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Solubility as a Function of Temperature of Selected Chlorophenols and Nitrophenols in Aqueous Solutions Containing Electrolytes or Surfactants

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The solubility of phenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2-nitrophenol, and 4-nitrophenol, was measured in aqueous solutions containing small concentrations of electrolytes or surfactants in the temperature range from 280 K to 345 K. The experimental determination of the solubility was performed using a light transmission technique. The results show that small amounts of surfactants or electrolytes can modify significantly the aqueous solubility of these compounds.

Introduction

Chlorinated phenols and nitrophenols are long-lived pollutants frequently found in industrial effluents. Their aqueous solubility is low and decreases with increasing number of hydrophobic chlorine or nitro groups. Reliable data of chlorophenol and nitrophenol solubility in pure water are reported in the literature.[1−6] However, measurements were usually performed at normal temperature (273 K or 298 K). Recently, Huang et al.[7] demonstrated the strong influence of pH at $T = 298$ K on the solubility of selected chlorophenols. Indeed, physical and chemical properties of chlorophenols and nitrophenols are strongly influenced by their capacity to form hydrogen bonds and by their partly ionic character in aqueous solutions. The acidity constant of chlorophenols increases with the number of chlorine atoms. Pentachlorophenol is an acid comparable in strength to acetic acid.

Numerous thermodynamic properties of aqueous solutions of chlorophenols are reported in the literature. Anderson et al.[8] studied the aqueous solubility of para-substituted phenols. Kojima and Davis[9] and Wenhui et al.[10] showed that the molecular transfer of chlorophenols in polyphase systems is strongly influenced by the presence of electrolytes. All of these results were reported at 298.15 K. Moreover, solubility and partition coefficients of chlorophenols were determined in the presence of large concentrations of salts.

In the present work, we investigated the influence of electrolytes (NaCl, NaOH, and HCl) on the solubility of selected phenols (phenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2-nitrophenol, and 4-nitrophenol) as a function of temperature. Temperature ranges and electrolyte concentrations concerned in this study were selected according to characteristic values of these parameters observed in river water. Thus, the influence of small concentrations of salts on the nitrophenol and chlorophenol aqueous solubility was dealt with.

Chlorophenols and nitrophenols are only slightly soluble in water. Atwood and Florence[11] discussed the mechanism of the micellar solubilization of hydrophobic solutes in aqueous solutions. Pramauro et al.[12] and Busserolles et al.[13] studied the micellar solubilization of phenol and chlorophenols. This phenomenon can be achieved when micelles are formed and the surfactant concentration is higher than the critical micellar concentration (cmc). Therefore, the aqueous solubilities reported by these authors were determined with relatively high concentrations of surfactants.

In ground or river water, small quantities of surfactants from domestic or industrial wastes are often present. Because their concentration is lower than the cmc, the usual micellar solubilization of hydrophobic pollutants cannot occur. The surfactants can aggregate, however, with pollutants and in certain cases may form mixed micelles. Consequently, the aqueous solubility of pollutants may be increased, and thermodynamic conditions of their environmental transfer can be seriously modified. In this work, we studied the solubility enhancement of nitrophenols and chlorophenols in aqueous solutions containing small quantities of selected surfactants. Sodium dodecyl sulfate (SDS), *N*-hexadecyl-*N*,*N*-dimethyl-3-ammonio-1-propanesulfonate (SB-16), poly(oxyethylene-4-lauryl ether) (Brij-30), and poly(glycol ether) (tergitol or NP-10) were used. The first of the group (SDS) is anionic, the second one (SB-16) is amphoteric, and the last two compounds (Brij-30 and NP-10) are nonionic. Some properties of these surfactants are given in Table 1. The cmc values were either taken from the literature or measured by ourselves using a KSV-5000 tensiometer (KSV, Finland).

Experimental Section

Materials. Deionized water was used, the purity of which was checked by determining the electrical conductivity. It was found to be 1−1.8 μS·cm^{-1}. Phenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2-nitrophenol, and 4-nitrophenol were from Merck. NaCl, SB-16, SDS, Brij-30, and NP-10 were from Sigma. Other chemicals were from Aldrich. The mass fraction purity of all compounds used was higher than 0.99, as checked by high-performance liquid chromatography.

Apparatus and Procedures. The laser light transmission technique was used to determine the aqueous solubility. A schematic diagram of the experimental setup is shown in Figure 1. Samples of known composition were

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Table 1. Selected Properties of Surfactants at T = 298 K

surfactant	designation	formula	M_w (g·mol^{-1})	cmc (mol·L^{-1})
anionic	SDS	$C_{12}H_{25}SO_4Na$	288.4	8.1 × 10^{-3} (ref 14) 8.3 × 10^{-3} (ref 15) (8.25 ± 0.07) × 10^{-3} [a]
amphoteric	SB-16	$CH_3(CH_2)_{15}N(CH_3)_2[(CH_2)_3SO_3)]$	391.7	(2.14 ± 0.05) × 10^{-4} [a]
nonionic	Brij-30	$C_{12}H_{25}(OCH_2CH_2)_4OH$	362.4	4.6 × 10^{-5} (ref 14) (4.50 ± 0.06) × 10^{-5} [a]
	NP-10	$C_9H_9(C_6H_4)(OCH_2CH_2)_{10}OH$	650.0	13.7 × 10^{-5} (ref 15) (7.19 ± 0.11) × 10^{-5} [a]

[a] Determined in this work from surface tension measurements.

Table 2. Correlation of the Solubility in Pure Water of Selected Chlorophenols and Nitrophenols Using Experimental Data of Jaoui et al.[6] and Achard et al.[18] $\ln(S°/S') = A + B/T$ Where S' = 1 mol·kg^{-1}

solute	temp range (K)	a	b (K)	R^2 [a]	no. of data points
phenol	288−313	7.3013	−853.62	0.9784	9
	313−332	10.731	−1931.7	0.9966	
4-chlorophenol	282−342	5.6451	−716.81	0.9828	7
2,4-dichlorophenol	288−298	11.846	−3025.1	1.0005	8
	298−347	5.0497	−981.37	0.9925	
2,4,6-trichlorophenol	292−303	23.367	−7096.7	0.9847	6
	303−334	6.6069	−2029.9	0.9964	
2-nitrophenol	288−308	16.237	−4672.3	0.9989	5
	308−332	6.9022	−1784.4	0.9807	
4-nitrophenol	288−314	17.110	−4273.4	0.9923	5

[a] R^2 is the correlation coefficient of the linear regression.

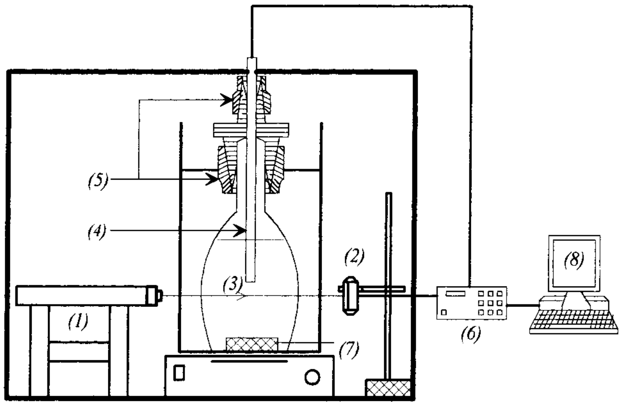

Figure 1. Scheme of the apparatus for solubility measurements: 1, He−Ne laser; 2, light sensor, selenium cell; 3, equilibrium vessel; 4, platinum resistance; 5, sealing system; 6, digital multimeter; 7, stirring bar; 8, acquisition computer.

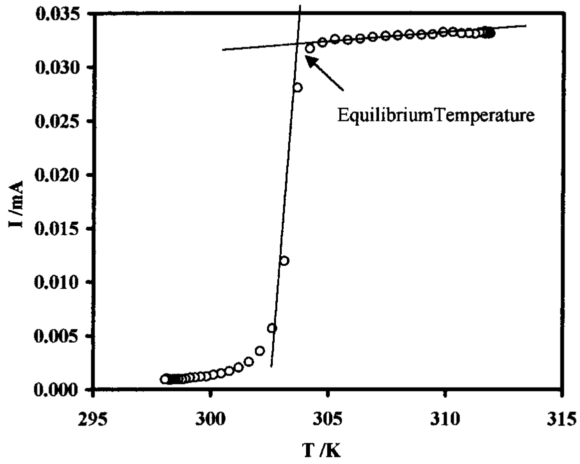

Figure 2. Light transmission plotted against temperature for a water + phenol mixture.

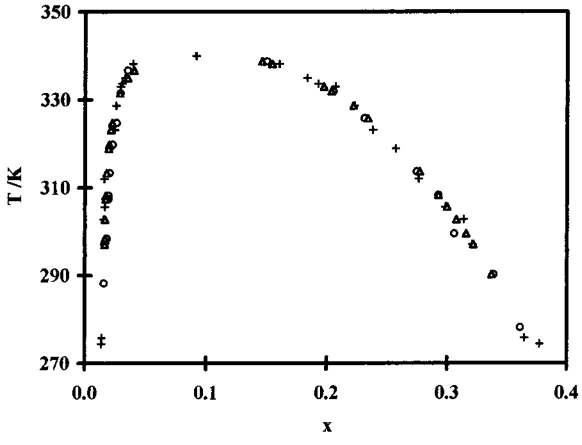

Figure 3. Liquid−liquid equilibria for the system water (1) + phenol (2): ○, ref 6; +, ref 16; △, laser light transmission method.

prepared by mass, using a OHAUS AS 120 balance with a precision of ±0.0001 g (purchase from Fisher Bioblock, France). Then, they were placed in a Pyrex cell (V = 300 mL) equipped with a magnetic stirrer and closed using a Swagelock fitting. The resulting concentration of compounds was given in moles of compound per kilogram of solution.

A platinum resistance Pt-100 probe, calibrated according to the ITS-90 scale at the triple point of water, was used for temperature measurements. This was connected with a Hewlett-Packard digital multimeter 34401A. The uncertainty of the temperature determination was ±0.1 K, and the resolution was ±0.01 K. The temperature of the cell was controlled with water circulating between the thermostat and the measuring system. The optical system was purchased from Optilas, France. It consisted of a light source (a He−Ne laser model GLG 5090 from NEC Co.; Max, 1 mW; CW, 632.8 nm) and a light sensor (selenium photocell model SM5-30A). Variations of the intensity of light transmitted through the solution contained in the cell were registered as a function of temperature using a personal computer. The solubility was determined as follows: first, the temperature was increased above the

Table 3. Solubility (in Moles of Solute per Kilogram of Solution) of Selected Chlorophenols and Nitrophenols in Pure Water ($S°$) and in Electrolyte Aqueous Solutions (S) as a Function of Temperature[a]

Water + NaCl (5.8179 × 10^{-3} mol·kg^{-1})								
phenol	T/K	296.1	300.2	305.8	313.3	326.8	333.6	
	S/mol·kg^{-1}	0.8233	0.8427	0.8716	0.9624	1.2225	1.3927	
	$S°$/mol·kg^{-1}	0.8816	0.9170	0.9660	1.0328	1.3180	1.4868	
	k_s/kg·mol^{-1}	5.11	6.31	7.68	5.27	5.61	4.88	
4-chlorophenol	T/K	298.0	305.2	315.3	319.7	323.8	332.7	341.2
	S/mol·kg^{-1}	0.1760	0.1856	0.2020	0.2125	0.2178	0.2346	0.2477
	$S°$/mol·kg^{-1}	0.1985	0.2101	0.2266	0.2338	0.2405	0.2552	0.2692
	k_s/kg·mol^{-1}	8.98	9.26	8.58	7.13	7.40	6.28	6.21
2,4-dichlorophenol	T/K	294.6	303.1	311.5	322.4	336.7		
	S/mol·kg^{-1}	0.0264	0.0308	0.0342	0.0388	0.0454		
	$S°$/mol·kg^{-1}	0.0297	0.0376	0.0410	0.0456	0.0519		
	k_s/kg·mol^{-1}	8.79	14.9	13.5	12.1	9.99		
2,4,6-trichlorophenol	T/K	294.9	304.6	308.6	314.6	320.9		
	S/mol·kg^{-1}	0.0020	0.0040	0.0045	0.0053	0.0060		
	$S°$/mol·kg^{-1}	0.0025	0.0048	0.0052	0.0059	0.0067		
	k_s/kg·mol^{-1}	16.6	13.6	10.8	8.01	8.24		
2-nitrophenol	T/K	290.5	304.4	310.0	322.7			
	S/mol·kg^{-1}	0.0074	0.0158	0.0202	0.0269			
	$S°$/mol·kg^{-1}	0.0084	0.0175	0.0226	0.0284			
	k_s/kg·mol^{-1}	9.46	7.63	8.38	4.05			
4-nitrophenol	T/K	285.9	291.3	296.8	307.7	314.2		
	S/mol·kg^{-1}	0.0494	0.0658	0.0826	0.1374	0.1826		
	$S°$/mol·kg^{-1}	0.0625	0.0825	0.1082	0.1803	0.2403		
	k_s/kg·mol^{-1}	17.6	16.9	20.2	20.3	20.5		
Water + HCl (1.6218 × 10^{-3} mol·kg^{-1})								
phenol	T/K	292.5	300.2	308.4	313.3	326.8		
	S/mol·kg^{-1}	0.6711	0.7256	0.8089	0.8862	1.1450		
	$S°$/mol·kg^{-1}	0.8509	0.9170	0.9890	1.0328	1.3180		
	k_s/kg·mol^{-1}	63.6	62.7	53.8	40.9	37.7		
4-chlorophenol	T/K	298.0	305.2	315.3	332.7	339.5		
	S/mol·kg^{-1}	0.1723	0.1856	0.2052	0.2341	0.2524		
	$S°$/mol·kg^{-1}	0.1985	0.2101	0.2266	0.2552	0.2664		
	k_s/kg·mol^{-1}	37.9	32.2	26.6	23.1	14.4		
2,4-dichlorophenol	T/K	295.2	303.7	312.4	318.1	323.2		
	S/mol·kg^{-1}	0.0271	0.0330	0.0375	0.0399	0.0428		
	$S°$/mol·kg^{-1}	0.0303	0.0378	0.0414	0.0438	0.0459		
	k_s/kg·mol^{-1}	29.9	36.4	29.5	25.0	18.7		
2,4,6-trichlorophenol	T/K	294.9	297.7	302.4	307.5	313.7		
	S/mol·kg^{-1}	0.0019	0.0026	0.0035	0.0045	0.0053		
	$S°$/mol·kg^{-1}	0.0025	0.0032	0.0046	0.0051	0.0058		
	k_s/kg·mol^{-1}	73.5	55.6	73.2	33.5	24.1		
2-nitrophenol	T/K	290.5	303.2	310.7	322.7			
	S/mol·kg^{-1}	0.0082	0.0154	0.0190	0.0259			
	$S°$/mol·kg^{-1}	0.0084	0.0164	0.0229	0.0284			
	k_s/kg·mol^{-1}	6.45	16.8	49.9	24.7			
4-nitrophenol	T/K	287.8	292.8	298.5	306.7	312.4		
	S/mol·kg^{-1}	0.0527	0.0712	0.0945	0.1358	0.1763		
	$S°$/mol·kg^{-1}	0.0690	0.0889	0.1175	0.1723	0.2221		
	k_s/kg·mol^{-1}	72.1	59.4	58.3	63.7	61.8		
NaOH (5.6230 × 10^{-3} mol·kg^{-1})								
	T/K	296.4	302.7	315.5	330.6			
	S/mol·kg^{-1}	1.0192	1.0286	1.1632	1.4892			
	$S°$/mol·kg^{-1}	0.8842	0.9388	1.0666	1.4107			
	$-k_s$/kg·mol^{-1}	11.0	7.06	6.70	4.18			
NaOH (1.0000 × 10^{-4} mol·kg^{-1})								
	T/K	299.1	302.9	304.9	315.2			
	S/mol·kg^{-1}	0.9958	1.0052	1.0147	1.1219			
	$S°$/mol·kg^{-1}	0.9075	0.9405	0.9581	1.0604			
	$-k_s$/kg·mol^{-1}	403	289	249	245			
Water + NaOH (1.0965 × 10^{-5} mol·kg^{-1})								
phenol	T/K	296.3	302.7	315.4	322.4	331.3		
	S/mol·kg^{-1}	0.9627	0.9769	1.1080	1.2364	1.4633		
	$S°$/mol·kg^{-1}	0.8833	0.9388	1.0645	1.2159	1.4282		
	$-k_s$/kg·mol^{-1}	3410	1576	1587	662	962		
4-chlorophenol	T/K	298.3	309.3	315.8	324.8	329.0	341.9	
	S/mol·kg^{-1}	0.2052	0.2241	0.2320	0.2462	0.2540	0.2764	
	$S°$/mol·kg^{-1}	0.1990	0.2168	0.2274	0.2421	0.2491	0.2704	
	$-k_s$/kg·mol^{-1}	1215	1312	753	665	772	870	
2,4-dichlorophenol	T/K	291.4	302.0	308.8	321.0	337.7		
	S/mol·kg^{-1}	0.0309	0.0392	0.0432	0.0495	0.0565		
	$S°$/mol·kg^{-1}	0.0265	0.0371	0.0399	0.0450	0.0523		
	$-k_s$/kg·mol^{-1}	6086	2181	3149	3776	3060		

Table 3 (Continued)

2,4,6-trichlorophenol	T/K	292.8	302.2	308.0	317.2	
	S/mol·kg^{-1}	0.0034	0.0054	0.0062	0.0071	
	$S°$/mol·kg^{-1}	0.0021	0.0045	0.0051	0.0062	
	$-k_s$/kg·mol^{-1}	19093	7224	7739	5371	
2-nitrophenol	T/K	290.5	304.4	310.0	322.7	
	S/mol·kg^{-1}	0.0105	0.0245	0.0271	0.0350	
	$S°$/mol·kg^{-1}	0.0084	0.0175	0.0226	0.0284	
	$-k_s$/kg·mol^{-1}	8842	13333	7195	8280	
4-nitrophenol	T/K	284.3	289.0	296.3	307.7	313.8
	S/mol·kg^{-1}	0.0690	0.0945	0.1380	0.2179	0.2714
	$S°$/mol·kg^{-1}	0.0575	0.0734	0.1056	0.1803	0.2361
	$-k_s$/kg·mol^{-1}	7224	10012	10603	7505	5521

[a] The salting coefficient k_s is given in kg·mol^{-1}.

equilibrium temperature to obtain a single phase; then, the sample was slowly cooled. The rate of cooling in the vicinity of the phase-splitting temperature was controlled to within 0.1 K·min^{-1}. The sharp decrease of the transmitted light intensity observed at the phase splitting is shown in Figure 2. The equilibrium temperature corresponds to the starting point of the transmitted light decrease. It was determined graphically with the intersection of two straight lines. Three determinations of the transition temperature were performed for each sample, and average values were calculated. Results were reproducible to within ±0.15 K. The resulting solubility uncertainty was calculated using the slope of the solubility curve versus temperature and the temperature uncertainty $\{\Delta S = (\mathrm{d}S/\mathrm{d}T)\ \Delta T\}$. The uncertainty in solution composition due to mass weighting was negligible. The highest solubility uncertainty was observed with phenol (0.0020 mol·kg^{-1}) and the lowest one with 2,4,6-trichlorophenol (0.0002 mol·kg^{-1}).

Results and Discussion

At first, the liquid−liquid solubility diagram of the water + phenol system was established to validate the experimental method. Results obtained were compared with literature data[6,16] and are shown in Figure 3. The average deviation of the present results with the data of Campbell and Campbell[16] is 3.5%. This confirms the utility of the experimental method to determine the liquid−liquid solubility.

Solubility data of phenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2-nitrophenol, and 4-nitrophenol in aqueous solutions of selected electrolytes and surfactants were obtained in the temperature range from 280 K up to 345 K.

Influence of Electrolytes on the Aqueous Solubility of Chlorophenols and Nitrophenols. The salting out (or salting in) effect on the solubility is usually taken into account using the Setschenow[17] equation:

$$\log \frac{S°}{S} = k_s C \tag{1}$$

where $S°/S$ corresponds to the ratio of solubility in pure water and in salt solution at concentration C and at the same temperature. The salting coefficient k_s is positive for the salting out ($S° > S$) and negative for the salting in ($S° < S$). Values of $S°$ were not available at all temperatures studied. Experimental data of Jaoui et al.[6] and Achard et al.[18] were used to establish a linear correlation of $\ln(S°)$ as a function of temperature. Corresponding parameters are listed in Table 2. The solubility curve of certain compounds shows a characteristic slope change. In this case, two linear relationships are needed to represent $S°$ as a function of temperature.

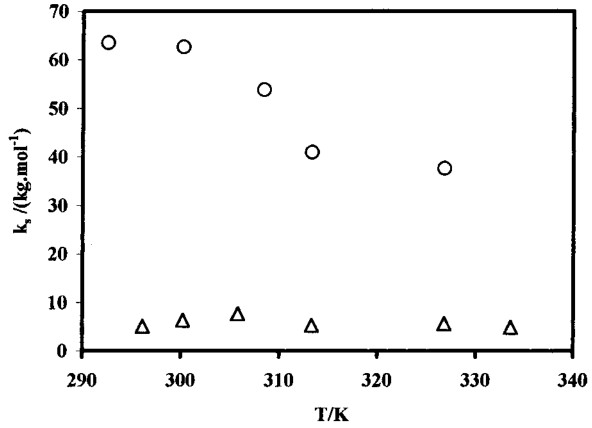

Figure 4. Salting parameter (k_s) of selected electrolytes measured in phenol aqueous solutions plotted against temperature: △, NaCl (5.8179×10^{-3} mol·kg^{-1}); ○, HCl (1.6218×10^{-3} mol·kg^{-1}).

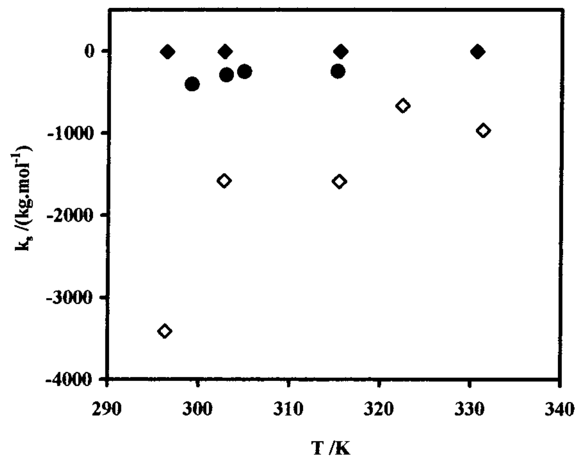

Figure 5. Salting parameter (k_s) of selected electrolytes measured in phenol aqueous solutions plotted against temperature: ◇, NaOH (1.0965×10^{-5} mol·kg^{-1}); ●, NaOH (1.0000×10^{-4} mol·kg^{-1}); ◆, NaOH (5.6230×10^{-3} mol·kg^{-1}).

Salting coefficients calculated from eq 1 are reported in Table 3 together with solubility data for each temperature. The evolution of the salting parameter of phenol as a function of temperature is plotted in Figures 4 and 5. The absolute value of the salting parameter is large and decreases significantly with temperature in the case of NaOH and HCl. It is negative in the former case and positive in the latter case. The value of k_s is small and positive with NaCl, and only a weak decrease is observed with increasing temperature. The same behavior is observed with all substituted phenols investigated in this work. The effect of low concentrations of electrolytes

Table 4. Solubility (in Moles of Solute per Kilogram of Solution) of Selected Chlorophenols and Nitrophenols in Pure Water ($S°$) and in Surfactant Aqueous Solutions (S) as a Function of Temperature[a]

		Water + SDS (3.8760×10^{-3} mol·kg^{-1})					
phenol	T/K	302.2	307.8	319.7	325.7	331.4	
	S/mol·kg^{-1}	0.9759	1.0089	1.1851	1.3296	1.4706	
	$S°$/mol·kg^{-1}	0.9344	0.9837	1.1559	1.2920	1.4307	
	C_m	10.7	6.50	7.53	9.70	10.3	
4-chlorophenol	T/K	296.9	306.6	312.1	319.9	331.0	
	S/mol·kg^{-1}	0.2102	0.2276	0.2381	0.2496	0.2699	
	$S°$/mol·kg^{-1}	0.1968	0.2124	0.2213	0.2341	0.2524	
	C_m	3.46	3.92	4.33	4.00	4.51	
2,4-dichlorophenol	T/K	294.7	299.5	307.1	315.1	325.5	
	S/mol·kg^{-1}	0.0345	0.0383	0.0426	0.0464	0.0483	
	$S°$/mol·kg^{-1}	0.0298	0.0361	0.0392	0.0425	0.0469	
	C_m	1.21	0.567	0.887	1.01	0.361	
2,4,6-trichlorophenol	T/K	290.9	303.0	311.4	315.3		
	S/mol·kg^{-1}	0.0026	0.0049	0.0061	0.0070		
	$S°$/mol·kg^{-1}	0.0018	0.0048	0.0055	0.0060		
	C_m	0.206	0.258	0.155	0.258		
2-nitrophenol	T/K	288.7	293.7	303.2	313.5	321.7	
	S/mol·kg^{-1}	0.0121	0.0144	0.0215	0.0282	0.0312	
	$S°$/mol·kg^{-1}	0.0076	0.0100	0.0164	0.0241	0.0279	
	C_m	1.16	1.13	1.31	1.06	0.851	
4-nitrophenol	T/K	286.7	291.9	297.5	305.2	311.7	
	S/mol·kg^{-1}	0.0836	0.0992	0.1207	0.1829	0.2406	
	$S°$/mol·kg^{-1}	0.0652	0.0850	0.1120	0.1609	0.2154	
	C_m	4.75	3.66	2.24	5.67	6.50	
		Water + Brij-30 (5.7250×10^{-5} mol·kg^{-1})					
phenol	T/K	293.8	299.1	307.2	317.2	324.8	329.3
	S/mol·kg^{-1}	1.1725	1.1771	1.2590	1.3531	1.4807	1.5927
	$S°$/mol·kg^{-1}	0.8619	0.9075	0.9784	1.1021	1.2709	1.3785
	C_m	5425	4709	4901	4384	3664	3741
4-chlorophenol	T/K	295.3	303.1	311.0	320.8	331.7	
	S/mol·kg^{-1}	0.2816	0.2950	0.3079	0.3300	0.3505	
	$S°$/mol·kg^{-1}	0.1942	0.2067	0.2195	0.2356	0.2535	
	C_m	1526	1542	1544	1649	1694	
2,4-dichlorophenol	T/K	295.2	303.7	312.4	318.1	323.2	
	S/mol·kg^{-1}	0.0505	0.0570	0.0635	0.0666	0.0689	
	$S°$/mol·kg^{-1}	0.0303	0.0378	0.0414	0.0438	0.0459	
	C_m	353	335	386	398	402	
2,4,6-trichlorophenol	T/K	295.3	303.7	313.3	319.9	327.0	
	S/mol·kg^{-1}	0.0066	0.0078	0.0095	0.0105	0.0121	
	$S°$/mol·kg^{-1}	0.0026	0.0047	0.0058	0.0066	0.0076	
	C_m	69.9	54.1	64.6	68.1	78.6	
2-nitrophenol	T/K	290.5	294.5	305.7	311.8	323.4	
	S/mol·kg^{-1}	0.0192	0.0209	0.0279	0.0314	0.0383	
	$S°$/mol·kg^{-1}	0.0084	0.0104	0.0186	0.0234	0.0287	
	C_m	189	183	162	140	168	
4-nitrophenol	T/K	287.8	292.8	298.5	306.2	312.4	
	S/mol·kg^{-1}	0.1497	0.1614	0.1895	0.2346	0.2936	
	$S°$/mol·kg^{-1}	0.0690	0.0889	0.1175	0.1684	0.2221	
	C_m	1409	1266	1258	1156	1249	
		Water + NP-10 (7.0500×10^{-5} mol·kg^{-1})					
phenol	T/K	293.8	302.2	307.8	319.7	325.7	
	S/mol·kg^{-1}	1.0287	1.0521	1.0755	1.2499	1.3974	
	$S°$/mol·kg^{-1}	0.8619	0.9344	0.9837	1.1559	1.2920	
	C_m	2366	1669	1302	1333	1495	
4-chlorophenol	T/K	296.9	306.6	312.1	319.9	331.0	
	S/mol·kg^{-1}	0.2388	0.2576	0.2665	0.2784	0.2986	
	$S°$/mol·kg^{-1}	0.1968	0.2124	0.2213	0.2341	0.2524	
	C_m	596	641	641	628	655	
2,4-dichlorophenol	T/K	295.2	300.8	306.6	311.8	317.5	
	S/mol·kg^{-1}	0.0434	0.0476	0.0499	0.0520	0.0546	
	$S°$/mol·kg^{-1}	0.0303	0.0366	0.0390	0.0411	0.0435	
	C_m	186	156	155	155	157	
2,4,6-trichlorophenol	T/K	292.8	300.6	309.5	314.3		
	S/mol·kg^{-1}	0.0040	0.0057	0.0067	0.0075		
	$S°$/mol·kg^{-1}	0.0021	0.0040	0.0053	0.0059		
	C_m	26.9	24.1	19.8	22.7		
2-nitrophenol	T/K	286.1	291.8	303.2	312.1	323.1	
	S/mol·kg^{-1}	0.0095	0.0142	0.0211	0.0263	0.0314	
	$S°$/mol·kg^{-1}	0.0065	0.0090	0.0164	0.0235	0.0286	
	C_m	42.5	73.7	66.7	39.7	39.7	
4-nitrophenol	T/K	291.0	294.6	301.5	306.1	310.4	
	S/mol·kg^{-1}	0.0891	0.1026	0.1572	0.1942	0.2304	
	$S°$/mol·kg^{-1}	0.0812	0.0972	0.1355	0.1676	0.2034	
	C_m	112	76.6	308	377	383	

Table 4 (Continued)

		Water + SB-16 (4.8450×10^{-5} mol·kg^{-1})				
phenol	T/K	298.2	303.4	317.4	323.5	331.0
	S/mol·kg^{-1}	1.0099	1.0334	1.2318	1.3753	1.5284
	$S°$/mol·kg^{-1}	0.8997	0.9449	1.1064	1.2409	1.4207
	C_m	2274	1827	2588	2774	2222
4-chlorophenol	T/K	298.4	303.4	308.8	318.5	333.2
	S/mol·kg^{-1}	0.2220	0.2310	0.2420	0.2571	0.2810
	$S°$/mol·kg^{-1}	0.1992	0.2072	0.2160	0.2318	0.2560
	C_m	471	491	537	522	516
2,4-dichlorophenol	T/K	294.7	299.5	307.1	315.1	325.5
	S/mol·kg^{-1}	0.0365	0.0403	0.0446	0.0484	0.0503
	$S°$/mol·kg^{-1}	0.0298	0.0361	0.0392	0.0425	0.0469
	C_m	138	86.7	111	122	70.2
2,4,6-trichlorophenol	T/K	293.3	303.0	311.4	323.0	
	S/mol·kg^{-1}	0.0034	0.0049	0.0061	0.0078	
	$S°$/mol·kg^{-1}	0.0022	0.0046	0.0055	0.0070	
	C_m	24.8	6.19	12.4	16.5	
2-nitrophenol	T/K	293.1	298.4	303.2	313.4	327.4
	S/mol·kg^{-1}	0.0142	0.0174	0.0211	0.0278	0.0331
	$S°$/mol·kg^{-1}	0.0097	0.0128	0.0164	0.0241	0.0307
	C_m	92.9	94.9	97.0	76.4	49.5
4-nitrophenol	T/K	288.7	293.9	299.5	307.2	313.7
	S/mol·kg^{-1}	0.0875	0.1112	0.1358	0.1942	0.2543
	$S°$/mol·kg^{-1}	0.0723	0.0939	0.1232	0.1762	0.2351
	C_m	314	357	260	371	396

[a] The capacity coefficient C_m is dimensionless.

observed in this study is significant and depends on the chemical properties of a given compound.

The variation of the solubility due to electrolytes can be determined from the values of S and $S°$ reported in Table 3. This variation is between 10 and 30%. Huang et al.[7] demonstrated that a larger enhancement of the solubility of chlorophenols at $T = 298$ K can be observed at pH higher than pK_a (pK_a is about 6 for 2,4,6-trichlorophenol). However, the pH of solutions investigated in our study was less than 7. In the case of NaOH solutions, the alkaline effect was weak at concentrations studied and was balanced by the acidic character of phenol derivatives. The pH encountered in ground and river water is usually acid and less than the pK_a of most of chlorophenols. Consequently, an increase of the solubility observed in natural conditions is comparable with the results presented in this work.

Influence of Surfactants on the Aqueous Solubility of Chlorophenols and Nitrophenols. All surfactants were used in this study at concentrations lower than the cmc. Consequently, the solubility enhancement of phenol derivatives is not due to the micellar solubilization. That could be tentatively explained either by hydrophobic aggregation or by formation of mixed micelles. To estimate the quantitative influence of a surfactant on the solubility of chlorophenols and nitrophenols, we defined capacity coefficient C_m, analogous to the salting coefficient, by

$$C_m = \frac{S - S°}{C} \tag{2}$$

C_m is given in moles of solute per moles of surfactant. It expresses an increase of the number of solute molecules present in the solution ($S - S°$) induced by one molecule of surfactant (C is the surfactant concentration in moles per kilogram). Values of the capacity coefficients are reported in Table 4 together with solubility data for each temperature. Figure 6 gives plots of C_m as a function of temperature for aqueous solutions of phenol. As is illustrated with these plots, C_m is not highly dependent on temperature, but it depends strongly on the nature of the surfactant. We hypothesize that formation of mixed surfactant−solute aggregates is responsible for this effect. The smallest effect is observed with SDS (the solubility increases between 5 and 40%). A larger enhancement of the solubility can be noted with NP-10 (20−50%) and SB-16 (15−50%). The strongest effect is induced by Brij-30 (40−150%).

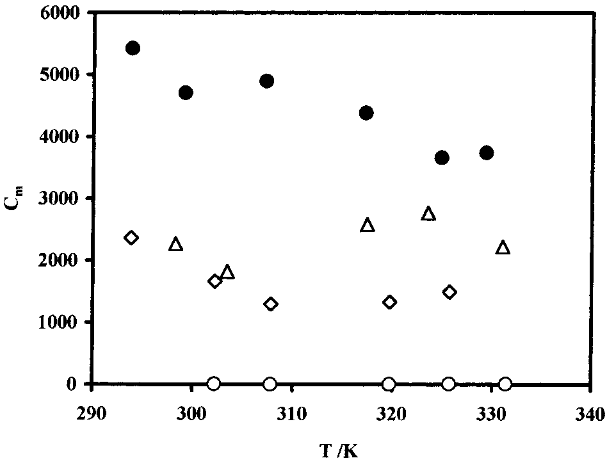

Figure 6. Capacity coefficient (C_m) of selected surfactants measured in phenol aqueous solutions plotted against temperature: ○, SDS (3.8760×10^{-3} mol·kg^{-1}); ●, Brij-30 (5.7250×10^{-5} mol·kg^{-1}); ◇, NP-10 (7.0500×10^{-5} mol·kg^{-1}); △, SB-16 (4.8450×10^{-5} mol·kg^{-1}).

The variation of C_m as a function of temperature is similar to that of all substituted phenols. However, it is strongly dependent on the number of chlorine atoms, n, and decreases as n increases. In the case of nitrophenols, the capacity coefficient C_m is significantly lower than that observed with phenol.

Conclusion

In the present work, we studied the influence of low concentrations of electrolytes or surfactants on the solubility of phenol and selected chlorophenols and nitrophenols in water. Special attention was paid to the evolution of this effect with temperature.

It was observed that the salting effect due to electrolytes is significant but decreases with temperature. The variation of the solubility in the presence of small amounts of electrolytes can be as high as 30%.

The solubility enhancement due to surfactants can be significant even below the cmc. This could be explained by aggregation phenomena occurring between surfactant and solute molecules. This hypothesis should be confirmed by an investigation of the solution structure. It was concluded that the influence of temperature was negligible in this case.

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