

Characterization of Lactam-Containing Binary Solvents by Solvatochromic Indicators

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Preferential solvation and intermolecular interactions of the solvatochromic indicators 4-nitroanisole, 4-nitroaniline, 4-nitrophenol, and Reichardt's dye is studied at 298.15 K in the binary solvents 2-pyrrolidinone/water, *N*-methylpyrrolidinone/water, and 2-pyrrolidinone/*N*-methylpyrrolidinone. From the experimental data the Reichardt's and Kamlet–Taft parameters were evaluated for the mixed solvents. A preferential solvation model was applied to analyze the solvation effect of the indicator by the different solvents used, and from these data useful information about solute–solvent and solvent–solvent interactions was deduced. Comparison with other thermophysical data reveals a relationship between the solvatochromic parameters and the partial molar volumes, mainly in water-containing solvents.

Introduction

Compounds containing the amide group are of great interest in connection with a number of structural problems in molecular biology and constitute a simple model system for proteins and peptides.¹ The basic element of this class of compounds, the very common in nature –NH–CO– peptide bond, contains the acidic NH and the basic CO groups and adopts a planar configuration in peptide chains. Due to its donor–acceptor properties, amides can interact with other amide molecules through N–H···O=C Hydrogen bonds. Of particular interest are lactams, which consist of cyclic amides composed of a ring of methylene groups linked to the N and C atoms of a peptide bond.¹ Lactams are an interesting class of amides not extensively studied; despite their use as solvents and biologic applications, their solution properties are still not well understood. *N*-Methylpyrrolidinone, with weakly basic behavior, is a stable, polar, aprotic solvent used in operations such as recovery of hydrocarbons, paint stripping, and cleaning;² water/lactam mixtures also are useful solvents in industrial applications.^{3,4}

Solvatochromism can be defined as the effect ascribed to the changes in the UV–vis absorption spectra caused by a change in solvent polarity. Solvent polarity involves the overall solvation capability of solvents and depends on the interactions between molecules. The differential solvation observed in mixed solvents depends on the intermolecular forces between the solute and the surrounding solvent molecules and is responsible for the changes in UV–vis spectra of solvatochromic dyes. Solvatochromic parameters are used to establish empirical solvent polarity scales often needed to properly select adequate media for chemical reactions;⁵ due to the ease of experimental determination, solvatochromic parameters are widely used as a measure of solvent–solvent and solute–solvent interactions. Among the different solvatochromic parameters available, those suggested by Reichardt⁶ and Kamlet–Taft⁷ are most used.^{5,8}

In this work, the structure and interactions of solvents containing the lactams 2-pyrrolidinone (PYR) and *N*-methylpyrrolidinone (NMP) were studied; although rigid, nonassociating

polar species in nature,⁹ some variable aggregation degree in NMP mixtures by dipole–dipole and/or H-bonding interactions is feasible due to the H-bonding acceptor ability of the CO oxygen.^{10,11} PYR, on the other hand, is self-associated by H-bonding to a noticeable extent, forming mainly dimers;⁹ this association, however, is strongly influenced by the particular cosolvent used.^{11,12} Some different solvent polarity parameters have been used to characterize the structure, polarity, and H-bond features of lactam-containing solvents. The solvatochromic indicators 4-nitroanisole (I), 4-nitroaniline (II), 4-nitrophenole (III), and 2,6-diphenyl-4-(2,4,6-triphenylpyridinio)-phenolate (IV, Reichardt's dye) were used to study the PYR/water, NMP/water, and PYR/NMP binary solvents.

Experimental Section

Materials. Ultrapure water (Milli-Q, Millipore, 18.2 mΩ·cm resistivity) and the solvents PYR (Fluka, 99.8%) and NMP (Fluka, 99.9%), of the highest purity commercially available, were used without further purification. The purity of the solvents was assessed by GC with a Perkin-Elmer 990 gas chromatograph, equipped with a Hewlett-Packard 3390A integrator, and also by comparing the densities and speeds of sound (measured with an Anton Paar DSA 5000 density and sound meter), viscosities (Anton Paar AMV 200 viscometer), and refractive indices (Leica AR 600 refractometer) with literature values. The pure liquids were degassed with ultrasound for several days before use and kept out of the light over Fluka Union Carbide 0.4 nm molecular sieves. The solvatochromic indicators 4-nitroanisole (Riedel Haën, 99%), 4-nitroaniline (Riedel Haën, 99%), 4-nitrophenole (Riedel Haën, 99%) and Reichardt's dye (Aldrich, 95%) were also used without further purification.

Instruments and Procedures. The binary liquid mixtures were prepared by syringing amounts and weighed to $\pm 10^{-5}$ g with a Mettler AT 261 Delta Range balance, into suitably stoppered bottles. The mixtures were completely miscible over the whole composition range. Proper small amounts of the indicator were added to each binary mixture up to 1×10^{-4} M concentration. UV–vis spectral curves were recorded using a Hewlett-Packard 8453 spectrophotometer (± 0.2 nm), and the

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TABLE 1: Experimental Wavenumbers, ν , and Solvatochromic Parameters of the Indicators I (4-Nitroanisole), II (4-Nitroaniline), III (4-Nitrophenol), and IV (Reichardt's Dye) in Pure Solvents at 298.15 K

solvent	$10^4\nu/\text{cm}^{-1}$				solvatochromic parameter				
	I	II	III	IV	π	β	α	$E_T/\text{kJ mol}^{-1}$	E_T^N
PYR	31.81	25.89	23.73	16.78	0.99	0.76	0.38	200.7	0.53
								202.5 ^a	0.547 ^a
NMP	31.86	25.96	22.97	14.79	0.97	0.76	0.03	176.9	0.36
					0.92 ^b	0.77 ^b		176.82 ^b	0.355 ^b
W	31.52	26.31	24.9	22.07 ^a	1.11	0.47	1.28	264.0 ^a	1.00 ^a
					1.13 ^c	0.50 ^c	1.26 ^c		

^a Reference 6. ^b Reference 8. ^c Reference 13.

temperature of the 1 cm quartz cells was controlled to ± 0.1 K using a Hewlett-Packard 89090A Peltier. The spectra were recorded using as a blank samples without indicator, and afterward recording the spectra of a sample of the same concentration containing the corresponding indicator. Maxima at the highest wavelength absorption bands were obtained by mathematical smoothing of the experimental absorption data using a Gaussian curve-fitting peak equation.¹³

Results

The UV-vis absorption spectra of the indicator recorded in a set of solvents of distinct polarity may change in shape, intensity, and wavenumbers due to solute-solvent interactions; this solvent effect can be evaluated by the changes in the spectral curves observed by changing the nature of the solvent. Table 1 lists the measured wavenumbers in pure solvents of the indicators used, Table 2 those in PYR/water binary mixtures, Table 3 those in NMP/water, and Table 4 those in PYR/NMP; the data for pure water and the Reichardt's dye were taken from the literature.⁶ Figure 1 shows the wavenumber vs x_1 plots for all four probes in the three mixed solvents used. Figure 2 plots the π , β , and α Kamlet-Taft solvatochromic parameters vs x_1 data pairs, the former being evaluated according to eqs 1–3,¹⁴ and the Reichardt's parameters E_T and E_T^N determined according to eqs 4 and 5,^{1,6}

$$\pi = 0.427(34.12 - \nu_I) \quad (1)$$

$$\beta = 0.358(31.10 - \nu_{II}) - 1.125\pi \quad (2)$$

$$\alpha = -0.186(10.91 - \nu_{IV}) - 0.72\pi \quad (3)$$

$$E_T = 119629\nu_{IV} \quad (4)$$

$$E_T^N = \frac{E_T - 30.7}{32.4} \quad (5)$$

Substitution of these values into eq 6 allows evaluation of the so-called mixing solvatochromic parameters, which account for the variation of the ΔP ($P = \pi, \beta, \alpha$, or E_T^N) mixing parameters compared to those of pure solvents,^{2,15}

$$\Delta P = P - x_1P_1 - x_2P_2 \quad (6)$$

where P and P_i are the corresponding parameters of the mixture and pure solvent, respectively, and x_i is the mole fraction, Figure 3 plots the variation of these mixing properties with mole fraction.

TABLE 2: Experimental Wavenumbers, ν , of Indicators I (4-Nitroanisole), II (4-Nitroaniline), III (4-Nitrophenol), and IV (Reichardt's Dye) in x_1 PYR + $(1 - x_1)$ W Binary Solvents at 298.15 K

I		II		III		IV	
x_1	$10^4\nu/\text{cm}^{-1}$	x_1	$10^4\nu/\text{cm}^{-1}$	x_1	$10^4\nu/\text{cm}^{-1}$	x_1	$10^4\nu/\text{cm}^{-1}$
0.0243	31.49	0.0221	26.03	0.0223	24.77	0.0999	20.16
0.0522	31.48	0.0487	25.91	0.0480	24.64	0.1987	19.42
0.0723	31.47	0.0712	25.83	0.0707	24.56	0.2974	18.85
0.0992	31.47	0.1022	25.75	0.0961	24.47	0.3991	18.35
0.1962	31.49	0.1999	25.71	0.2024	24.29	0.4935	18.00
0.2951	31.53	0.2984	25.74	0.2980	24.20	0.6005	17.67
0.3951	31.58	0.4003	25.78	0.4046	24.14	0.6963	17.41
0.4927	31.62	0.5032	25.81	0.5206	24.07	0.8037	17.17
0.6010	31.67	0.6112	25.83	0.6039	24.02	0.9074	16.95
0.7041	31.71	0.7084	25.85	0.6997	23.97		
0.8022	31.76	0.8039	25.86	0.8007	23.90		
0.9018	31.79	0.9029	25.88	0.9017	23.82		

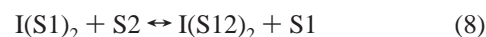
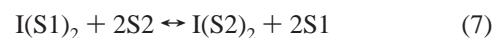
TABLE 3: Experimental Wavenumbers, ν , of Indicators I (4-Nitroanisole), II (4-Nitroaniline), III (4-Nitrophenol), and IV (Reichardt's Dye) in x_1 NMP + $(1 - x_1)$ W Binary Solvents at 298.15 K

I		II		III		IV	
x_1	$10^4\nu/\text{cm}^{-1}$	x_1	$10^4\nu/\text{cm}^{-1}$	x_1	$10^4\nu/\text{cm}^{-1}$	x_1	$10^4\nu/\text{cm}^{-1}$
0.0102	31.48	0.0239	25.94	0.0240	24.72	0.1008	19.57
0.0239	31.46	0.0487	25.80	0.0492	24.54	0.2043	18.59
0.0732	31.44	0.0733	25.73	0.0734	24.43	0.3012	17.79
0.0913	31.44	0.0987	25.69	0.1085	24.31	0.4011	17.16
0.1840	31.45	0.2215	25.67	0.2168	24.10	0.5050	16.61
0.2889	31.49	0.3043	25.70	0.3193	23.98	0.5997	16.13
0.3938	31.55	0.4054	25.73	0.4182	23.87	0.7036	15.77
0.4774	31.59	0.5035	25.76	0.5230	23.76	0.8005	15.40
0.5907	31.66	0.6074	25.80	0.6229	23.66	0.8744	15.15
0.6877	31.70	0.7028	25.84	0.7133	23.57		
0.7754	31.74	0.7865	25.88	0.7949	23.45		
0.8946	31.80	0.8975	25.92	0.9056	23.22		

TABLE 4: Experimental Wavenumbers, ν , of Indicators I (4-Nitroanisole), II (4-Nitroaniline), III (4-Nitrophenol), and IV (Reichardt's Dye) in x_1 PYR + $(1 - x_1)$ NMP Binary Solvents at 298.15 K

I		II		III		IV	
x_1	$10^4\nu/\text{cm}^{-1}$	x_1	$10^4\nu/\text{cm}^{-1}$	x_1	$10^4\nu/\text{cm}^{-1}$	x_1	$10^4\nu/\text{cm}^{-1}$
0.0969	31.87	0.1014	25.93	0.0911	23.18	0.1006	15.29
0.1895	31.86	0.1939	25.91	0.1942	23.34	0.1959	15.63
0.2910	31.84	0.2880	25.90	0.2880	23.43	0.2906	15.86
0.3915	31.83	0.3854	25.89	0.3850	23.49	0.3938	16.05
0.4964	31.82	0.4908	25.88	0.4893	23.54	0.4926	16.20
0.5957	31.82	0.5895	25.88	0.5868	23.58	0.5981	16.34
0.6789	31.82	0.6758	25.88	0.7082	23.62	0.6937	16.45
0.7963	31.82	0.7919	25.88	0.7939	23.65	0.7976	16.59
0.9028	31.82	0.9057	25.88	0.8972	23.69	0.8952	16.70

Preferential Solvation Model. Interest on preferential solvation in mixed solvents has increased noticeably in recent years. The interpretation of the main features requires simple models that may describe the behavior of solvatochromic indicators and the structure of binary solvents; these models may provide valuable solute-solvent and solvent-solvent structural information.¹⁶ Preferential solvation was analyzed in this work with the Buhvestov¹³ and Skwierczynski¹⁷ models, which are based on a simple exchange of two solvents according to eqs 7 and 8,



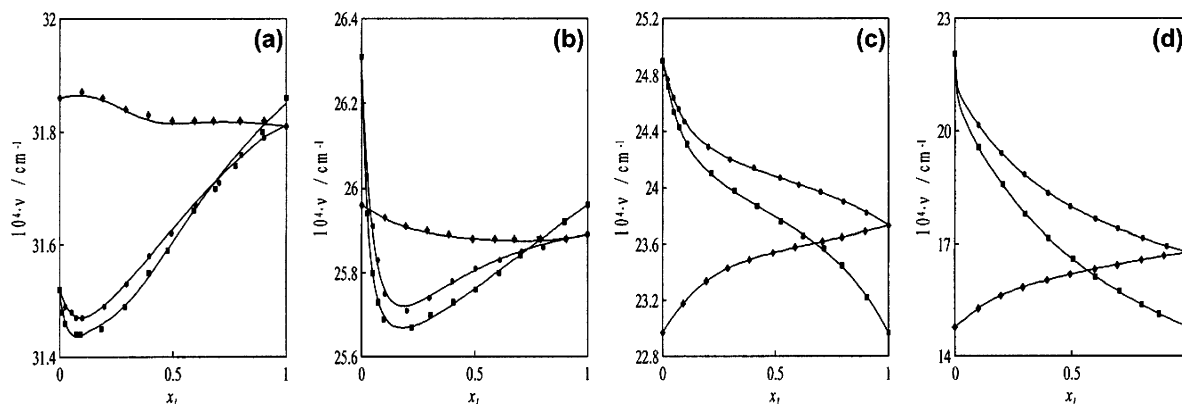


Figure 1. Wavenumbers of the absorption maxima of (a) 4-nitroanisole, (b) 4-nitroaniline, (c) 4-nitrophenol, and (d) Reichardt's dye, in x_1 PYR + $(1 - x_1)$ W (●), x_1 NMP + $(1 - x_1)$ W (■), and x_1 PYR + $(1 - x_1)$ NMP (◆) binary mixtures at 298.15 K. Continuous lines obtained from the preferential solvation model according to eqs 9–13.

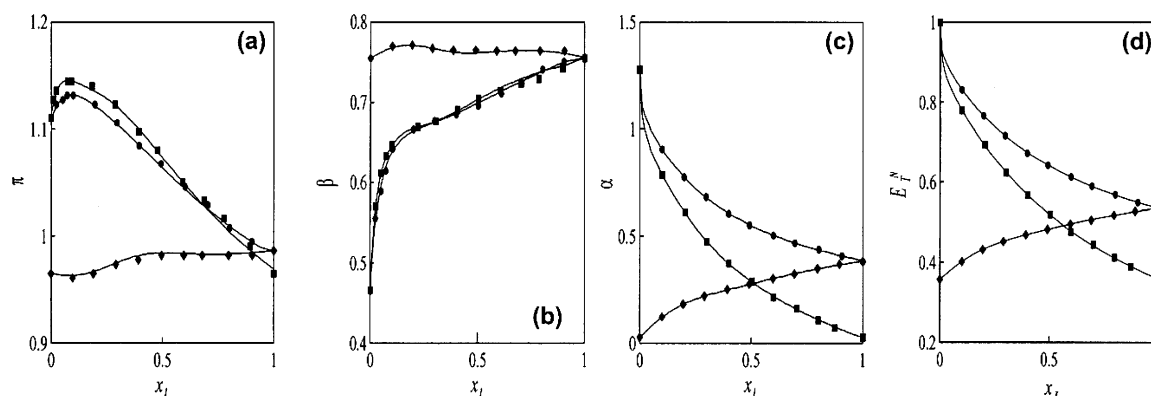


Figure 2. Solvatochromic parameters (a) π , (b) β , (c) α , and (d) E_T^N , calculated according to eqs 1–5. Symbols as in Figure 1.

where I stands for the corresponding indicator, S1 and S2 for the pure solvents, and S12 for the mixed solvent. $I(S1)$ represents the indicator solvated by the S1 component, $I(S2)$ by the S2 component, and $I(S12)$ by the S12 mixed solvent. Equation 7 reflects the total exchange of solvent 1 by solvent 2 in the solvation sphere of the indicator, and eq 8 corresponds to the exchange by the mixed solvent. The constants $f_{2/1}$, corresponding to the process described by eq 7, and $f_{12/1}$, corresponding to that by eq 8, can be evaluated using eqs 9 and 10,

$$f_{2/1} = \frac{x_2^S/x_1^S}{(x_2/x_1)^2} \quad (9)$$

$$f_{12/1} = \frac{x_{12}^S/x_1^S}{x_2/x_1} \quad (10)$$

where x_i^S is the mole fraction of the solvent i in the solvation sphere of the indicator, and x_i represents the bulk mole fraction. The $f_{12/2}$ parameter, corresponding to the 12/2 exchange, was evaluated with eq 11.

$$f_{12/2} = \frac{f_{12/1}}{f_{2/1}} \quad (11)$$

Thus the solvatochromic mixture property Y can be evaluated from those of pure solvents, Y_1 and Y_2 , according to eqs 12 and 13:

$$\Delta Y = \frac{kf_{2/1}(x_2)^2[(1 - x_2)^2 + f_{12/1}(1 - x_2)x_2/2]}{[(1 - x_2)^2 + f_{2/1}(x_2)^2 + f_{12/1}(1 - x_2)x_2]^2} \quad (12)$$

$$Y = \frac{Y_1(1 - x_2)^2 + Y_2f_{2/1}(x_2)^2 + Y_{12}f_{12/1}(1 - x_2)x_2}{(1 - x_2)^2 + f_{2/1}(x_2)^2 + f_{12/1}(1 - x_2)x_2} + \Delta Y \quad (13)$$

The wavenumbers recorded for each solvent/indicator couple were correlated according to eqs 12 and 13, and the parameters were evaluated by a global minimization procedure introducing a simulated annealing algorithm that has been applied efficiently to some chemical and engineering problems;¹⁸ the results are reported in Table 5, the continuous lines in Figures 1–3 showing the values of the corresponding property provided by the model.

Discussion

The solvatochromic probes used in this work have different features. 4-Nitroanisole displays positive solvatochromism (increasing solvent polarity causes a bathochromic shift of the absorption maxima)⁷ owing to the high polarity of the excited state relative to the ground state;¹⁹ this probe has often been regarded as sensitive to solvent polarity–polarizability, and insensitive to specific H-bonding with other solvents.^{6,7,19} 4-Nitroaniline and 4-nitrophenol also display positive solvatochromism; in addition to their polarity–polarizability sensitivity, these probes also are sensitive to the H-bond acceptor (HBA), and H-bond donor (HBD) solvent ability, respectively.^{14,15,19} Reichardt's dye displayed negative solvatochromism due to the solvation of its highly dipolar ground state and the increasingly less dipolar Franck–Condon excited state, with an increase in solvent polarity;⁶ likewise, this probe was sensitive to solvent polarity–polarizability and HBD ability.^{6,13}

The thermophysical properties of the PYR/W and NMP/W mixed solvents indicate strong solvation by H-bonding;^{7,11} hence

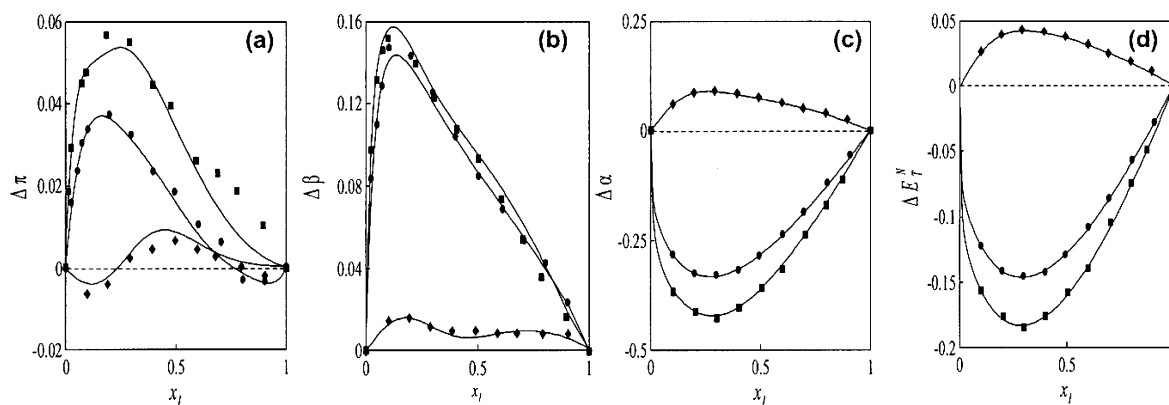


Figure 3. Mixing solvatochromic parameters (a) $\Delta\pi$, (b) $\Delta\beta$, (c) $\Delta\alpha$, and (d) ΔE_T^N , calculated according to eq 6. Symbols as in Figure 1.

TABLE 5: Parameters and Standard Deviation, σ , Obtained by Application of the Preferential Solvation Model, Eqs 9–13, to the Experimental Wavenumbers, $10^4\nu$ (cm^{-1}), of Indicators I (4-Nitroanisole), II (4-Nitroaniline), III (4-Nitrophenol), and IV (Reichardt's dye) in $x_1\text{PYR} + (1 - x_1)\text{W}$, $x_1\text{NMP} + (1 - x_1)\text{W}$, and $x_1\text{PYR} + (1 - x_1)\text{NMP}$ Binary Solvents at 298.15 K

	mixture	Y_1	Y_2	Y_{12}	$f_{2/1}$	$f_{12/1}$	$f_{12/2}$	k	σ
I	PYR + W	31.82	31.52	30.73	0.094	0.259	2.755	0.660	0.005
	NMP + W	31.85	31.51	29.99	0.054	0.194	3.593	1.573	0.010
	PYR + NMP	31.81	31.86	35.33	0.453	0.015	0.033	-0.197	0.003
II	PYR + W	25.89	26.30	25.75	0.062	0.671	10.823	-1.648	0.013
	NMP + W	25.96	26.31	25.51	0.012	0.856	71.333	1.193	0.005
	PYR + NMP	25.89	25.96	25.86	0.582	4.963	8.527	0.134	0.002
III	PYR + W	23.73	24.90	24.14	0.124	2.677	21.589	1.127	0.005
	NMP + W	22.97	24.90	23.96	0.143	3.313	23.168	1.362	0.010
	PYR + NMP	23.73	22.97	23.29	0.284	0.902	3.176	1.085	0.002
IV	PYR + W	16.79	22.07	21.10	0.001	0.381	381.000	0.000	0.012
	NMP + W	14.80	22.07	20.66	0.002	0.448	224.000	0.000	0.026
	PYR + NMP	16.79	14.79	14.75	0.117	0.456	3.897	2.727	0.010

these lactams strongly interact with water, giving rise to a pronounced hydration effect. Although self-association of the PYR dimers still remains in the bulk PYR/W solvent, heteroassociation yields the formation of 1:2 PYR:W aggregates.⁷ The NMP/W solvent also gives rise to 1:2 NMP:W aggregates,¹¹ but in contrast with the low association degree reported for NMP,^{2,20} these aggregates are short-lived species.

The wavenumbers of the three binary systems exhibit a complex behavior for all four indicators. 4-Nitroanisole shows a pronounced minimum in the water-rich region (Figure 1a); this probe displays positive solvatochromism due to the polarity–polarizability effect. The minima recorded were ascribed to the enhancement in the water-rich regions of the water structure upon lactam addition, with the result of a higher solvent polarity–polarizability. The PYR/NMP solvent showed no noticeable variation with composition, and the polarity–polarizability effect was similar to that observed in the mixture across the full composition range. The observed increase in the absorption maxima of the pure solvents according to the preferential solvation model was in the order $\text{W} < \text{PYR} \cong \text{NMP}$ (Table 5), and the increase for mixed solvents in the order $\text{NMP/W} < \text{PYR/W} < \text{PYR/NMP}$; therefore pure PYR and pure NMP displayed similar polarity–polarizability effects, although somewhat lower compared to pure W. Mixed NMP/W displays strong polarity–polarizability compared to PYR/W, and even stronger compared to PYR/NMP; this effect, however, was higher for lactam/W solvents, as inferred from the Y_{12} value, which was lower than the Y_1 and Y_2 values of the pure solvents. The PYR/NMP system, with higher Y_{12} solvatochromic property, displayed somewhat lower polarizability.

The $f_{2/1}$ parameters of 4-nitroanisole indicate that hydration is not preferential in lactam/W solvents, but this effect increases in the order $\text{NMP/W} < \text{PYR/W}$. The small $f_{2/1}$ values deduced

indicate that the probe is preferentially solvated by the lactam. Likewise, the $f_{12/1}$ and $f_{12/2}$ parameters reveal that this indicator is not preferentially solvated by the mixed solvent; instead, only some preferential solvation referred to water is remarkable. For lactam/W systems (the two solvents displayed close polarizability) 4-nitroanisole becomes preferentially solvated by the lactam referred to water. For mixed PYR/NMP lactams, 4-nitroanisole is preferentially solvated by NMP, no preferential solvation being observed compared to pure PYR or pure NMP.

4-Nitroaniline was sensitive to both HBA solvents and polarity–polarizability effect; it displayed a minimum for PYR/W and NMP/W in the water-rich region, whereas for PYR/NMP only a slight decreasing profile appears (Figure 1b). The wavenumbers recorded in pure PYR and pure NMP, close to each other, were somewhat low compared to pure W (Table 5), the HBA ability being in the order $\text{PYR} \cong \text{NMP} > \text{W}$. The strong minima in the water-rich regions and the shift in wavelengths observed for PYR/W and NMP/W mixtures show that enhancement of the water structure upon lactam addition increases the HBA solvent ability, but this decreases for increasing lactam contents. The preferential solvation parameters indicate that, in lactam/W solvent, 4-nitroaniline is preferentially solvated by the lactam (low $f_{2/1}$), and by the lactam/W mixed solvent (low $f_{12/1}$ and high $f_{12/2}$). For PYR/NMP the high $f_{12/1}$ and $f_{12/2}$ values show that the indicator is preferentially solvated by the mixed solvent compared to the pure components.

4-Nitrophenol (Figure 1c) is sensitive to HBD solvents and polarity–dipolarizability effects, the wavenumbers of pure solvents being in the order $\text{NMP} < \text{PYR} < \text{W}$ and those for the mixed solvent being intermediate. An analysis of the preferential solvation parameters show that in lactam/W systems the probe was preferentially solvated by the mixed solvent

compared to pure W. In PYR/NMP preferential solvation by the mixed solvent also occurs.

Reichardt's dye (Figure 1d) is particularly sensitive to HBD solvents and polarity–polarizability effect and displays strongly negative solvatochromism; hence, in the pure solvents the HBD ability, as for 4-nitrophenole, follows the same order as the wavenumbers: NMP < PYR < W. The wavenumbers in the three mixed solvents studied are intermediate to those of the pure components and follow the order PYR/NMP < NMP/W < PYR/W and so does the HBD ability. An analysis of the preferential solvation parameters shows that this probe is preferentially solvated by the lactam and the mixed solvent, as inferred from the very low $f_{2/1}$ and the very high $f_{12/2}$ values. For PYR/NMP the indicator is preferentially solvated by the mixed solvent compared to pure NMP.

The Kamlet–Taft parameter π for lactam/W (Figure 2) indicates that polarity–polarizability increases with the water content; a maximum at $x_1 = 0.06$ appears due to reinforcement of the water structure at low lactam concentrations, this effect being only slightly greater for NMP compared to PYR. The parameter π varies linearly for PYR/NMP, and the polarity–polarizability effect in the mixture was not very different from that in the pure components. The parameter β , which is a measure of the HBA solvent ability, decreased for lactam/W with an increase in the water content, and for PYR/NMP it was nearly linear, though somewhat greater compared to lactam/W. The α and E_T^N parameters measure the HBD solvent ability. HBD ability increased in lactam/W with the water content (no maximum); although HBD also increased in PYR/NMP with the PYR content, it was lower than for lactam/W.

The solvatochromic parameter $\Delta\pi$ calculated with eq 6 was positive for lactam/W, showing a maximum in the water-rich region, and a S-shaped profile for PYR/NMP with negative sign in the NMP-rich region. Reinforcement of the water structure by addition of small lactam amounts produces an increase in polarity–polarizability of the solvent mixture in the water-rich edges. On the contrary, for PYR/NMP addition of small PYR amounts produces a slight decrease in polarity–polarizability. $\Delta\beta$ was positive for the three binary systems (Figure 3b). For lactam/W the observed decrease in the β parameter reveals that the HBA ability decreases with the W content; however, the pronounced maxima in water-rich zones show that HBA was always greater than in the additive case. The behavior of $\Delta\alpha$ and ΔE_T^N is parallel to β : positive values for PYR/NMP and negative for lactam/W follow. Positive β values indicate preferential solvation of the probe by the more polar component, and negative values preferential solvation by the less polar component;² hence these indicators are preferentially solvated by the lactam in lactam/W, and by NMP in the PYR/NMP mixtures.

Conclusions

In PYR/W and NMP/W mixtures a strong enhancement of the water structure by lactam addition is observed in the water-rich region, a result consistent with the behavior of partial molar volume.¹¹ This heteroassociation leads to a pronounced decrease in polarity and to an increasing HBA and HBD ability of the lactam/W solvents. For PYR/NMP the mixing does not substantially change the properties of the mixed solvent compared with pure components.

Solute–solvent interactions showed with the different probes that in lactam/W and PYR/NMP mixed solvents dipolar sensitive molecules such as 4-nitroanisole become preferentially solvated

by the lactam. On the other hand, 4-nitroaniline, 4-nitrophenole, and Reichardt's dye which, in addition to dipolarity–polarizability, are sensitive to HDA, HBD, and HBD, respectively, become preferentially solvated by the mixed solvents in the lactam/W and PYR/NMP systems.

List of Symbols

- x_i = mole fraction of the i solvent
- x_i^S = mole fraction of i solvent in the solvation sphere of the indicator
- ν = wavenumber
- π = Kamlet–Taft parameter calculated for 4-nitroanisole according to eq 1
- β = Kamlet–Taft parameter calculated for 4-nitroaniline according to eq 2
- α = Kamlet–Taft parameter calculated for Reichardt's dye according to eq 3
- E_T = Reichardt parameter calculated for Reichardt's dye according to eq 4
- E_T^N = Reichardt normalized parameter for Reichardt's dye according to eq 5
- ΔP = mixing solvatochromic parameter according to eq 6, with $P = \pi, \beta, \alpha$, or E_T^N
- f_{ij} = constant of the exchange process of j by i in the solvation sphere of the indicator, eqs 9–11
- k = proportionality constant in eq 13
- I = 4-nitroanisole
- II = 4-nitroaniline
- III = 4-nitrophenole
- IV = Reichardt's dye
- HBA = Hydrogen bond acceptor basicity
- HBD = Hydrogen bond donor acidity

Uncertainties

- $x_i = \pm 10^{-4}$
- $\nu/10^{-4} \text{ cm}^{-1} = \pm 10^{-2}$
- $\pi = \pm 10^{-2}$
- $\beta = \pm 10^{-2}$
- $\alpha = \pm 10^{-2}$
- $E_T = \pm 10^{-2}$
- $E_T^N = \pm 10^{-2}$
- $\Delta P = \pm 10^{-2}$

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