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Solvation of *o*- and *p*-Nitroanilines in Some Organic Solvents at 25°C

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From the experimental solubility measurements of *o*-nitroaniline (ONA) and *p*-nitroaniline (PNA) in the organic solvents acetonitrile (MeCN). N-methylformamide (NMF), ethanol (EtOH), N-N, dimethylformamide (DMF), propylene carbonate (PC), dimethyl sulphoxide (DMSO), and N-methylpyrrolidone (NMePy), the free energies of solvation ($\Delta G°$), free energies of transfer ($\Delta G_t°$) from water to the organic solvents for both solutes and the hydrogen bonding free energies ($\Delta G°_{H\text{-}bond.}$) for ONA in the organic solvents were evaluated.

INTRODUCTION

Free energy of solvation gives us good information about solute-solvent[1-3], solvent-solvent[4-6] and solute-solute[7-11] interactions. This work concentrates with the solute-solute interactions of the organic molecules *o*-nitroaniline (ONA) and *p*-nitroaniline (PNA) in some organic solvents. For inorganic salts, the solute-solute interactions can be expressed by the activity coefficient values, which is not permitted in the case of neutral organic molecules. The aim of the present work is to evaluate the free energies of solvation of both *o*-nitroaniline (ONA) & *p*-nitroaniline (PNA) in the organic solvents under consideration and investigate the solute-solute interactions of ONA.

EXPERIMENTAL

The ONA and PNA used were of the type Cambrian Chemicals. The organic solvents MeCN, EtOH, DMF and DMSO were from BDH Co., whereas the other solvents were from Merck (Zur Analyse) Co. The solubility measurements of the saturated solutions of ONA and PNA in the organic solvents under consideration were done experimentally by measuring their absorbance using Jobin Yvon JV 101 spectrophotometer in ethanol. These were achieved by evaporating the saturated solutions under vacuum in a closed vessel till dryness, dissolving the residue in ethanol, measuring the absorbance and estimating the solubilities using a calibration curve.

RESULTS AND DISCUSSION

From the experimental molal solubilities (S) of ONA and PNA listed

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in Table 1, the free energies of solvation were estimated[4] from Eq. 1

$$\Delta G^\circ = -2.303\ RT \log S \qquad (1)$$

where $-\log S = pK$.

Also the free energies of transfer of ONA and PNA from water to the organic solvents were evaluated on applying Eq. 2 and their results are tabulated also in Table 1.

$$\Delta G_t^\circ = \Delta G_s^\circ - \Delta G_w^\circ \qquad (2)$$

where ΔG_s^0 and ΔG_w^0 are the free energies of solvation of solutes in the organic solvents and water, respectively.

TABLE 1
SOLUBILITIES, FREE ENERGIES OF SOLVATION OF ONA & PNA AND THE HYDROGEN BONDING FREE ENERGIES OF TRANSFER OF ONA IN SOME ORGANIC SOLVENTS UNDER CONSIDERATION

Solvent	ONA				
	Solubility (S) in molal scale	pK	ΔG° (in KJ mole^{-1})	ΔG_t°	$\Delta G^\circ_{H\text{-bond}}$
MeCN	1.734×10^{3}	−3.239	−18.485	−34.499	−12.344
NMF	1.215×10^{3}	−3.085	−17.606	−33.619	−10.232
EtOH	18.44	−1.266	−7.225	−23.238	−4.416
DMF	1.998×10^{3}	−3.301	−18,839	−34.852	−10.084
PC	2.613×10^{2}	−2.417	−13.794	−29.808	−8.310
DMSO	1.892×10^{3}	−3.277	−18.702	−34.716	−9.822
NMePy	2.587×10^{3}	−3.413	−19.478	−35.492	−10.736
H_2O	1.561×10^{-3}	2.806	16.014	0	0

Solvent	PNA			
	Solubility (S) in molal scale	pK	ΔG° (in KJ. mole^{-1})	ΔG_t°
MeCN	13.274	−1.123	−6.409	−22.515
NMF	21.823	−1.339	−7.642	−23.387
EtOH	3.467	−0.539	−3.076	−18.822
DMF	38.098	−1.581	−9.023	−24.768
PC	10.195	−1.008	−5.753	−21.498
DMSO	40.079	−1.603	−9.148	−24.894
NMePy	37.962	−1.579	−9.011	−24.756
H_2O	1.743×10^{-3}	2.759	15.746	0

S Values are in g. mole/1000 g solvent.

Since the neutral molecules ONA and PNA having the same diameter, which is the predominant factor for estimating the theoretical free energies, therefore the difference between the solute free energy values are due to the functional groups they belong to. On subtracting the ΔG_t^0 values of ONA from that of PNA, the hydrogen bonding free energies were obtained and their values are shown in Table 1.

$$\Delta G^0_{\text{H-bond.}}(\text{ONA}) = \Delta G^0_t(\text{ONA}) - \Delta G^0_t(\text{PNA}) \quad (3)$$

The solvents discussed here are classified into many classes according to Bronsted and other authors[3] (Table 2). This classification is based on four properties; they are: the dielectric constant (ϵ) which will be + for solvents with values greater than 30, dipole moment (+ for solvents greater than 3), acidic property and lastly basic property. These classes could not explain the ability to enhance the hydrogen bonding in ONA. On using the new parameters of the solvents which are the donor number (DN) and the acceptor number (AN)[5,6], better results were obtained.

TABLE 2

CLASSIFICATION OF THE ORGANIC SOLVENTS UNDER CONSIDERATION

Class	Dielectric constant (ϵ)	Dipole moment (μ)	Acidic property	Basic property	Solvents
Amphiprotic	+	−	+	+	H_2O
Protophilic	++(*)	+	−	+	NMF
Aprotic	+	+	−	−	MeCN
Amphiprotic	−	−	+	+	EtOH
Dipolar-aprotic	+	++(*)	−	−	PC & NMePy
Aprotic	+	+	−	+	DMSO&DMF

*very high value.

On drawing the DN or AN values against $\Delta G^0_{\text{H-bond,}}$ of ONA, a decrease in the hydrogen bonding ability was observed on increasing both DN and AN values (Fig. 1). This explains that the intra-hydrogen bonding free energy between the hydroxyl and amino groups in ONA molecules will increase when the solvents became less active towards ONA. That is to say the $\Delta G^0_{\text{H-bond.}}$ of ONA will increase with a decrease in both the solvent donating and accepting properties.

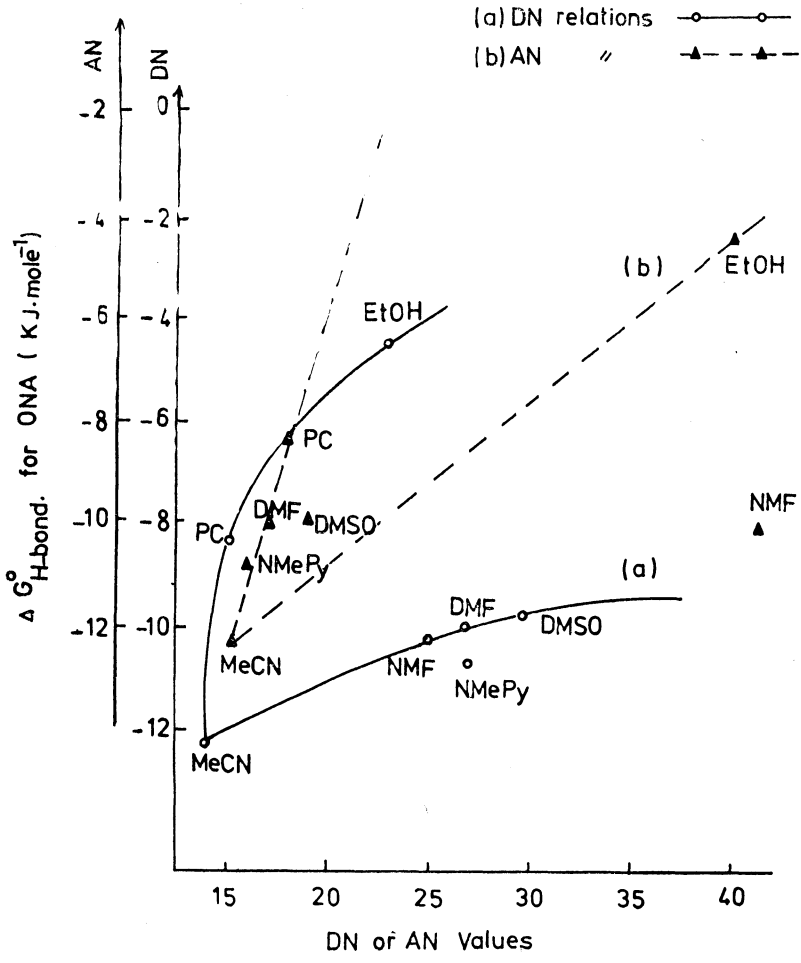

Fig. 1. $\Delta G^0_{H\text{-bonding}}$ for ONA dependence on both the donor and aceptor numbers of the organic solvents.

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