0.71	0.74	0.72	0.90	0.93	0.95	0.97	0.97	0.97	0.96
	π^*	1.04	1.05	1.05	1.05	1.05	1.06	1.07	1.07	1.10	1.13
	β	0.76	0.76	0.72	0.70	0.66	0.60	0.61	0.60	0.65	0.51
	α	0.57	0.65	0.87	0.99	1.08	1.12	1.16	1.15	1.13	1.11
AcN	E_T^N	0.94	0.95	0.96	0.97	0.97	0.96	0.97	0.97	0.97	0.97
	π^*	0.84	0.87	0.92	0.95	1.01	1.06	1.09	1.09	1.12	1.16
	β	0.44	0.47	0.52	0.54	0.56	0.56	0.55	0.51	0.51	0.50
	α	1.32	1.32	1.29	1.27	1.23	1.18	1.19	1.15	1.13	1.10
MeOH	E_T^N	0.90	0.91	0.94	0.95	0.96	0.96	0.96	0.96	0.96	0.96
	π^*	0.84	0.89	0.96	0.99	1.04	1.06	1.08	1.08	1.11	1.13
	β	0.65	0.63	0.59	0.57	0.53	0.52	0.50	0.51	0.49	0.48
	α	1.20	1.19	1.20	1.20	1.18	1.16	1.15	1.14	1.12	1.08
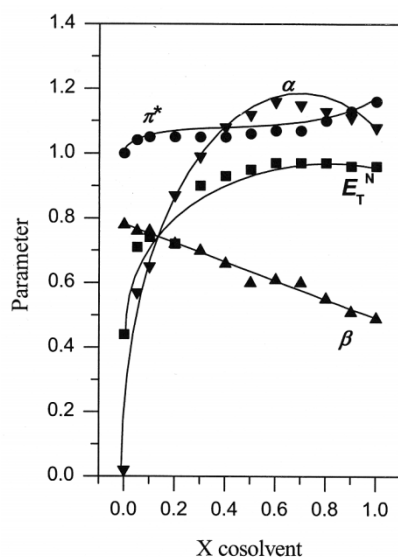
FIGURE 1.   Plots of solvatochromic solvent parameters vs. cosolvent mole fraction for DMSO/EAN system.

In contrast to this, E_T^N and α parameters are always higher than the values expected for the ideal behavior. Moreover, some parameter values are higher than those of the pure solvents showing a synergistic effect on the property. This effect is particularly marked on the acidity α. Of particular interest is the mixed-solvent corresponding to $X_{EAN} = 0.6$, which exhibits high dipolarity/polarizability ($\pi^* = 1.07$), moderate hydrogen bond basicity ($\beta = 0.61$) and high hydrogen bond acidity ($\alpha = 1.16$), even higher than the one corresponding to EAN.

AcN/EAN System

By adding small quantities of the ionic liquid, the E_T^N parameter increases abruptly and then remains constant at values close to the value of pure EAN. As can be seen,
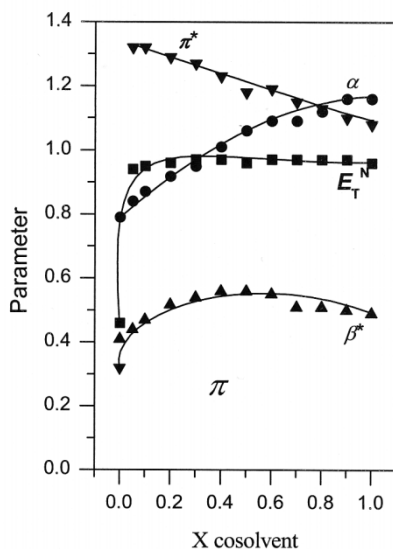
FIGURE 2   Plots of solvatochromic solvent parameters vs. cosolvent mole fraction for AcN/EAN system.
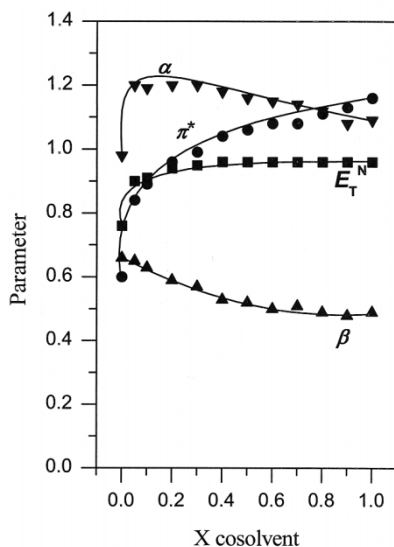
FIGURE 3   Plots of solvatochromic solvent parameters vs. cosolvent mole fraction for MeOH/EAN system.

π^* values exhibit positive deviations from the ideal behavior, while β values show a synergistic effect on the property (the basicity of the pure components has similar property values). In all cases, α values are higher than those of the pure solvents, manifesting synergism on the acidity. Focusing on $X_{EAN} = 0.05$ binary mixture, the dipolarity/polarizability and basicity are close to those of AcN since their hydrogen bond donor ability is higher than that corresponding to the EAN.

MeOH/EAN System

The addition of EAN to MeOH rapidly increases E_T^N and π^* values producing a positive deviation from the ideal behavior. The β property exhibits small negative deviations from ideality, a fact which suggests that this property is dominated by the anion. The behavior of α is similar to the one observed for mixtures with AcN, exhibiting synergism on the property values. Special interest should be given to EAN-poor mixtures since the dipolarity/polarizability and acidity are maximized whereas the basicity is minimized.

In order to understand the changes in the microscopic properties, the formation of inter-solvents associated species through specific molecular interactions has to be considered. Moreover, in mixed solvents, different (in terms of type and strength) and often simultaneous solute–solvent interactions can be established.

By comparing the response patterns of microscopic properties to changes in solvent mixtures composition (reflected by the shape of the curves presented in Figs. 1–3) the following observations can be made:

(1) All explored systems show basically similar $E_T(30)$ response patterns: the parameter values abruptly increase with small increases in cosolvent content exhibiting positive deviations from the ideal behavior. Moreover, low synergistic effects on the property are observed at some mixtures of DMSO and AcN systems. The halochromism of phenoxide dyes, probes which mainly reflect the acidity of solvent, has received particular attention [1,7]. The specific hydrogen-bonded interactions between the highly dipolar ground-state of the Reichardt's dye and the ethylammonium cation is responsible for the striking shifts in the transition energy of the indicator in mixtures of EAN and organic solvents [3,6]. The π^* parameter response patterns suggest preferential solvation of the indicator by the more dipolar/polarizable solvent (except for EAN-rich mixtures of DMSO/EAN system). This behavior can be related to the influence of the possible contamination of π^* parameter values (which mainly reflect the nonspecific interactions with the solvents) with specific interactions: the indicator N,N-diethylnitroaniline can provide contaminated dipolarity/polarizability values because it is capable of accepting hydrogen bonds [8]. At first, the shape of the curves suggests that the behavior of mixtures with DMSO are dominated by the nonspecific interactions, whereas the behavior of mixtures with AcN and MeOH are influenced by specific interactions. This observable effect is greater in the less dipolar/polarizable and more acidic solvent MeOH.

(2) The property β clearly exhibits different response patterns for the explored systems: no general trend can be discerned. The EAN is moderately basic as expected since the anion is the conjugated base of the strongly acidic ethylammonium cation. The results suggest that the behavior of mixtures with DMSO and MeOH (which are the more basic of the explored molecular solvents) shows the influence of the anion, whereas the synergism on β values exhibited by AcN-system indicates the presence of complexes which add enhanced basicity to the mixtures.

(3) The dependent parameter α behaves in an unexpected way. The general tendency is for solvent mixtures to have a higher ability to donate a hydrogen atom than the pure solvent part of the mixtures, exhibiting strong synergistic effects on the property. The degree of synergism is AcN > MeOH > DMSO. In a first instance, it appears that the hydrogen bond donor ability of the cation increases in EAN

diluted mixtures. This fact can be related, on the one hand, to the abrupt increments observed in $E_T(30)$ values when small amounts of EAN are added to molecular solvents due to a preferential interaction of the ionic liquid with the ground state of the betaine dye [3(a)]. On the other hand, it could be related to the structural features of the mixtures. In connection with this, previous studies on the characterization of mixed solvents by means of empirical solvatochromic parameters report that binary mixtures of molecular solvents in which the components are solvent-active to one another forming complexes or associated species through hydrogen-bonding interactions exhibit synergism on the microscopic properties in some cases [9].

Binary mixtures of solvents can be deliberately used to improve their chemical characteristics to affect reaction rates, mechanisms, selectivity, chemical equilibria, position and intensity of spectral absorption bands and liquid chromatographic separations. In connection with this, we have focused our attention on the most remarkable microscopic property of the explored systems (the acidity) in order to select mixtures of particular compositions with relevant microscopic characteristics. We propose individual solvent mixtures, which were selected from the explored systems on the basis of their hydrogen-bonding ability, as liquids suitable to provide a medium with particular solvating properties (Table II).

In Fig. 4, the selected liquids and the pure solvents in the three-dimensional solvatochromic space are presented in order to point out the differences. Obviously,

TABLE II   Selected mixed solvents and their microscopic molecular solvent properties

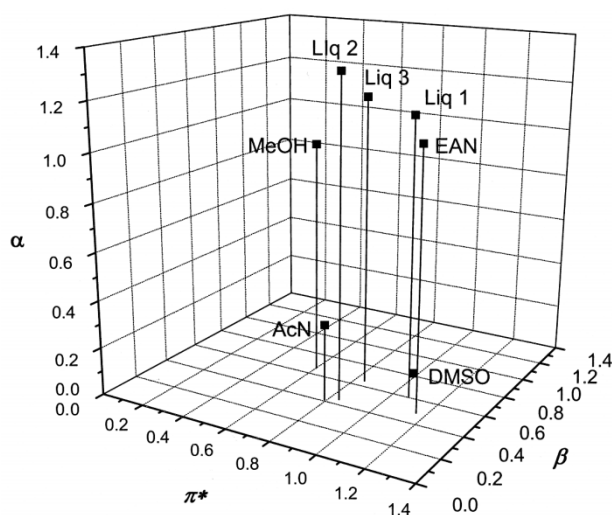| Solvent	Composition	E_T^N	π^*	β	α
Liquid 1	$X_{DMSO}0.6/X_{EAN}0.4$	0.97	1.07	0.61	1.16
Liquid 2	$X_{AcN}0.95/X_{EAN}0.05$	0.94	0.84	0.44	1.32
Liquid 3	$X_{MeOH}0.95/X_{EAN}0.05$	0.90	0.84	0.65	1.20

FIGURE 4   The selected liquids and the pure solvents presented in the three-dimensional solvatochromic space.

the differences appear more relevant in the case of the molecular solvents DMSO and AcN.

CONCLUSIONS

In the case of the explored systems, the addition of the ionic liquid to the molecular solvent increases abruptly the ability to donate a hydrogen atom to the formation of a hydrogen bond. Moreover, the general tendency is for mixtures to exhibit α values even higher than those of pure EAN reflecting synergistic effects on the microscopic property. This fact can be related to the formation of hydrogen bonded complexes on the solvation shell.

The results presented here show that it is possible to prepare strongly hydrogen bond donating solvent mixtures of the molecular solvent/ionic liquid type, as a 'new solvent' with particular microscopic solvent feature. In the first instance, these observations could be extended to similar systems.

It should be noted that one advantage of this type of mixtures is that the ionic liquid need not be a liquid at room temperature, but soluble in the selected molecular solvent.

EXPERIMENTAL

Ethylammonium nitrate (EAN) was prepared from a concentrated aqueous solution of ethylamine (70%) and nitric acid (70%) [10]. The solvatochromic indicators and the molecular solvents were prepared and/or purified as reported previously [6].

The spectroscopic data were obtained with a Perkin-Elmer Lambda 40 UV–Vis spectrophotometer, equipped with a thermostatic cell holder. The binary mixtures and the indicator solutions were prepared just prior to use.

The $E_T(30)$ and E_T^N parameters are calculated according to the procedure reported elsewhere [1]. The microscopic properties π^*, β and α were calculated according to the general expressions collected by Marcus [11]:

(i)   Indicator: N,N-diethyl-4-nitroaniline (I), $\pi^* = 0.314[27.52 - \nu_I]$
(ii) Indicator: 4-nitroaniline (II), $\beta = 0.358[31.10 - \nu_{II}]$
(iii) $\alpha = 0.0692 E_T(30) - 2.090 - 0.900\ \pi^* - 0.147\beta$

References

[1] (a) C. Reichardt (1990). *Solvent and Solvent Effects in Organic Chemistry*, 2nd Edn. Verlag Chemie, Weinheim; (b) C. Reichardt (1994). *Chem. Rev.*, **94**, 2319; (c) G. Wypych editor (2001). *Handbook of Solvents*. Chem Tec Publishing, Canada.

632   P.M. MANCINI *et al.*

[2] (a) J.D. Holbrey and K.R. Seddon (1999). *Clean Products and Processes*, **1**, 223; (b) T. Welton (1999). *Chem. Rev.*, **99**, 2071; (c) P. Wassescheid and W. Keim (2000). *Angew. Chem. Int. Ed. Engl.*, **39**, 3772; (d) H. Z. Zhao (2003). *Phys. Chem. Liq.*, **41**, 545.

[3] (a) S.K. Poole, P.H. Shetty and C.F. Poole (1989). *Anal. Chim. Acta.*, **218**, 241; (b) I.M. Herfort and H. Schneider (1991). *Liebigs Ann. Chem.*, 27; (c) K.A. Fletcher and S. Pandey (2003). *J. Phys. Chem. B*, **107**, 13532; (d) K.A. Fletcher and S. Pandey (2002). *Appl. Spectrosc.*, **56**, 266; **56**, 1498;

[4] (a) M.J. Kamlet and R.W. Taft (1976). *J. Am. Chem. Soc.*, **98**, 377; (b) R.W. Taft and M.J. Kamlet (1976). *J. Am. Chem. Soc.*, **98**, 2886; (c) M.J. Kamlet, J.L. Abboud and R.W. Taft (1977). *J. Am. Chem. Soc.*, **99**, 6027.

[5] (a) Y. Marcus (1994). *J. Chem. Soc. Perkin Trans.*, **2**, 1015; (b) Y. Marcus (1991). *J. Chem. Soc. Faraday Trans.*, 1339.

[6] (a) P.M. Mancini, C. Adam, A. del C. Pérez and L.R. Vottero (2000). *J. Phys. Org. Chem.*, **13**, 221; (b) P.M. Mancini, A. del C. Pérez and L.R. Vottero (2003). *Phys. Chem. Liq.*, **41**, 45.

[7] L. Crowhrst, P.R. Mawdsley, J.M. Perez-Arlandis, P.A. Salter and T. Welton (2003). *Phys. Chem. Chem. Phys.*, **5**, 2790.

[8] (a) C. Reichardt, S. Asharin-Fard and G. Schaefer (1993). *Chem. Ber.*, **126**, 143; (b) S.P. Zanotto, M. Seremin, C. Machado and M.C. Rezende (1993). *J. Phys. Org. Chem.*, **6**, 637.

[9] (a) C. Laurence, M. Berthelot, M. Lucon and D.G. Morris (1994). *J. Chem. Soc. Perkin Trans.*, **2**, 491; (b) J. Catalán (1995). *J. Org. Chem.*, **60**, 8315; (c) P.M. Mancini, A. del C. Pérez and L.R. Vottero (2001). *J. Sol. Chem.*, **30**, 695.

[10] (a) M. Rosés, C. Ràfols, J. Ortega and E. Bosch (1995). *J. Chem. Soc. Perkin Trans.*, **2**, 1607; (b) P.M. Mancini, A. Terenzani, C. Adam, A. del C. Pérez and L.R. Vottero (1999). *J. Phys. Org. Chem.*, **12**, 713.

[11] C.F. Poole, B.R. Kersten, S.S.J. Ho, M.E. Coddens and K.G. Furton (1986). *J. Chrom.*, **352**, 407.

[12] Y. Marcus (1993). *Chem. Soc. Rev.*, 409.