with η in mPa s and T in K, which yields viscosities higher than ours particularly at low temperature.

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Solubilities of Some Electrolytes in Water–Pyridine and Water–Acetonitrile Solvent Mixtures

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The solubilities of various organic and inorganic salts have been measured in aqueous pyridine and acetonitrile solutions. For low saturated concentrations of the solute (C_{sat} < 0.1 M), the solubilities are linearly correlated; they are also correlated with the solubilities of nonionic species (e.g., ferrocene).

Introduction

The solubilities of ionic species in various nonaqueous solvents or in solvent mixtures have received renewed interest over the last few years (e.g., ref *1–4*) in order to examine whether they correlate with some solvent parameters such as Kosower's Z index. These data were also used to estimate the medium effect for an electrolyte, which is measured by the free energy change upon transferring 1 mol of the electrolyte (i) from its standard state in water (W) (or in the reference medium) to its standard state in the nonaqueous solvent (S) (or in the solvent mixture):

$$\Delta G°(\mathrm{i}) = n_\mathrm{i}[{}^{\mathrm{S}}\mu°(\mathrm{i}) - {}^{\mathrm{W}}\mu°(\mathrm{i})] = n_\mathrm{i}RT \ln \gamma_t(\mathrm{i}) \qquad (1)$$

For a 1:1 electrolyte, the transfer activity coefficient γ_t(i) is given by the square of the ratio of the mean activity $a_\pm$(i) in water and in S:

$$\gamma_t(\mathrm{i}) = \gamma_{t\pm}(\mathrm{i})^2 = [{}^{\mathrm{W}}a_\pm(\mathrm{i})/{}^{\mathrm{S}}a_\pm(\mathrm{i})]^2 = {}^{\mathrm{W}}a(\mathrm{i})/{}^{\mathrm{S}}a(\mathrm{i}) \qquad (2)$$

For very dilute solutions, the concentrations can be considered instead of the activities and γ_t(i) is given by the ratio of the concentrations of i in water and in S: ${}^{\mathrm{W}}C_{sat}(\mathrm{i})/{}^{\mathrm{S}}C_{sat}(\mathrm{i})$.

The literature reports numerous data for solubilities in pure solvents, but few results relevant to solvent mixtures are available. The water-pyridine mixtures (W-Py) have been carefully investigated through their acid-base properties (*5–7*), but only a few solubility data are published (*8–10*). We selected some particular salts such as the picrates, which have been considered in other solvents (*4*, *11–13*), and potassium hexacyanoferrate(III), which has been examined electrochemically in a previous paper (*5*).

In order to develop an electrochemical study of the water–acetonitrile mixtures (W-AN) which is presently in progress, we measured also solubilities in these media, and we selected the same solutes with the view of completing the literature data (*14–17*). (Unfortunately phase separation of the $K_3Fe(CN)_6$ solution occurs in most of the W-AN mixtures and a limited number of results could be obtained. Consequently, we chose to examine another complex of the same charge: the hexamminecobalt(III) chloride.

Table I. Solubilities (−log C_{sat}(i) in the Molar Scale) in Water–Pyridine Mixtures at t = 20 °C

Py, vol %	NEt_4Pic (20 °C)	PyHPic (20 °C)	K_3-$Fe(CN)_6$ (20 °C)	NaCl (25 °C)[a]	KCl (10 °C)[b]	ferrocene (20 °C)
0	1.60	1.97	0.02	−0.79	−0.50	4.47
10	1.07	1.56	0.05		−0.42	3.54
20	0.66	1.19	0.13		−0.34	3.09
30	0.46	0.91	0.30		−0.25	2.65
40	0.31	0.78	0.45		−0.13	2.23
50	0.26	0.67	0.70		−0.07	2.00
60	0.21	0.58	1.15		−0.35	1.68
70	0.21	0.51	1.93	0.22	−0.78	1.37
80	0.18	0.43	3.42	0.75	−1.49	0.97
90		0.38		1.71	−2.27	0.45
100		0.37				0.08

[a] Interpolated from ref *9*. [b] Reference *10*.

Table II. Solubilities (−log C_{sat}(i) in the Molar Scale) in Water–Acetonitrile Mixtures at t = 25 °C

AN, vol %	KPic	NEt_4Pic	PyHPic	Co-$(NH_3)_6$-Cl_3	ferrocene	BPh_4^- [a]
0	1.61		1.97	0.78		3.53
10	1.15	1.04	1.47	0.78	3.58	
20	1.01	0.94	1.21	0.76	3.28	3.34
30	0.85	0.58	0.95	0.81	2.82	
40	0.59	0.35	0.78	0.98	2.57	3.26
50	0.47	0.14	0.62	1.17	2.16	
60	0.59	0.06	0.50	1.43	1.80	3.19
70		0.05	0.43	1.85	1.52	
80		0.01	0.44	2.16	1.32	3.13
90			0.45		1.05	
100					0.73	

[a] Determined from ref *16*.

In addition we determined the solubilities of a particular uncharged species, ferrocene, in order to compare the two series of mixtures.

Experimental Section

Water, AN, Py and Me_2SO were distilled before use. The hexamminecobalt(III) chloride was synthesized (*18*) and analyzed satisfactorily.

The solubility determinations were performed as in other studies (*19*). Saturated solutions of a given solute were prepared by stirring the suspension for 24–48 h in each mixture in a thermostated bath and filtering. The solutions were then

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Table III. Solubilities (–log C_{sat}(i) in the Molar Scale) in Water-Me_2SO and Methanol-Acetonitrile Mixtures at t = 25 °C

Me_2SO, vol %	PyHPic	ferrocene[a]	Ag_2SO_4[b]	$AgBrO_3$[c]	$AgIO_3$[c]
0	1.99	4.47	1.60	2.01	3.49
10	1.86	4.27	1.77	2.04	3.49
20	1.84	4.05	1.92	2.06	3.50
30	1.72	3.80	2.08	(2.85)	3.51
40	1.63	3.48	2.25	2.10	3.53
50	1.49	3.12	2.45	2.15	3.56
60	1.23	2.76	2.67	2.10	3.61
70		2.44	2.94		
80		1.88	3.28		
90		1.20	3.76		
100		0.69	4.39		

AN, vol %	PyHPic	ferrocene	AN, vol %	PyHPic	ferrocene
0	1.72	1.05	40	1.18	
10	1.52	1.00	50	1.15	0.89
20	1.40		60	1.09	0.81
30	1.27	0.91	70	0.99	0.80

[a] Reference *20*. [b] C_{sat}(i) in the molal scale, ref *21*. [c] C_{sat}(i) in the molal scale, ref *22*.

diluted with the solvent mixture, and their absorbances measured at the wavelength of the absorption peak. The determination of the concentration was made by comparison with a Beer-Lambert calibration curve performed under the same conditions (solvent composition, temperature).

Each solubility measurement was performed at least on two independent series of experiments. The solubility data reported in Tables I-III are the average values of –log C_{sat}(i); they differ from the raw values by less than 0.05 log units, which represents the accuracy of our results.

Results and Discussion

The organic and inorganic electrolytes give inverse results when the solvent composition changes: the solubility of the organic salts increases as the organic percentage in the mixture increases and that of the inorganic solutes decreases. In addition, the solubilities of both kinds of solutes tend to become independent of the solvent composition when they are greater than 0.16 M. The concentrations C_{sat}(i) are then too high for being taken in place of the activities, and the determination of the transfer free energy becomes hazardous.

Tables I and II suggest other conclusions if one considers only the concentration range $C_{sat}(i) \leq 0.1$ M: (i) A linear correlation can be found between the solubilities of the various electrolytes examined (i.e., both organic and inorganic salts); this correlation is confirmed by data taken from the literature (e.g., ref *16*). This result is not particular to the solvent mixtures considered in this work since a similar correlation can be verified approximately from the literature data relevant to other media (*2*). (ii) Another linear correlation can also be found between the solubilities of the ionic species and those of uncharged species such as ferrocene (or SO_2 in W–AN mixtures according to ref *17*). This unexpected behavior is also verified in other media for ferrocene and pyridinium picrate (Table III).

The preceding remarks are illustrated by Figure 1, which shows the variations of –log C_{sat}(i) with the solubility of ferrocene in the two series of hydroorganic mixtures considered. It should be pointed out that the graphs relevant to a given salt are independent of the organic cosolvent (*19*, *23*) although exceptions to this behavior are known. A good illustration is provided by the solubilities of ferrocene and pyridinium picrate in W–Me_2SO and CH_3OH–AN mixtures (Table III).

Our results suggest that, for a given series of mixtures, the solubilities of the various ionic species are linearly correlated and are also linearly dependent on the solubilities of molecular species. It is then easy to assume that the plots of any "ionic function" (e.g., acidity constants, stability constants of complexes, etc.) vary also linearly with the solubility parameters. This assumption has been verified occasionally (*24*) but cannot hold for the mixtures examined in this paper, as shown by the graphs of pK_a vs. solubility. The acidity constants previously determined (*6*) in the W–Py mixtures were plotted vs. the solubility of a molecular species, 3-nitroaniline, the solubility of which is linearly correlated with that of ferrocene. The resulting curves are composed of linear sections of different slopes, the changes in which occur for various compositions of the mixtures. This example demonstrates that the use of a solvent function based on solubility parameters needs extreme care, as already mentioned (*2*).

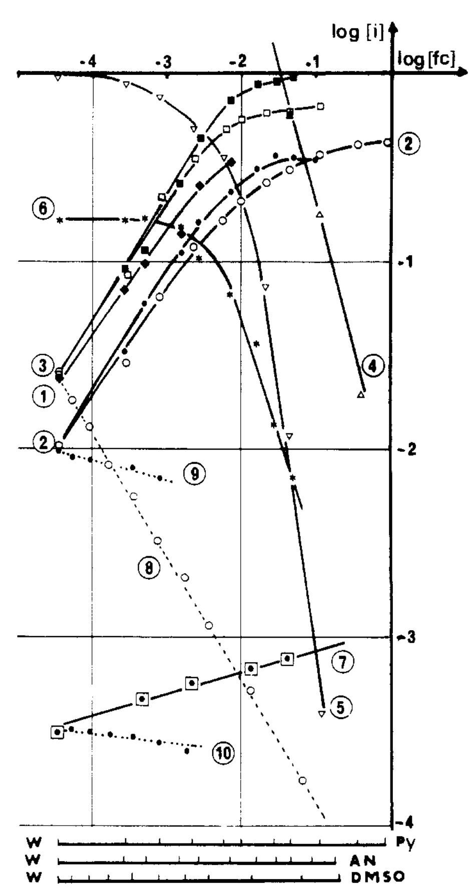

Figure 1. Solubilities (expressed in the molar scale) of various electrolytes in the mixtures considered. The values of log C_{sat}(i) are plotted against log C_{sat}(ferrocene). Full lines: (1) KPic in W–AN (◆); (2) PyHPic in W–Py (○) and in W–AN (●); (3) NEt_4Pic in W–Py (□) and in W–AN (■); (4) NaCl in W–Py (△); (5) $K_3Fe(CN)_6$ in W–Py (▽); (6) $Co(NH_3)_6Cl_3$ in W–AN (*); (7) BPh_4^- in W–AN (⊡). Dotted lines refer to W–Me_2SO mixtures: (8) Ag_2SO_4; (9) $AgBrO_3$; (10) $AgIO_3$.

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Salting-Out Parameters for Organic Acids

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The salting-out parameter was determined for formate, acetate, and adipate, and the same value was obtained for all three ions. Using the standard state where the salting-out parameter for H^+ is zero, the present study has revealed a salting-out parameter of 0.034 for the three ions.

Background

Interest has been focused on the addition of organic acids to scrubbing solutions for control of air pollutants. The organic acid can act as a reactive species for the gaseous pollutant or as a buffer whereby the mass transfer rate of the gaseous pollutant is enhanced. Acetic acid is an example of a reactive species that is used for simultaneous scrubbing of SO_2 and NO_x; the Japanese company Kureha Chemical has developed such a process. Adipic acid and formic acid are used to enhance mass transfer. For instance, Chang and Rochelle (*1*) investigated the influence of acetic and adipic acids on the absorption of SO_2 in an aqueous solution; improvement of wet scrubbing now relies on the addition of adipic acid. Also, the Saarberg-Holter process, in operation on a 40 MW_e scale in Germany to control SO_2 from a coal-fired boiler, is based on the addition of formic acid to the scrubbing solution, in order to enhance mass transfer.

Generally speaking, the solubility of a gaseous species is depleted when ions are added to the aqueous solution. This is noticed as an increase in the Henry's law constant. According to Danckwerts (*2*), the following expression is pertinent to account for the mentioned depletion:

$$\log (H/H_0) = I(h_+ + h_- + h_g) \qquad (1)$$

The ionic strength of the solution is

$$I = 0.5\sum C_i z_i^2 \qquad (2)$$

where C_i is the concentration of the ions of valency, z_i. The Henry's law constant is defined by

$$p = HC \qquad (3)$$

where p and C are the partial pressure and the concentration of the gaseous species. The subscript 0 indicates pure water. The salting-out parameters, h_+, h_- and h_g refer to anion, cation and gas, respectively.

Table I. Measured and Calculated Solubilities of Oxygen at Various Concentration Levels of Sodium Chloride

	O_2 solubility, mg of O_2/L	
[NaCl], mol/L	measured	calcd
0	9.2	
0.52	7.7	7.7
1.12	6.3	6.3
2.23	4.4	4.3
3.47	2.9	2.9
4.85	1.9	1.8

The salting-out parameters are known for many common species; however, they are not known for organic anions. In the present study, h_- is determined for formate, acetate, and adipate.

Experimental Section

The following procedure was applied to obtain the Henry's law constant as a function of the ion strength at 20 °C. Sodium salts of the three organic acids were dissolved in water. Air from a gas cylinder was bubbled through the samples to obtain a certain content of dissolved oxygen in equilibrium with the gas. The samples were "fixed" with solutions of iodized alkaline iodide, $MnSO_4$, and H_2SO_4, according to the procedure described in ref 3. The amount of dissolved oxygen was determined indirectly by titration, utilizing $Na_2S_2O_3$. The ion strength was varied from zero upwards for each solution; the ion strength was calculated as if all of the salt were dissociated completely. According to ref 3, it is possible to determine the oxygen solubility with a precision of 0.03 mg of O_2/L and within 0.05 mg of O_2/L of the true value by using the above-described method.

Result

A number of experiments were first made using sodium chloride solution, to check the applicability of the method. The measured data are shown in Table I. The values have been adjusted to 10^5 Pa by multiplying by the actual pressure in Pa

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