504 J. Chem. Eng. Data **1996,** *41,* 504−507

Aqueous Solubilities of Phenol Derivatives by Conductivity Measurements

C. Achard, M. Jaoui, M. Schwing, and M. Rogalski*

Laboratoire de Thermodynamique et d'Analyse Chimique, Université de Metz, Ile du Saulcy, F-57045 Metz Cedex, France

The aqueous solubilities of five chlorophenols and three nitrophenols were measured by conductimetry at temperatures between 15 and 48 °C. The solubilities of 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol, 2-nitrophenol, 4-nitrophenol, and 2,4-dinitrophenol were studied. Automatic conductivity measurements allow the determination of the solute concentration and, hence, the determination of the solubility. Emulsion formation can also be followed. Results obtained are in good agreement with literature values.

Introduction

Chlorophenols are used extensively as fungicides, herbicides, algicides, insecticides, ovicides, pharmaceuticals, and dyes, as preservatives for wood, glue, paint, vegetable fibers, and leather, and as intermediates in chemical syntheses. They may also be formed by the degradation of chlorinated pesticides and by the reaction of chlorinated water supplies with phenol in the environment (Bourguignon *et al.*, 1993). They have a relatively high toxicity. The nitrophenols, with the exception of the trinitro derivatives, are classed as slight fire hazards and moderate explosion hazards. They are very toxic compounds when ingested, inhaled, or absorbed through the skin (Othmer, 1987).

The environmental fate and hence effects of these substances depend on their physical−chemical properties. The literature contains considerable information on the toxicological and analytical characteristics of these compounds. However, the lack of physical−chemical properties renders an adequate understanding of their fate in the environment difficult and unreliable (Suntio *et al.*, 1988).

Aqueous solubility is a particularly important parameter for assessing environmental partitioning. Ma *et al.* (1993) determined the aqueous solubility at 25 °C for 16 chlorophenols by using high-pressure liquid chromatography with UV detection. Solubility data for nitrophenols at 25 °C were reported by Buchholz and Pawliszyn (1994). Values at temperatures higher than 40 °C are also available in the literature for mononitrophenols (Seidell, 1941).

The precipitation of ionized species can be detected by measurement of the electrical conductivity. Several studies were reported in the literature for strong electrolyte aqueous mixtures in the conductivity ranges between mS cm^{-1} and S cm^{-1} (Berthet and Counioux, 1992). However, few applications to low conductivity systems (from nS cm^{-1} to 100 $\mu S\ cm^{-1}$) were reported. Fotland *et al.* (1993) made studies on the asphaltene solubility in low dielectric constant media.

The aim of the present work was to determine the aqueous solubilities of some nitrophenols and chlorophenols at temperatures between 15 and 48 °C by conductivity measurements. An experimental arrangement made it possible to determine the solubility for slightly ionized liquids within the conductivity range from 0.01 to 400 $\mu S\ cm^{-1}$.

Experimental Section

Experimental Setup. The apparatus is shown in Figure 1. Measurements were performed in a glass sample cell (a) of the volume $V = 250\ cm^3$ equipped with a magnetic stirrer (b). The temperature was maintained constant to within ±0.1 deg by a double jacket surrounding the cell and connected to the Lauda RM6 thermostat (c). A platinum resistance probe (PT 100) with a Hewlett-Packard digital multimeter (34401A) was used to measure the cell temperature (d). The conductivity measurements were carried out using an electrode immersed in the solution and connected to a Tacussel CDM 92 conductimeter (e). The working frequency of this apparatus ranged from 94 Hz to 50 kHz (conductivity from 10 nS cm^{-1} to 6 S cm^{-1} when using a cell constant of 1 cm^{-1}) and enabled the conductivity studies of both low and high conductivity solutions. An automatic piston buret (Schott T90/20) was used to modify the initial quantity of the solvent (f). The piston buret, the multimeter, the conductimeter, and the magnetic stirrer were connected with the four serial ports of a PC computer via the standard RS-232 interface (g). Measurement control and data acquisition were automated via the computer.

Materials. Chlorophenols and nitrophenols purchased respectively from Aldrich Chemical Co. and Merck Co. were of purity higher than 99%. They were used without any further purification. Deionized water used for solution preparation had a conductivity of about 1−1.8 $\mu S\ cm^{-1}$. The corresponding pH was 5.6.

Experimental Procedure. Weighted amounts of the chlorophenol or the nitrophenol and deionized water were placed in the sample cell. The amount of solute was in excess with respect to saturation. The solution was stirred for 2 h at a temperature sufficiently high to solubilize all of the solute. The temperature was then decreased to the value selected for the measurement, and the solid deposition or a phase splitting of the solute excess was observed. The mixture was stirred 2 h before starting solubility measurements.

The excess solute was dissolved by injecting known volumes of water (from 0.5 to 2.5 cm^3). After each injection, the solution was vigorously stirred for at least 5 min to ensure thermal and chemical equilibria. Absolute conductivity measurements cannot be performed when the solution is stirred. Therefore, the stirring was stopped before every measurement. In the case of the low conductivity determinations, the apparatus made it pos-

0021-9568/96/1741-0504$12.00/0

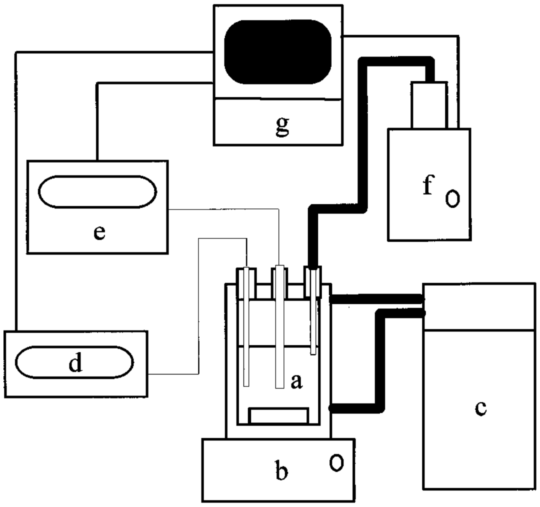

Figure 1. Experimental setup: (a) sample cell; (b) magnetic stirrer; (c) thermostat; (d) multimeter; (e) conductimeter; (f) piston buret; (g) PC computer.

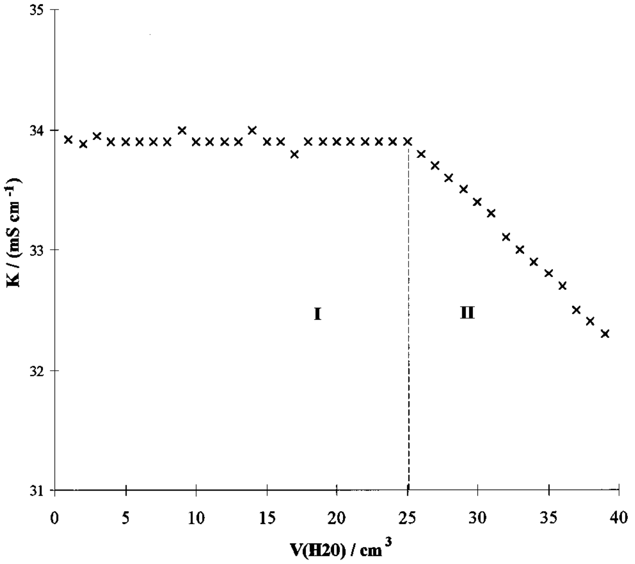

Figure 2. Conductivity K as a function of the water volume added to an aqueous NaCl solution (I, liquid solution + solid NaCl; II, liquid solution).

sible to obtain conductivities with a relative accuracy to within ±0.1%.

The experimental procedure was initially tested with solutions of a strong electrolyte. Results obtained with sodium chloride are presented in Figure 2. A break observed on the plot of the conductivity versus volume corresponds to the complete dissolution of the solute. The solute solubility can then be calculated using a simple mass balance. The magnetic stirring affects conductivity measurements but does not modify the break location on the composition scale. This allows solubility measurements to be performed using continuous stirring. However, we preferred to use the real absolute values of the conductivity obtained without the perturbation effect of the magnetic stirring.

Results and Discussion

Solubility Measurements. In Table 1, experimental results obtained in the present study are compared with values reported in the literature and expressed in g L^{-1}. To convert our results in g L^{-1}, densities of saturated solutions should be known. They were measured at 25 °C with an Anton Paar DMA 35 densimeter and ranged between 0.998 g cm^{-3} (pentachlorophenol) and 1.004 g cm^{-3} (phenol, 4-chlorophenol). The average value of the density, 1.000 g cm^{-3}, was used in conversion of g kg^{-1} to g L^{-1}.

The pK_a values and the melting points of phenols were obtained from the literature.

Each solubility was established as an average value of four experiments. The resulting standard deviation was in the range between 0.5 and 7%. The uncertainty of the method was estimated using the error propagation formula and was found to be 1−4 % depending on the compound solubility. The most important error was observed in the case of the pentachlorophenol.

For monochlorophenols, the organic liquid phase remains in equilibrium with the aqueous phase over the whole temperature range. 2,4-Dichlorophenol is solid at low temperatures. The liquid organic phase appears between 20 and 25 °C. For higher chlorophenols and nitrophenols, the two liquid phase system is never observed. It should be emphasized that the conductivity measurements lead to good solubility results in the case of both liquid−liquid and liquid−solid systems.

It can be observed that the aqueous solubilities of 2-nitrophenol and 4-nitrophenol are very different. This might be due to the stabilization of the nondissociated form of 2-nitrophenol by intramolecular hydrogen bonding between nitro and hydroxyl groups (Schwarzenbach *et al.*, 1988). As a consequence, the higher solubility of 4-nitrophenol as compared to 2-nitrophenol is due to easier solvation and intermolecular hydrogen bonding. It is interesting to note that both compounds exhibit nearly the same value of pK_a. A very important difference of melting temperature is observed however.

Solubility values presented in the literature are often discordant. A scatter of about 100% is observed in the case of pentachlorophenol. Results presented in this work are in good agreement with the recent literature data when they are available.

Aqueous solubilities of the substituted phenols are small and in general do not exceed 0.025 mass fraction. The presence of the chlorine or the nitro groups in the molecules decreases the aqueous solubility with respect to phenol. The logarithm of solubility dependence on temperature is linear for chlorophenols, as shown in Figure 3. In the case of nitrophenols (Figure 4), the increase of log(S) is not always linear. The faster increase of the solubility observed in the case of 4-nitrophenol at higher temperatures is due to the relatively low value of the upper critical solution temperature.

Emulsion Effect. When two liquid phases are present in the solution, emulsion formation is often observed. This phenomenon can be followed by conductimetric measurements. In the plot of the conductivity versus the volume of water, three breaks can be seen, as illustrated in Figure 5 for 4-chlorophenol. The first break (i) corresponds to the formation of the emulsion occurring in the saturated solution remaining in equilibrium with the organic liquid phase. The second one (ii) marks the disappearance of the organic liquid phase. The last one (iii) corresponds to the emulsion disappearing and at the same time the full dissolution of the 4-chlorophenol in water. Therefore, the conductimetric studies provide more details about the structural evolution of the solution.

The size of the particles in the emulsion was measured by a particle size analyzer (Malvern Instruments) and they were about 0.5 μm. This corresponds to the limit between microemulsions (less than 0.1 μm) and emulsions (more

Table 1. Aqueous Solubilities in Grams per Liter (and Standard Deviations) of Solution for the Chlorophenols and the Nitrophenols in the Temperature Range 15−48 °C

compound	pK_a at 25 °C	t_m/°C	t/°C	S/(g L^{-1})	S(lit.) at t/°C	physical state of the organic phase
phenol	9.92[b]	41[b]	15.1	76.044 ± 0.014	75.000/10[d]	liquid
			25.0	84.045 ± 0.011	83.000/20[d]	liquid
			35.0	93.098 ± 0.029	88.000/30[d]	liquid
					96.000/40[d]	liquid
2-chlorophenol	8.52[b]	9[b]	15.4	20.838 ± 0.130		liquid
			24.6	22.660 ± 0.217	23.256/25[b] 11.350/25[b] 24.650/25[b]	liquid
			34.5	24.007 ± 0.192		liquid
4-chlorophenol	9.37[b]	43−44[b]	15.1	23.337 ± 0.017		liquid
			25.2	25.540 ± 0.020	26.390/25[b] 26.250/25[b] 27.000/25[b]	liquid
			34.6	28.499 ± 0.053		liquid
2,4-dichlorophenol	7.90[b]	42−43[b]	15.3	3.896 ± 0.003		solid
			25.2	5.517 ± 0.064	6.194/25[b] 5.547/25[b]	liquid
			29.8	6.075 ± 0.031		liquid
			35.1	6.501 ± 0.005		liquid
2,4,6-trichlorophenol	5.99[b]	69.5[b]	19.5	0.410 ± 0.005		solid
			20.1	0.427 ± 0.005		solid
			24.9	0.692 ± 0.005	0.434/25[b] 0.708/25[b]	solid
			30.0	0.928 ± 0.007		solid
pentachlorophenol	4.74[b]	174[b]	25.1	0.0214 ± 0.001	0.0184/25[b] 0.0096/25[b] 0.0154/25[b] 0.0108/25[b] 0.0140/25[b]	solid
			34.5	0.0578 ± 0.001		solid
			46.8	0.0862 ± 0.002		solid
2-nitrophenol	7.23[a]	45−46[c]	15.6	1.076 ± 0.017		solid
			24.8	1.697 ± 0.031	2.100/25[a]	solid
			34.7	2.935 ± 0.125	3.300/40[d]	solid
4-nitrophenol	7.15[a]	114−116[c]	15.3	10.162 ± 0.018		solid
			25.0	15.599 ± 0.033	16.000/25[a]	solid
			30.3	19.600 ± 0.032	38.800/40[d]	solid
			34.9	26.845 ± 0.419		solid
2,4-dinitrophenol	4.09[a]	115−116[c]	15.1	0.415 ± 0.019		solid
			25.0	0.691 ± 0.046	0.560/25[a]	solid
			35.0	0.975 ± 0.030		solid

[a] Buchholz and Pawliszyn (1994). [b] Ma *et al.* (1993). [c] Weast (1981). [d] Seidell (1941).

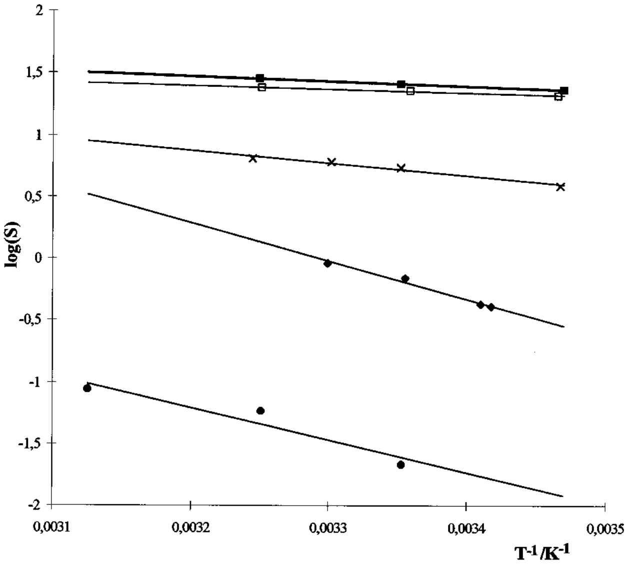

Figure 3. Logarithm of the solubility of chlorophenols versus T^{-1}/K^{-1} (□, 2-chlorophenol; ■, 4-chlorophenol; ×, 2,4-dichlorophenol; ♦, 2,4,6-trichlorophenol; ●, pentachlorophenol).

than 1 μm) (Berthod, 1983). These emulsions are stable at ambient conditions and 1 week is usually necessary to obtain complete phase splitting.

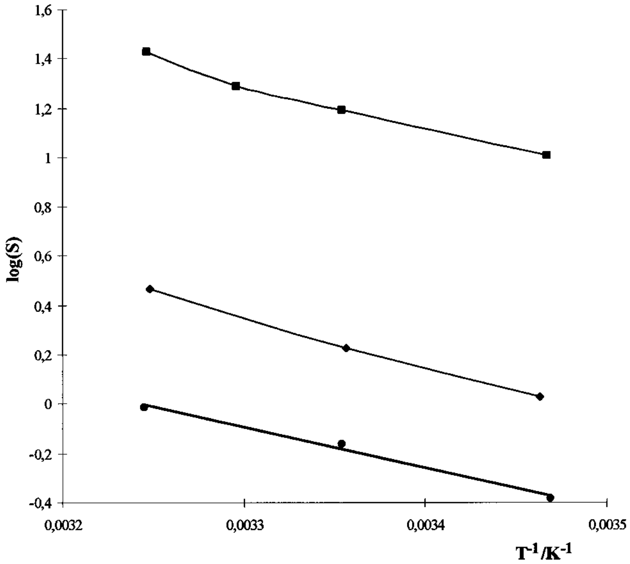

Figure 4. Logarithm of the solubility of nitrophenols versus T^{-1}/K^{-1} (♦, 2-nitrophenol; ■, 4-nitrophenol; ●, 2,4-dinitrophenol).

Conclusion

Results of the present study show that the aqueous solubility of weak organic electrolytes of environmental

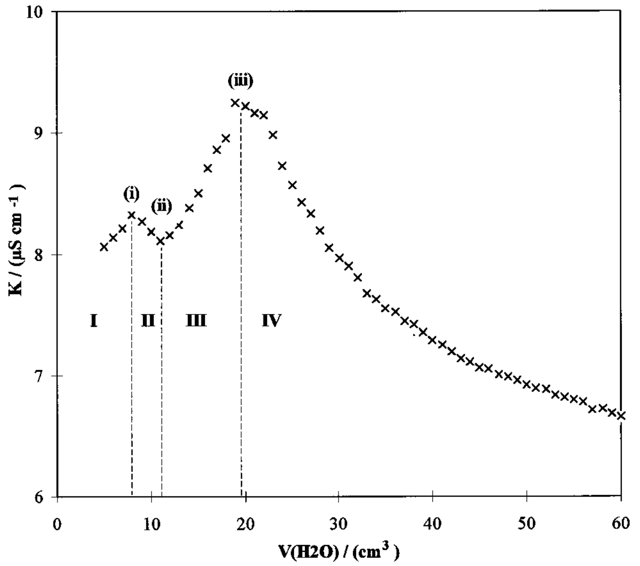

Figure 5. Conductivity measurements in 4-chlorophenol aqueous solutions at 25 °C (I, aqueous phase + organic phase; II, aqueous phase + organic phase + emulsion; III, aqueous phase + emulsion; IV, aqueous phase).

interest, such as substituted phenols, can be accurately determined by conductivity measurements. The accuracy of results obtained by the present method in the case of weak electrolytes is comparable with the most accurate data published in the literature. It is about 1−4% depending on the physical properties of the compound considered. In the case of the chlorinated phenols, conductivity measurements allow one to determine the emulsion existence domain in the two liquid phase range.

Literature Cited

Berthet, J.; Counioux, J. J. Automated conductimetric analysis of solid-liquid equilibria. *Thermochim. Acta* **1992**, *194*, 137−147.

Berthod, A. Review article. Physical-chemical structures of liquid disperse systems, micellar media, emulsions and microemulsions. *J. Chim. Phys.* **1983**, *80*, 407−424.

Bourguignon, B.; Marcenac, F.; Keller, H. R.; De Aguiar, P. F.; Massart, D. L. Simultaneous optimization of pH and organic modifier content of the mobile phase for the separation of chlorophenols using a Doehlert design. *J. Chromatogr.* **1993**, *628*, 171−189.

Buchholz, K. D.; Pawliszyn, J. Optimization of Solid-Phase Microextraction Conditions for Determination of Phenols. *Anal. Chem.* **1994**, *66*, 160−167.

Fotland, P.; Anfindsen, H.; Fadnes, F. H. Detection of asphaltene precipitation and amounts precipitated by measurement of electrical conductivity. *Fluid Phase Equilibr.* **1993**, *82*, 157−164.

Ma, K. C.; Shiu, W. Y.; Mackay D. Aqueous Solubilities of Chlorinated Phenols at 25 °C. *J. Chem. Eng. Data* **1993**, *38*, 364−366.

Othmer, K. *Encyclopedia of Chemical Technology*; Wiley Interscience: New York, 1987.

Schwarzenbach, R. P.; Stierli, R.; Folsom, B. R.; Zeyer, J. Compound Properties Relevant for Assessing the Environmental Partitioning of Nitrophenols. *Environ. Sci. Technol.* **1988**, *22*, 83−92.

Seidell, A. *Solubility of organic compounds*; Van Nostrand Co.: New York, 1941; Vol II.

Suntio, L. R.; Shiu, W. Y.; Mackay, D. *Chemosphere* **1988**, *17*, 1259−1290.

Weast, R. C. *Handbook of Chemistry and Physics*, 61st ed.; CRC Press: Boca Raton, FL, 1981.

Received for review August 9, 1995. Accepted January 24, 1996.⊗

JE950202O

⊗ Abstract published in *Advance ACS Abstracts,* March 15, 1996.