The Effects of Temperature and Inorganic Salts on the Aqueous Solubility of Selected Chlorobenzenes

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The experimental results reported in this paper are the first in a wider research program aiming to test, in a laboratory, the behavior of selected hydrophobic compounds in an aqueous system. The generator column method was used to determine the solubility in water of biphenyl, 1,2-dichlorobenzene (1,2-DCBz), and hexachlorobenzene (HxCBz) at 25 °C. The solubilities of 1,2-DCBz and HxCBz were measured at temperatures ranging from 15 to 55 °C, and the enthalpies of solutions were derived from van't Hoff plots. The effects of three electrolytes on the solubility of HxCBz were determined at 25 °C, and their newly obtained Setschenow constants are reported.

Introduction

Chlorobenzenes created during chemical and industrial processes and released into the environment can lead to taste and odor problems in drinking water and fish; also, they may accumulate in organically rich sediments, soils, and groundwater, causing a variety of adverse health effects.[1] To assess precisely the transport and distribution of chlorobenzenes in the aquatic system, the knowledge of their physical and chemical properties is needed, especially of their aqueous solubility. Since various environmental factors, such as temperature, dissolved salts (in a marine environment), dissolved organic matter (in soil), or pH, may strongly affect the solubility of chemicals as well as their sorption into and desorption from soils and sediments, it also is necessary to take these factors into consideration when studying the behavior of chlorobenzenes.

Most organic pollutants are present in the environment at very small concentrations below saturation levels. At a laboratory, their solubility in water as well as vapor pressure are measured at saturation conditions. These saturated values are useful for estimating air−water partition coefficients.[2]

The considerable discrepancies between the reported aqueous solubility data[2−6] reflect an important problem associated with difficulties in the preparation of their saturated solutions, especially for sparingly soluble hydrophobic compounds such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), and biphenyls (BiPh, PCBs), including chlorobenzenes (CBZs). We must mention that there are two accepted methods of equilibration. The first is the shake-flask method,[7] in which an excess amount of the solute is added to water and shaken gently (or stirred) until equilibrium is achieved. In practice, this simple technique is not suitable for compounds with solubilities below 10 mg·L^{-1}. The second is the generator column method,[8] in which an inert support is coated with the analyte and packed into the column; then water, at a precise flow rate, is passed through to achieve equilibrium. This method is accepted to determine the water solubility of chemicals in the range from 10^{-3} to 5000 mg·L^{-1}.

Among the published articles, only a few provide detailed information about and explanations of the solubility behavior and its temperature dependence of chlorobenzenes,[9,10] polycyclic aromatic hydrocarbons,[5,6,11] polychlorinated BiPhs,[9,12−14] polychlorinated-*p*-dioxins,[12,15−17] and dibenzofurans.[9,12]

A few articles provide information about the effect of salts on the solubility of organic compounds. Among them, only two articles report data for the lower chlorinated benzenes.[18,19] The others report the salting effect for polycyclic hydrocarbons,[11] toluene, xylenes, benzene, and derivatives.[20,24,25] To this point, no new data have been reported for PCDDs, PCDFs, PCBs, and other CBZs.

In this study, the generator column method is applied to the determination of the solubilities of 1,2-dichlorobenzene (1,2-DCBz), hexachlorobenzene (HxCBz), and BiPh, and the effect of temperature on the solubility of two different chlorobenzenes is studied. The enthalpies of solutions are derived, the activity coefficients are calculated from determined solubilities, and the effect of temperature on the activity coefficient is reported. Finally, the effect of dissolved inorganic salts on the solubility of HxCBz is analyzed, and the Setschenow constants are calculated. These data can be helpful for predicting the behavior of chlorobenzenes under environmental conditions.

Experimental Section

Materials. The BiPh (99.5%), and ethyl acetate (99.8% HPLC-grade) were obtained from Aldrich Chemical Co., Inc.; the 1,2-DCBz (98.0%), hexane (97.8%), anhydrous Na_2SO_4, NaCl (99.5%), KCl (99.9%), and $CaCl_2$ (99.9%) were purchased from Wako Pure Chemical Industries, Ltd.; the HxCBz (99.0%) was provided by Cambridge Isotope Laboratories, Inc. The reagent-grade water was obtained from a NANOpure Diamond TOC−UV system. In the solid-phase-extraction (SPE) process, cartridges (200 mg/3 mL, J. T. Baker) packed with reversed-phase octadecylsilane (C_{18}) bonded onto silica gel were used.

The salt solutions were prepared by accurately weighing one of the salts (NaCl, KCl, $CaCl_2$) and dissolving them in the nano-ultrapure water. Each solution was filtered through a membrane filter (0.22 μm, Duvapore). The concentration of each solution was analyzed before and

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Table 1. Aqueous Solubilities of 1,2-DCBz, HxCBz, and BiPh: Mean Value and Standard Deviations at 25 °C

	this study		literature data	
compound	flow rate/mL·min^{-1}	generator column S_{w}[a]/mg·L^{-1}	generator column S_{w}[a]/mg·L^{-1}	other methods S_{w}[a]/mg·L^{-1}
1,2-DCBz	0.50	93.7 ± 3.60	92.3[27]	149.4;[4] 137;[2] 154;[4,2] 169;[4,2] 155.8;[4,2] 152.9;[4] 97.0;[4] 109;[4] 149;[10] 145;[30] 92.7;[31] 79.0;[2] 92.8;[32] 154;[2] 99.1[33]
	1.10	94.4 ± 4.57		
HxCBz	0.74	0.010 ± 0.0006	0.005;[4,2] 0.00544;[9] 0.047;[27] 0.00966[7]	0.006;[4,2] 0.11;[4,2] 0.0039;[33] 0.0054;[4,2] 0.0052;[4] 0.005;[4,2] 0.38;[4] 0.0012−0.014[31]
	1.51	0.0096 ± 0.0005		
BiPh	0.66	5.37 ± 0.37	6.71(28)	7.00;[2] 7.45;[2] 7.48;[2] 7.50;[2] 7.08;[2] 5.94;[2] 3.87;[2] 8.08;[29] 8.05;[2]
	1.13	5.32 ± 0.28		

[a] Mean value ± standard deviation; a student's T-test was applied to the means of determined solubility values (*n*) for level of significance 0.99.

after passing through the generator column by inductively coupled plasma spectrometry (Perkin Elmer Optima 3300 SYS).

Stock standard solutions (100 mg·L^{-1}) were prepared in hexane for the BiPh, 1,2-DCBz, and HxCBz. The working standard solutions for the calibration curves were obtained by dilution with hexane from the stock solutions.

Preparation of the Saturated Solution Using a Generator Column. The generator column (300 mm × 3 mm i.d.) was made of Pyrex glass, and enclosed in a water jacket connected to an isothermal bath (ThermoHaake K 10 ± 0.01 K). The tubing and connections were made of Teflon. Each compound was dissolved in hexane or ethyl acetate and coated on Chromosorb W (60−80 mesh, Merck). The solvent was removed using a rotary evaporator for 2−3 h; then the coated chromosorb was dry packed into the generator column. The amount of coating applied was ca. 3.0 (w/w), 0.2 (w/w), and 2.0% (w/w) for BiPh, HxCBz, and 1,2-DCBz, respectively. The pure water or salt solution was pumped at a flow rate of 0.5−1.8 mL/min by a Metarol pump, from a thermostatic glass reservoir vessel, through the generator column; finally, it was directed either to a tared flask or through the extractor cartridge. For the initial conditioning of the generator column, 100−300 mL of water was used.

Extraction of the Saturated Solution. A liquid−liquid extraction was used for the aqueous saturated solutions of BiPh and 1,2-DCBz. Each solution was collected in the tared flask then drained into a separator funnel and extracted with an appropriate volume of hexane. A solid-phase extraction was used for the HxCBz. Before connection, the cartridge was washed sequentially with 3 mL of hexane, 4 mL of methanol, and 5 mL of reagent-grade water. The saturated aqueous solution eluting from a generator column was passed directly through the SPE cartridge, and the quantities of aqueous eluate collected in the tared flask were weighed. After collection of a sufficient volume of eluate, the SPE cartridge was disconnected, washed with reagent-grade water (3 mL), and dried under vacuum for 40 min. The analyte was eluted with 3 × 0.3 mL of hexane under vacuum. Each portion of hexane was left in contact with the sorbent for 2 min to reach equilibrium. The collected extract was dried with anhydrous sodium sulfate to remove any remaining water.

Recovery tests for the liquid−liquid and solid-phase extractions were carried out by extraction procedure protocols. A measured volume of the compound of interest was dissolved in reagent-grade water in a glass vessel and extracted with an appropriate volume of hexane. The procedure was repeated in triplicate for three different concentrations of each compound. The mean recovery amounted to 98% for 1,2-DCBz, 96% for BiPh, and 99% for HxCBz. The experimental samples were analyzed by the same method.

Chromatographic Analysis of Extract. A 2-μL aliquot was injected into the GC-MS or GC-ECD systems. The analyses of the HxCBz and the 1,2-DCBz were performed with a Hewlett-Packard (Model 1991Z-413) GC-ECD system, fitted with a methylsiloxane capillary column (HP-1, 30 m × 0.32 μm × 0.25 μm). An analysis of the BiPh was performed with a Hewlett-Packard 5973 GC-MSD system fitted with a phenylmethyl−siloxane capillary column (HP-5MS 5% 30 m × 250 μm × 0.25 μm). Each concentration was determined by measuring the peak area and comparing this response to a standard curve. The calibration curves were linear with correlation coefficients ranging from 0.9965 to 0.9999.

Results and Discussion

Aqueous Solubility at 25 °C. In accordance with the Office of Prevention, Pesticides and Toxic Substances (OPPTS) guidelines,[7,8] the preliminary test of reference compounds was carried out at 25 °C at two independent flow rates for the calibration of the generator column. The aqueous solubility values were determined as the average of at least 5 measurements and are summarized in Table 1, with the reported literature values.

The calculated percentage standard deviation between the observed measurements amounted to 6.0 and 5.2% for HxCBz, 6.9 and 5.3% for BiPh, and 3.8 and 4.8% for 1,2-DCBz, in two independent runs. These values meet the OPPTS guideline stating that the repeatability of the concentration of the eluated saturated solution as a function of time should not exceed 30%.

As can be seen from Table 1, the reported literature solubilities are divergent. The largest discrepancies were found for 1,2-DCBz where the values occur in the ranges of 79−109 mg·L^{-1} and 137−169 mg·L^{-1}. The solubility of 1,2-DCBz obtained in this study agrees very well with three of the published determinations. Two of those were produced by the shake-flask method (92.8 mg·L^{-1} [32] and 99.1 mg·L^{-1}),[33] and one was measured by a generator column (92.3 mg·L^{-1}).[27] Large differences can be also observed among the aqueous solubility values of HxCBz. The data obtained in this study agree well with two values: 0.00996 mg·L^{-1} measured by elution chromatographic method[7] and

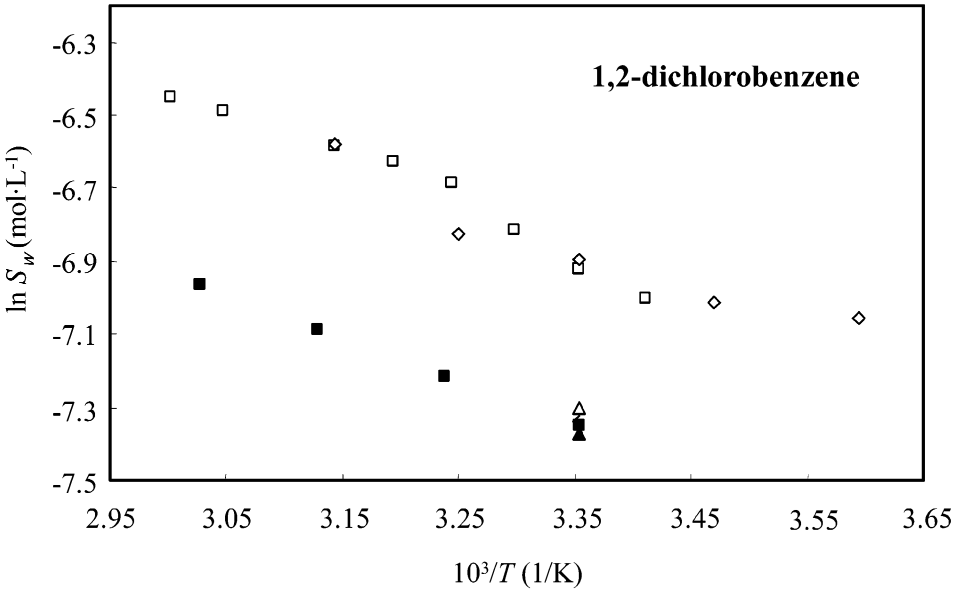

Figure 1. van't Hoff plot of the logarithm of the molar solubility of 1,2-DCBz from this and previous studies: ■, this study; ◇, Ma et al.;[10] ▲, Miller et al.;[27] □, Klemenc and Low;[30] −, Yalkowsky et al.;[32] △, Konemann.[33]

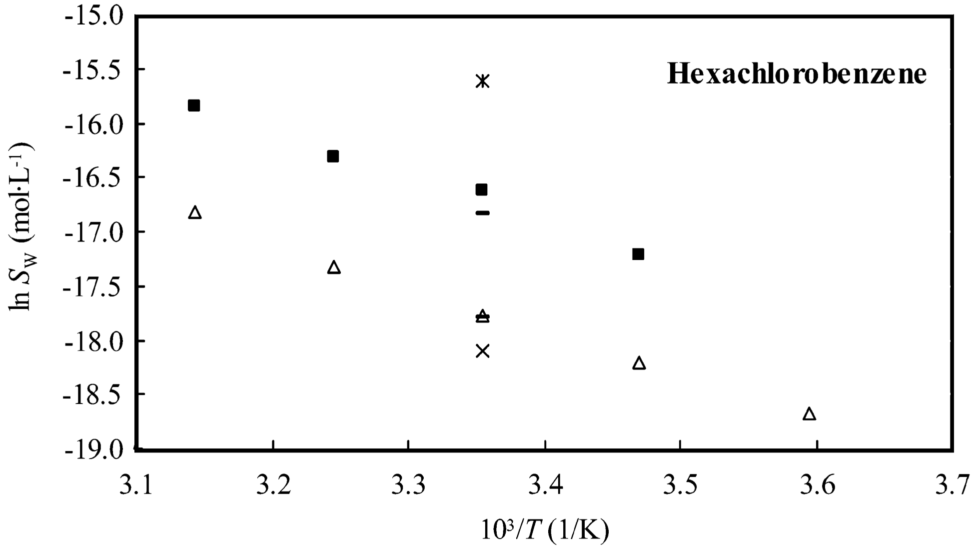

Figure 2. van't Hoff plot of the logarithm of the molar solubility of HxCBz from this and previous studies: ■, this study; △, Shiu et al.;[9] *, Miller et al.;[27] −, Hashimoto et al.;[31] ×, Konemann et al.[33]

0.014 mg·L^{-1} obtained by a shake-flask method.[31] The lowest discrepancies are for the solubilities of BiPh. Both the literature values and those determined in this study range from 3.87 to 8.08 mg·L^{-1}.

The very good agreement of our data with some of the previously reported solubilities determined by two different methods allows us to suppose that the use of the generator column in this study produces accurate data. However, the wide divergence from other aqueous solubility values may be a reflection of the impact on determinations of such variables as the solute purity, equilibration time, temperature, and analysis method.

Effect of Temperature on the Aqueous Solubility. The influence of temperature on aqueous solubility strongly depends on the physical state of the solute and generally is small for organic liquids.[21] In this study, the temperature dependencies of the aqueous solubility of a solid (HxCBz) and a liquid (1,2-DCBz) have been determined. The enthalpies of solutions were derived from the slope of the van't Hoff plots (Figures 1 and 2) according to the following equation

$$\ln(S_w/\text{mol}\cdot\text{L}^{-1}) = -\Delta_{sol}H/RT + C \qquad (1)$$

where S_w is the molar aqueous solubility, T the absolute temperature, R the gas constant, and C an empirical constant. The estimated precision expressed as standard deviations amounts to ±0.97% and ±4.8% for 1,2-DCBz and HxCBz, respectively.

The temperature dependence of the aqueous solubility of 1,2-DCBz was previously determined by thevolumetric[30] and shake-flask[10] methods. These values are much higher than those produced by our generator column. As previously mentioned, among the reported solubilities at 25 °C, several values have been found that were similar to those obtained in this study. Unfortunately, the determinations did not encompass a wide temperature range, and it may be supposed that a continuation of those measurements

Table 2. Aqueous Solubilities and Activity Coefficients of 1,2-DCBz and HxCBz at Different Temperatures, with Their Enthalpies of Solution ($\Delta_{sol}H$)

	S_w/mg·L^{-1}					$\Delta_{sol}H$/kJ·mol^{-1}	
compound	15 °C	25 °C	35 °C	45 °C	55 °C	this study	ref values
1,2-DCBz		94.4 ± 4.6	108.0 ± 3.1	122.7 ± 7.5	139.1 ± 5.5	10.49 ± 12.3	
γ_w		8.65×10^4	7.55×10^4	6.66×10^4	5.87×10^4		
HxCBz	0.007 ±0.0006	0.0096 ±0.0005	0.018 ±0.0007	0.024 ±0.0018	0.038 ±0.0051	33.5 ±192.4	33.7[9] 36.9[4]
γ_w[a]	8.25×10^7	7.41×10^7	5.20×10^7	4.76×10^7	3.70×10^7		

[a] γ_w the activity coefficient is calculated using ref 4 ($\Delta_{fus}H = 18.7$ kJ/mol, $T_m = 227$ °C).

Table 3. Experimental Values of the Solubilities (S_w) of HxCBz in Various Aqueous Salt Solutions (C_s) at 25 °C

salt	C_s/mol·L^{-1}	S_w[a]/mg·L^{-1}	no. samples	K_s/L·mol^{-1}
S_w	0	0.0096 ± 0.0004	5	0.343 ± 0.007
NaCl	0.022	0.0096 ± 0.0007	9	
	0.089	0.0089 ± 0.0017	7	
	0.185	0.0084 ± 0.0014	5	
	0.505	0.0065 ± 0.0004	8	
KCl	0.011	0.0095 ± 0.0006	7	0.266 ± 0.002
	0.046	0.0094 ± 0.0004	8	
	0.325	0.0078 ± 0.0012	9	
	0.530	0.0069 ± 0.0015	9	
$CaCl_2$	0.073	0.0082 ± 0.0012	9	0.707 ± 0.03
	0.158	0.0073 ± 0.0025	5	
	0.240	0.0066 ± 0.0006	7	
	0.410	0.0048 ± 0.0012	6	

[a] Mean value ± standard deviation; a student's T-test was applied to the means of determined solubility values (*n*) for level of significance 0.99.

would give values for the temperature dependence behavior of 1,2-DCBz near to those presented in this study.

From Figure 1, we can see that the solubilities determined previously[10,30] do not exhibit linear behavior in all ranges of temperatures studied, and for that reason the enthalpies of solutions have not been derived. This study's linear regression of the van't Hoff plot for the solubilities of 1,2-DCBz gives a value for the correlation coefficient equal to 0.9999. The enthalpy of solution derived from the slope of this plot amounts to 10.49 kJ·mol^{-1}.

The solubilities of HxCBz obtained here are higher than the solubilities reported by Shiu et al.[9] (Figure 2). These differences have no effect on the value of the enthalpy of solution which amounts to 33.5 kJ·mol^{-1}, and agrees very well with values previously reported by Shiu et al.[9] (33.7 kJ·mol^{-1}) and by Opperhuizen et al (36.9 kJ·mol^{-1}).[4]

The experimental solubilities have been used for calculation of the relevant activity coefficients (Table 2). The thermodynamic equation for solid compounds relates solubilities to activity coefficients as follows

$$S_w = [1/(\gamma_w V_w)]\exp[-\Delta_{fus}H/R(1/T - 1/T_m)] \qquad (2)$$

where S_w is the molar aqueous solubility, γ_w is the activity coefficient in pure water, $\Delta_{fus}H$ is the enthalpy of fusion, T_m is the melting temperature, T is an experimental temperature, R is the gas constant, and V_w is the molar volume of aqueous solution, assumed equal to the molar volume of water. This assumption is correct only for aqueous solutions of sparingly soluble compounds where the contribution of the organic solute to the molar volume of the mixture is very small and can be neglected.[21] The effect of temperature on the density[22] and molar volume of water has been taken into account.

When the liquid compound is equilibrated with water, its aqueous activity coefficient (γ_w) is expressed by the inverse of its molar aqueous solubility (S_w)

$$\gamma_w = 1/(S_w V_w) \qquad (3)$$

The influence of the temperature on the activity coefficient is significant. In pure water, the activity coefficient of HxCBz decreases with the increasing solubility of this compound. In other words, the activity coefficient decreases as the temperature increases. The same behavior is observed for the activity coefficient of 1,2-DCBz.

Effect of Dissolved Salts on the Solubility of HxCBz. Originally, the salt effect was expressed by an empirical eq 4 proposed by J. Setschenow

$$\log(S_w/S_s) = K_s C_s \qquad (4)$$

where S_s and S_w are the solubilities of solute in a salt solution and pure water, respectively, C_s is the molar

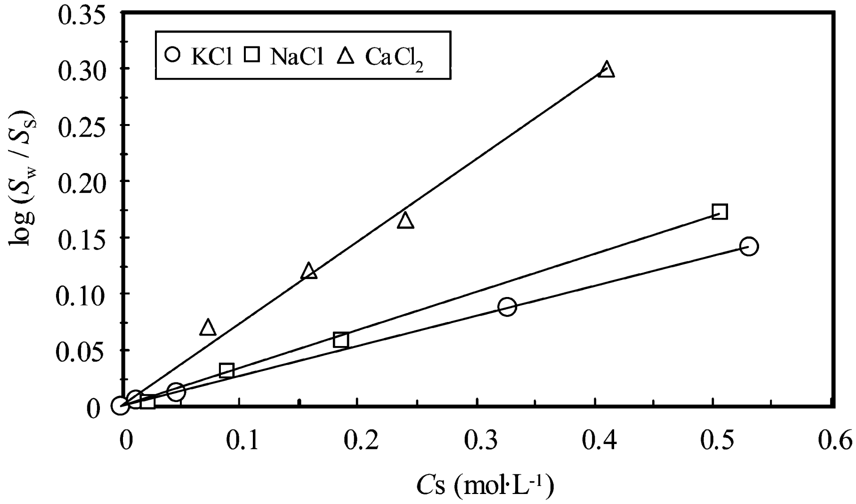

Figure 3. Effect of various salt concentrations (C_s) on the aqueous solubility of HxCBz.

concentration of the salt solution, and K_s is the salt effect parameter.[23]

The solubilities of HxCBz determined in various salt solutions at 25 °C have been summarized in Table 3. Each value is an average of 5−10 replicate determinations with the percentage deviation ranging from 5.0% to 19.6% for the sodium chloride solution, from 4.6% to 20.0% for the potassium chloride solution, and from 10.4% to 34.0% for the calcium chloride solution.

The Setschenow constants have been derived from the plots presented in Figure 3. The estimated precision is expressed for each solution as a standard deviation ranging from ±0.8% to ±4.8%. The solubility of HxCBz decreases when the salt is added to the solution; this behavior is called the "salting-out" effect, and the nonelectrolyte is said to be "salted-out". In this case, the electrolyte increases the activity coefficient of the solute. A detailed explanation of the phenomena can be found in the literature.[21,26] The salting-out effect is strongly dependent on the type of electrolyte and its concentration. As can be seen from Figure 3, the influence of the $CaCl_2$ solution on the solubility of HxCBz is the strongest, and the effects decrease in the following order: $Ca^{2+} > Na^{+} > K^{+}$. This tendency can be explained as an aspect of the differences in ionic strength, which is larger for bivalent ions (Ca^{2+}) than for monovalent ions (K^+, Na^+). Previously[18,19] a similar behavior has been noted in the solubilities of other chlorobenzenes in salt solutions.

We should mention that the first theory relating the Setschenow constant with liquid molar volume was developed by McDevit and Long[24] for hydrocarbons; it then was confirmed by May et al.[11] for the salting out of selected polycyclic aromatic hydrocarbons. Then, Xie et al.[18] observed that the Setschenow constants rose with the molar volume of chlorobenzenes in the order $K_{MoCB} < K_{DiCB} < K_{TrCB}$ for KCl, NaCl, and $CaCl_2$ solutions. They also found that the position of the chlorine in the molecular structure of dichlorobenzenes (1,2-, 1,3-, 1,4-) did not affect the salting parameter. The data reported by Xie at al.[18] and the new data reported in this study expand our range of knowledge of Setschenow constants and may be very useful in efforts to predict them for other chlorobenzenes.

Conclusion

The experimental aqueous solubilities reported in this study at 25 °C agree well with some of the selected literature values. While some of the data agree independent of the methods used in the determinations, for some compounds large discrepancies are observed in the range of solubilities measured both by different and similar methods. In contrast to previous reports, the van't Hoff plots of 1,2-DCBz show good linearity over the studied temperature ranges and, for the first time, permitted the derivation of values for the enthalpy of solution. The generator column method was successfully applied to the measurement of the solubilities of HxCBz in three electrolyte solutions; these data may be helpful for the prediction of the behavior of chlorobenzenes under environmental conditions. Our expanded knowledge of the Setschenow constants may facilitate our prediction of them for other chlorobenzenes.

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