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Hydrogen Bonding of O-Nitroaniline in Water-DMSO Mixtures

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Abstract. From solubilities of O-nitroaniline (ONA) and p-nitroaniline (PNA) at 25°C in H_2O-DMSO mixtures, the free energies of transfer ($\Delta_w^s G^0$) from water to mixed solvents were estimated. From $\Delta_w^s G^0$ values for both ONA and PNA, the internal hydrogen bonding of ONA has been evaluated. Furthermore the ion-pair formation constant ($K_{ass.}$) between similar molecules in each ONA and PNA were also theoretically calculated. The transfer free energies for ONA and PNA molecules were increased by increasing in the mole fraction of DMSO (X_s) in the mixed solvents, due to the increase in solute-solvent interactions.

Introduction

Solubility of a solute in a solvent involves a consideration of the attractive forces which exist between the species in the mixture, i.e. solute-solvent, solvent-solvent and solute-solute. Fundamentally, three factors affecting the interactions between molecular substances:- the polarities of the molecules involved, the magnitude of the dispersion forces and the ability of the molecules to interact in a specific manner, e.g. hydrogen bonding [1,2]. In this work two molecules were used, ONA and PNA as they have similar polarities and they interact with the same magnitude of dispersion energies. Therefore information will be obtained about the hydrogen bonding forces in discussing the free energies of transfer values for ONA and PNA from water to mixed H_2O-DMSO solvents.

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Experimental

O-nitroaniline (2-nitroaniline) and p-nitroaniline (4-nitroaniline) of analytical grade from Merck Co. were used. The saturated solutions of ONA and PNA in aqueous-DMSO mixtures were prepared by dissolving them in the mixed solvents and passing nitrogen gas in closed test tubes. The tubes were shaken in a water thermostate "Assistant" at 25°C for three days, then left for another day without shaking to reach the necessary equilibrium. The solubilities of ONA and PNA were determined gravimetrically by taking 1 ml of the saturated solutions, putting them in small aluminium disks and evaporated using infrared lamp.

Results and Discussion

The solubilities of ONA and PNA in mixed H_2O-DMSO solvents on the molal scale were determined experimentally at different mole fractions of DMSO (X_s) and their values are tabulated in Table 1. The pK values of both nitroanilines which are electrically neutral bases under our experimental conditions were calculated by using eq. 1.

Table 1. Molal solubilities and pK's of O-nitroaniline and p-nitroaniline in mixed H_2O-DMSO solvents at 25°C.

Volume % of DMSO	X_s DMSO	r (A°)	O-nitroaniline		p-nitroaniline	
			C	pK	C	pK
0	0	6.541	4.864×10^{-5}	4.313	6.414×10^{-3}	2.193
50	0.237	7.191	0.1499	0.824	0.1049	0.979
60	0.327	7.391	0.3949	0.404	0.3749	0.426
70	0.433	7.631	0.6759	0.170	0.5758	0.240
80	0.504	7.771	1.4299	0.155	0.7883	0.130
90	0.696	8.131	2.5586	0.408	1.9170	0.283
100	1.0	8.481	3.6575	0.563	2.9223	0.466

$$pK = -\log C \qquad (1)$$

where C is the molal solubility (g. mole/1000 g. solvent). The free energies (ΔG^o) for both ONA and PNA in the mixed H_2O-DMSO solvents were calculated by applying eq. 2.

$$\Delta G^o = 2.303\ RT\ pK \qquad (2)$$

The transfer free energies of ONA and PNA from water (w) to mixed solvents (s) were calculated using equations 3 & 4.

$$\Delta_{w}^{s} G^{o}_{ONA} = 2.303\ RT \log \frac{C_{ONA(w)}}{C_{ONA(s)}} \tag{3}$$

$$\Delta_{w}^{s} G^{o}_{PNA} = 2.303\ RT \log \frac{C_{PNA(w)}}{C_{PNA(s)}} \tag{4}$$

The calculated free energies ($\Delta\ G^{o}$) for both ONA and PNA listed in Table 1, decrease with the addition of DMSO, whereas the free energies of transfer ($\Delta_{w}^{s} G^{o}$) increase. The increase of the latter is an indication that the anilines are more solvated through the positively charged amino group by the more negative oxygen atoms of DMSO, while the small free energies in case of water, indicate that the solvation process took place through the negatively charged nitro group. Therefore, the affinity of interaction for ONA & PNA in mixed H_2O-DMSO solvents seems to be greater than that in water. Also the increase in solubilities for ONA & PNA in the mixed solvents under consideration may be caused by dispersion forces.

Internal hydrogen bonding free energies for ONA

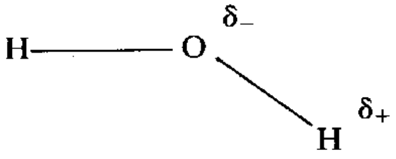
Since ONA and PNA have the same molecular weight and the same elemental composition, similar polarities, their dipole moments are 4.40 and 5.79 D for ONA and PNA [3, p. 2070]. Therefore, ONA and PNA interact externally in the solvents with the same magnitude. The difference in dipole moments for both anilines give difference in ion-dipole interaction [4]. On the other hand, the internal interactions between molecules of the same kind only occurs in ONA. Therefore, the internal hydrogen bonding free energies ($\Delta\ G^{o}_{H\text{-bonding}}$) in ONA can be calculated by subtracting their free energies of transfer in the mixed solvents from that of PNA as explained in eq. 5.

$$\Delta_{w}^{s} G^{o}_{H\text{-bonding}} = \Delta_{w}^{s} G^{o}_{ONA} - \Delta_{w}^{s} G^{o}_{PNA} \tag{5}$$

The calculated values of the internal hydrogen bonding for ONA are given in both Table 2 and Fig. 1, with nearly a constant value in H_2O-DMSO mixtures having 12.1 k.J./mole as a mean value.

Solvation process and the self association of ONA and PNA

The isolated dipoles of water and DMSO can be represented as follows:



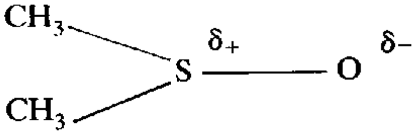


Table 2. Free energies of ONA & PNA, free energies of transfer from water to mixed H_2O-DMSO solvents for ONA & PNA, and the free energies of hydrogen bonding of ONA in mixed H_2O-DMSO solvents at 25°C (k.J./mole) and $K_{ass.}$ for ONA & PNA.

X_s DMSO	ONA		PNA		$\Delta G^o_{H\text{-bonding}}$ for ONA	$K_{ass.} \times 10^3$
	ΔG^o	$\Delta_w^s G^o$	ΔG^o	$\Delta_w^s G^o$		
0	24.614	0	12.514	0	0	0.98
0.237	4.703	− 19.91	5.586	− 6.93	− 12.98	1.08
0.327	2.395	− 22.31	2.431	− 10.08	− 12.23	1.11
0.433	0.971	− 23.64	1.368	− 11.15	− 12.50	1.11
0.504	0.883	− 23.73	0.586	− 11.93	− 11.80	1.17
0.696	2.330	− 22.28	1.615	− 10.90	− 11.39	1.23
1.0	3.213	− 21.40	2.661	− 9.85	− 11.55	1.29

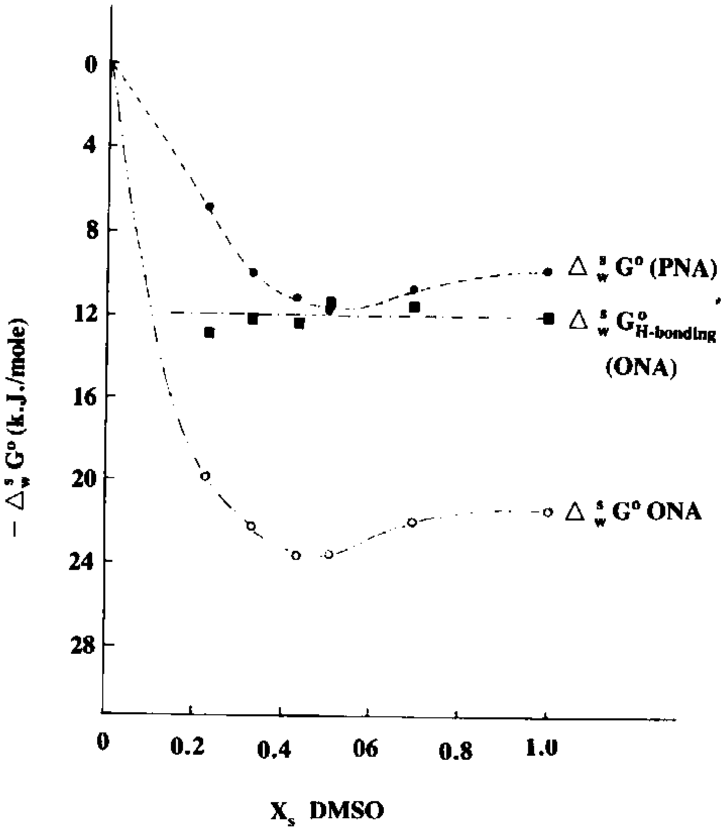
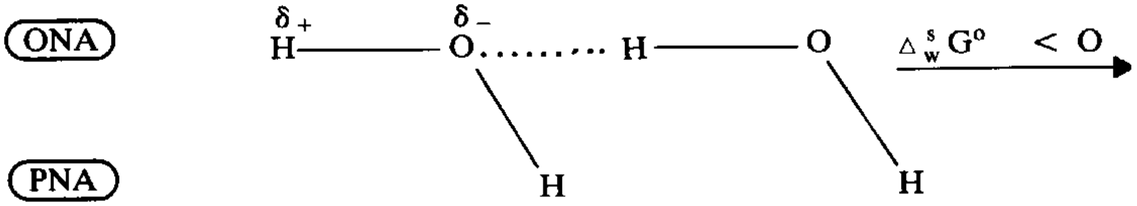
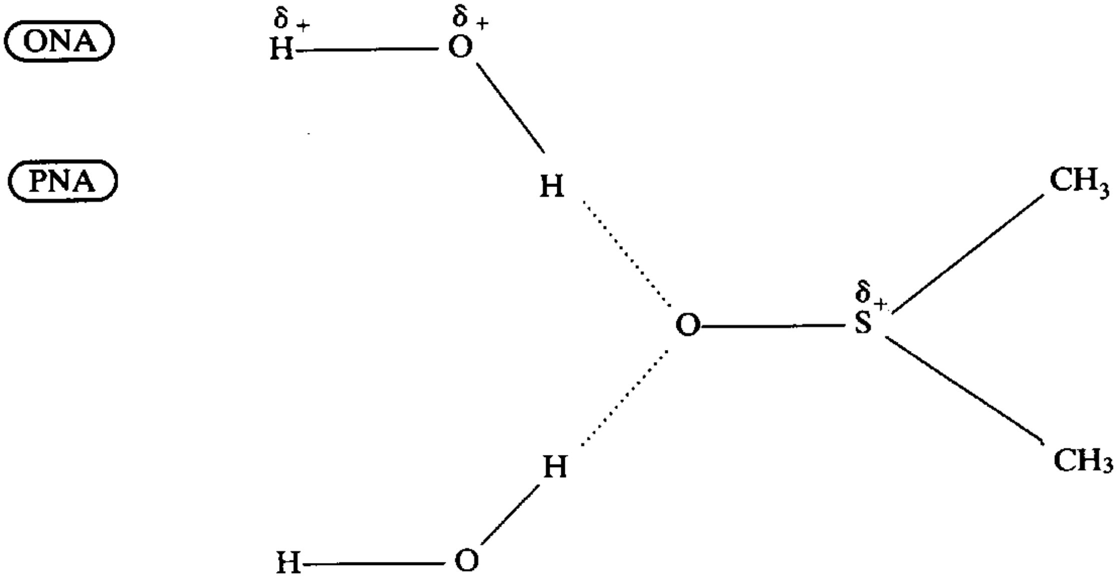


Fig. 1. Free energies of transfer of O- & p-nitroanilines and $\Delta_w^s G^o_{H\text{-bonding}}$ of o-nitroaniline in mixed H_2O-DMSO solvents.

Due to the inductive effect of the methyl group in DMSO, the negative charge density on the oxygen atom is somewhat larger than the corresponding quantity in water dipoles. The transfer free energies of ONA and PNA from water to mixed H_2P-DMSO give negative values, because both solute molecules are more bonded to water in pure water than in the case of mixed solvents. This is due to the decrease of the charges in the mixed solvents resulting from the interaction between DMSO with water to form complex compound with ratio 1:2 (DMSO : H_2O) [5,6, p. 51].





For further calculation the solvated radius (r) was calculated by adding the Van der Waals radius of solute to the hard sphere radius of the mixed solvent [5]. The Van der Waals radii of both ONA and PNA were calculated by applying the Bondi model [7] and found to be 3.81 A° for both the organic anilines. The self association constant ($K_{ass.}$) for both ONA & PNA were calculated theoretically after Fuoss equation [8] as follows:

$$K_{ass.} = 4/3 \, \pi \, N \, r^3 \, . \, \exp \left(\frac{e^2}{r \, \varepsilon \, k \, T} \right) \tag{6}$$

where N is Avogadro's number, r is the solvated radius and ε is the dielectric constant of the medium [5] and k is Boltzmann's constant. The calculated values for the self association constants ($k_{ass.}$) for the neutral organic molecules under consideration in mixed H_2O-DMSO solvents are given in Table 2 also, showing an increase in their values in DMSO rich solvents, indicating the increase in solute-solvent interactions, also.

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بحث مختصـــر

طاقة الربط الهيدروجينية لأورثونيتروانيلين في مخاليط الماء مع ثنائي ميثيل السلفوكسيد

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(استلم في ٢١ صفـر ١٤٠٩هـ، قُبل للنشر في ١٩ جمادي الآخرة ١٤١٠هـ)

ملخص البحث. تم حساب طاقة الربط الهيدروجينية لأورثونيتروانيلين من قياسات الذوبانية لكل من أورثونيتروانيلين وبارانيتروانيلين في مخاليط الماء مع ثنائي ميثيل السلفوكسيد عند ٢٥°م. كذلك تمت دراسة كل من تفاعل المذاب مع المذيب وثابت التجمع الذاتي للمركبين العضويين. وجد أن قيم الطاقات الحرة للمركبات المستخدمة تزداد بزيادة الكسر الجزيئى لثنائي ميثيل السلفوكسيد في المخلوط نتيجة للزيادة في تفاعلات المذاب مع المذيب.

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