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Solubilities of Various Nitroanilines in Water–Pyridine, Water–Acetonitrile, and Water–Ethylene Glycol Solvents

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The solubilities of various nitroanilines have been determined in aqueous solutions of pyridine, acetonitrile, or ethylene glycol in a large range of composition, and the corresponding transfer free energies calculated. The solubilities increase with the amount of organic cosolvent in the mixtures. Besides, under their logarithm form, they are linear functions of that of a particular species, ferrocene. This result is independent of the nature of the organic solvent and may be considered as an argument in favor of the use of a solvent function based on the solubility of molecular species.

Introduction

Many attempts have been made to characterize a given nonaqueous solvent (or a solvent mixture) by means of a "solvent parameter". The solubility parameters have been recently reviewed in the literature (*1*). In this paper we are concerned with the solubilities of several mono-, di-, and trinitroanilines in aqueous solutions of pyridine (PY), acetonitrile (AN), or 1,2-ethanediol (ethylene glycol, ETG) in a great range of compositions. The selection of a new series of binary mixtures as the solvents allows us to develop previously reported values (*2*–*4*) of the solubilities of the nitroanilines. Besides, our data match the solubilities of some electrolytes in the same media which have been already determined (*5*). They improve also our knowledge of the considered mixtures which have been otherwise examined electrochemically by Kalidas et al. (*6*) or by us (*7*, *8*) since they allow the determination of the transfer free enthalpy of a given solute i from water (W) to a particular mixture (S). The relevant $\Delta G_t^\circ(i)$ value is defined for one molecule of i taken in the standard state in water and in the mixture S by the change of the standard Gibbs energy:

$$\Delta G_t^\circ(i) = {}^{s}G^\circ(i) - {}^{w}G^\circ(i) \qquad (1)$$

$\Delta G_t^\circ(i)$ can be determined experimentally from solubility measurements of i in water and in the mixture S, if one assumes that the solubilities are low enough to allow one to consider the concentrations $C_{sat}(i)$ instead of the activities:

$$\Delta G_t^\circ(i) = RT \ln ({}^{w}C_{sat}(i)/{}^{s}C_{sat}(i)) \qquad (2)$$

$\Delta G_t^\circ(i)$ is also related to the transfer activity coefficient $\gamma_t(i)$ by

$$\Delta G_t^\circ(i) = RT \ln \gamma_t(i) \qquad (3)$$

which is the usual parameter to evaluate the medium effects.

Experimental Section

Ferrocene (E) and most of the selected nitroanilines are commercially available chemicals: 4-nitroaniline (A), 2,4-dinitroaniline (B), 2,6-dinitroaniline (H), 2,4,6-trinitroaniline or picramine (C), 3-nitroaniline (F). The 2,4,6-trinitrodiphenylamine or picrylaniline (D) was prepared by slowly adding freshly distilled aniline (0.2 mol) to a methanolic solution of picryl chloride (0.2 mol). The mixture was heated at 60 °C for 2 h. D precipitated on cooling.

All the solutes were recrystallized several times before use. Pure solvents were freshly distilled and stored under N_2.

The general procedure for the solubility measurements which were performed spectrophotometrically has been reported (*5*). A similar precision for the values of $-\log C_{sat}(i)$ (i.e., 0.05 log unit) can then be expected.

Results and Discussion

The solubility data for the nitroanilines in W–PY, W–AN, and W–ETG mixtures are listed in Tables I–III, respectively, while Table IV is devoted to the corresponding values in CH_3OH–AN mixtures.

Tables I–III illustrate a general trend of the $C_{sat}(i)$ values which are very low in pure water and increase with the proportion of the organic compound in the solvent mixture. Such a behavior has already been observed for molecular species in other aquoorganic mixtures (*2*–*4*) as well as for various picrates in the same solvents (*5*).

If one assumes that the solubility of i in a particular mixture S (water and organic cosolvent OS in a given ratio) is due to the solvation by water or by OS molecules, the following equilibria are involved:

$$i_{solid} + pH_2O \rightleftharpoons i_{aq} \qquad (4)$$

$$i_{solid} + qOS \rightleftharpoons i_{solv} \qquad (5)$$

Then

$${}^{s}C_{sat}(i) = (i_{aq}) + (i_{solv}) \qquad (6)$$

Experimental data relevant to pure water or pure organic solvent show that (i_{aq}) is much lower than (i_{solv}). Equilibrium 4 can thus be discarded as a first approximation. The equilibrium

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Table I. Solubilities and Transfer Free Enthalpies in Water–Pyridine Mixtures at 25 °C[a]

${}^{s}X$(PY)	A	B	C	D	E	F	H
0.00	2.52 (0.00)	3.37 (0.00)	4.06 (0.00)	4.23 (0.00)	4.47 (0.00)	2.27 (0.00)	3.36 (0.00)
0.02	1.86 (3.77)	2.67 (4.02)	3.28 (4.54)	3.85 (1.60)	3.55 (5.28)	1.64 (3.60)	2.82 (3.10)
0.05	1.30 (6.97)	2.10 (7.27)	2.88 (6.71)	3.55 (3.31)	3.09 (7.89)	1.11 (6.62)	2.29 (6.10)
0.08	0.89 (9.26)	1.67 (9.71)	2.48 (9.00)	3.10 (5.88)	2.65 (10.39)	0.76 (8.64)	1.93 (8.17)
0.13	0.55 (11.24)	1.42 (11.15)	2.21 (10.59)	2.67 (8.29)	2.23 (12.81)	0.51 (10.04)	1.67 (9.64)
0.18	0.34 (12.48)	1.14 (12.75)	2.02 (11.65)	2.38 (9.99)	2.00 (14.09)	0.27 (11.42)	1.45 (10.93)
0.24		0.87 (14.30)	1.78 (13.02)	2.12 (11.48)	1.68 (15.91)		1.24 (12.08)
0.32		0.61 (15.76)	1.48 (14.76)	1.69 (13.93)	1.37 (17.68)		0.98 (13.57)
0.45		0.34 (17.33)	1.06 (17.12)	1.18 (16.84)	0.96 (20.06)		0.64 (15.52)
0.63		0.13 (18.52)	0.71 (19.13)	0.53 (20.56)	0.45 (22.98)		0.20 (18.06)
1.00			0.21 (22.00)		0.08 (25.08)		0.10 (18.62)

[a] The ${}^{s}C_{sat}$(i) values are expressed on the molar scale. Upper line: values of $-\log {}^{s}C_{sat}{}^{s}C_{sat}$(i). Lower line, in parentheses: $-\Delta G_t°$(i) values in kJ.

Table II. Solubilities and Transfer Free Enthalpies in Water–Acetonitrile Mixtures at 25 °C[a]

${}^{s}X$(AN)	A	B	C	D	E
0.04	2.00 (2.97)	2.90 (2.68)	3.50 (3.19)	3.84 (1.60)	3.82 (3.71)
0.08	1.50 (5.82)	2.32 (5.99)	3.08 (5.59)	3.60 (2.97)	3.27 (6.84)
0.13	1.12 (7.98)	1.90 (8.38)	2.66 (7.98)	3.13 (5.65)	2.81 (9.47)
0.19	0.82 (9.69)	1.60 (10.09)	2.22 (10.49)	2.72 (7.98)	2.42 (11.69)
0.25	0.53 (11.35)	1.39 (11.29)	1.92 (12.20)	2.40 (9.81)	2.16 (13.17)
0.34		1.13 (12.77)	1.60 (14.03)	2.05 (11.80)	1.80 (15.23)
0.45		0.88 (14.20)	1.38 (15.28)	1.73 (13.63)	1.52 (16.82)
0.58		0.70 (15.23)	1.16 (16.54)	1.45 (15.23)	1.28 (18.19)
0.75		0.52 (16.25)	0.96 (17.68)	1.21 (15.59)	1.05 (19.50)
1.00		0.30 (17.51)	0.78 (18.70)	1.02 (17.68)	0.85 (20.64)

[a] Same notation as in Table I.

Table III. Solubilities and Transfer Free Enthalpies in Water–Ethylene Glycol Mixtures at 25 °C[a]

${}^{s}X$(ETG)	A	C	D	F
0.04	2.49 (0.06)	3.42 (3.65)	3.22 (5.14)	2.26 (0.06)
0.12	2.22 (1.60)	3.25 (4.62)	3.14 (5.60)	1.98 (1.66)
0.24	1.85 (3.71)	2.80 (7.19)	2.90 (6.97)	1.69 (3.32)
0.43	1.29 (6.92)	2.41 (9.42)	2.61 (8.62)	1.30 (5.53)
0.76	0.70 (10.28)	1.98 (11.88)	2.38 (9.93)	0.81 (8.36)
1.00	0.57 (11.04)	1.86 (12.56)	2.27 (10.56)	0.71 (8.91)

[a] Same notation as in Table I.

Table IV. Solubilities and Transfer Free Enthalpies in Methanol–Acetonitrile Mixtures at 25 °C[a]

${}^{s}X$(AN)	C	D	E
0.00	1.64 (0.00)	2.18 (0.00)	1.05 (0.00)
0.07	1.49 (0.86)	1.90 (1.60)	0.99 (0.34)
0.16	1.36 (1.60)	1.74 (2.51)	
0.25	1.29 (2.00)	1.57 (3.49)	0.91 (0.80)
0.34	1.19 (2.57)	1.44 (4.23)	
0.43	1.09 (3.14)	1.31 (4.97)	0.84 (1.20)
0.53	1.00 (3.66)	1.19 (5.66)	0.81 (1.37)
0.63	0.92 (4.11)	1.02 (6.63)	0.80 (1.43)
0.75	0.85 (4.51)	0.99 (6.80)	
0.87	0.75 (5.09)	0.91 (7.26)	0.76 (1.66)
1.00	0.78 (4.91)	0.86 (7.54)	0.85 (1.14)

[a] Same notation as in Table I.

constant K_5 for eq 5 links the activity of i in the solvent mixture to that of the organic cosolvent which can be represented by the mole fraction ${}^{s}X$(OS) of OS in the mixture S, provided the mixture is either very dilute of very concentrated in OS. Then

$$ {}^{s}C_{sat}(i) = K_5[{}^{s}X(OS)]^{q} \qquad (7) $$

Equation 7 suggests that for a given solute i, log ${}^{s}C_{sat}$(i) is linearly correlated to log ${}^{s}X$(OS) with the slope q. This is illustrated in Figure 1, which is relevant to the W–AN mixtures. The underlying assumption is verified for concentrated mixtures (i.e., roughly for $0.5 < {}^{s}X(OS) < 1$). In this range of compositions the graphs representing the various solutes are nearly parallel and tend to be linear with the same slope. This suggests that the number of AN molecules involved in the solvation process (eq 5) is independent of the solute and cannot be correlated with its structure.

Examination of the experimental data obtained for the other solvent mixtures leads to similar conclusions. The limiting q values in the W–PY mixtures are however higher for the bicyclic molecules (ferrocene and picrylaniline) than for the monocyclic anilines.

A direct consequence of the parallel behavior of the graphs log ${}^{s}C_{sat}$(i) vs. log ${}^{s}X$(OS) is that log ${}^{s}C_{sat}$(i) is proportional to log ${}^{s}C_{sat}$(j) for a given series of mixtures. This feature has been pointed out by Letellier (*3*) and used to introduce a new solvent function, g(s), which is defined from the solubilities of 3-nitro-

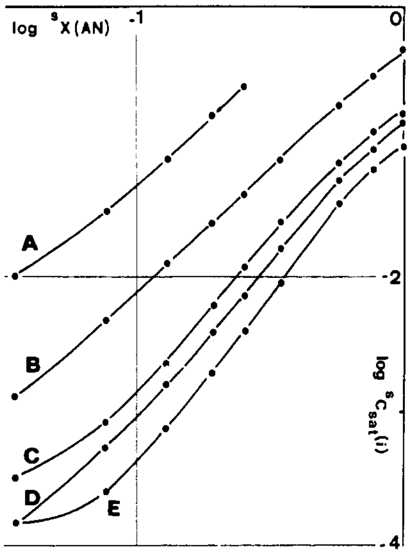

Figure 1. Solubilities (log $^sC_{sat}$(i)) at 25 °C of ferrocene and of various anilines in water-acetonitrile mixtures as a function of log ^sX(AN).

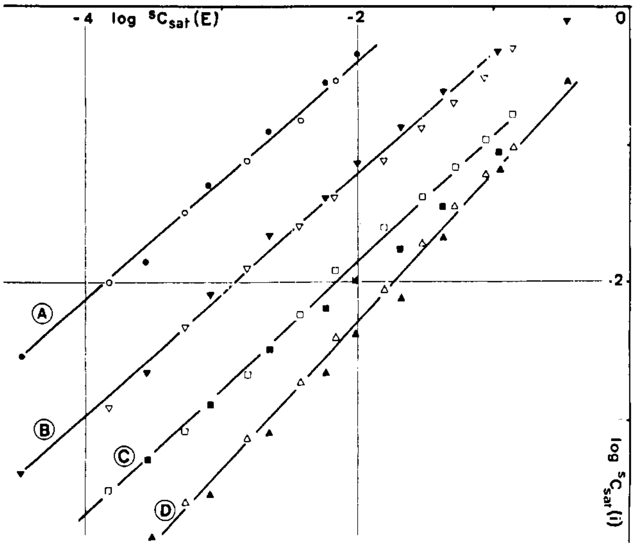

Figure 2. Solubilities (log $^sC_{sat}$(i)) at 25 °C of various anilines vs. log $^sC_{sat}$(E) in water-pyridine (full dots) and water-acetonitrile (open dots) mixtures.

aniline (F). In this work, ferrocene (E) was preferred to F because of its lower solubility, which allows one to explore a larger range of solvent compositions, and also because the ferrocenium/ferrocene system is the base of a very popular extrathermodynamic assumption used to evaluate the transfer parameters of ions in nonaqueous media. Figure 2 represents the graphs log $^sC_{sat}$(i) vs. log $^sC_{sat}$(E) and reports data relevant to W-PY and W-AN mixtures. For a given solute the experimental points fit well on a single straight line, in a concentration range of 3 decades or more, except for C, for which a limited discrepancy can be observed. This result confirms Letellier's findings on molecular solubilities and brings them a more general character.

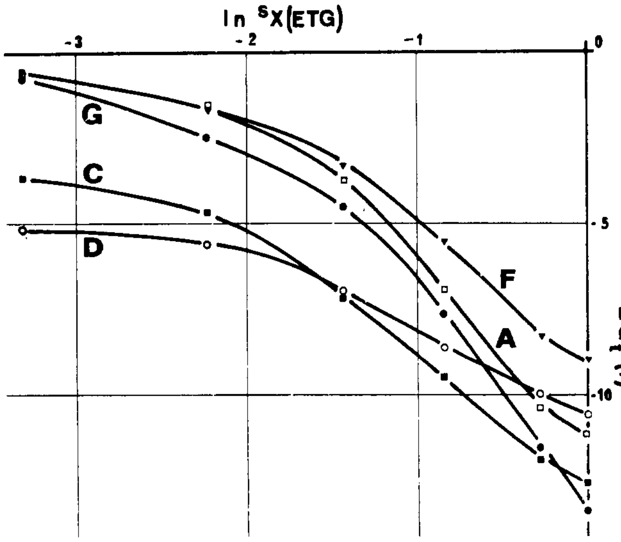

Figure 3. Transfer free enthalpies of anilines and of I_2 (curve G) between water and W-ETG mixtures as a function of the mole fraction of ETG (log ^sX(ETG)).

In addition, eq 2 and 3 show that ΔG_t^o(i) or ln γ_t(i) are directly dependent on ln $^sC_{sat}$(i). Then the transfer parameters of any solute i are also proportional to ln ^sX(OS) in a large range of solvent composition. The calculated ΔG_t^o(i) values for the various mixtures are listed in Tables I–IV. Figure 3 illustrates the variations of ΔG_t^o(i) with the solvent composition (e.g., ln ^sX(ETG)), with additionally literature data (*9*) relevant to iodine. For all the solutes studied ΔG_t^o(i) is a decreasing function of ln ^sX(OS), which illustrates the solvating power of the organic cosolvent, but the ΔG_t^o(i) values for pure solvents depend strongly on the nature of OS as expected. For example, ΔG_t^o(C) is about −22 kJ in pure pyridine, −19 kJ in acetonitrile, and −13 kJ in ethylene glycol.

Registry No. Pyridine, 110-86-1; acetonitrile, 75-05-8; ethylene glycol, 107-21-1; 4-nitroaniline, 100-01-6; 2,4-dinitroaniline, 97-02-9; 2,6-dinitroaniline, 606-22-4; 2,4,6-trinitroaniline, 489-98-5; 3-nitroaniline, 99-09-2; ferrocene, 102-54-5.

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