

Solubility of Hexafluorobenzene in Aqueous Salt Solutions from (280 to 340) K

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The aim of this work was to study the solubility of hexafluorobenzene in aqueous salt solutions because, despite its interest, information about the solubility of perfluorocarbons in aqueous solutions was previously not available. The solubility of the perfluorocarbon in water and aqueous salt solutions was measured using a liquid–liquid extraction method. The method was validated by comparing the measured solubility of ethylbenzene in water with the literature data. The estimated uncertainty in the experimental data is less than 6%. The effect of the salt concentration and the cation/anion effect on the solubility were also established. Solubility data was measured in the temperature range from (280 to 340) K at atmospheric pressure. Thermodynamic functions such as the Gibbs energy, enthalpy, and entropy of solution were obtained from the temperature dependence of the solubility data. From the data on the enthalpies of solution, values of the enthalpy of solvation in the solvents were determined and discussed.

Introduction

Fluorinated molecules such as perfluorocarbons (PFCs) and their derivatives represent a very interesting and stimulating class of chemicals because of their specific and unusual properties. Perfluorocarbons are nonpolar, highly fluorinated compounds that, as a result of strong intramolecular bonding, are chemically and biochemically inert.¹

These substances can be used in a wide variety of areas such as surfactants in supercritical solvents, environmental probes, anticorrosive and antifriction components, flame retardants, and water repellents. It is, however, in the biomedical field that the most relevant applications are found. PFCs can be used in tissue oxygenation fluids as blood substitutes, anti-tumor agents, perfusates for isolated organs, gas carriers in eye surgery, diagnostic imaging agents, in lubrication and cushioning for articular disorders, cell culture media, and in drug delivery.^{2–5}

The determination of the solubilities of perfluorocarbons in water holds particular interest because the solubilities determine their fate in the body and environment and may help us to understand the aging mechanisms of the perfluorocarbon emulsions used as blood substitutes.⁶ Solubility measurements at different temperatures also allow the determination of thermodynamic parameters of the solution and provide information about the organization of the hydrophilic solvent around the hydrophobic solute.

The solubility of perfluorocarbons in water and aqueous salt solutions is important for two of the most important applications of these compounds: as drug delivery systems and as cell culture media.

Experimental Section

Materials. The oil-in-water solubility was measured for hexafluorobenzene, (C₆F₆) 99+% pure, from Fluorochem

and for ethylbenzene, (C₈H₁₀) 99% pure, from Janssen Chimica, both used without further purification. This last compound was used to validate the experimental method used in this work by comparison of the measured values with literature data. The organic phases were kept in equilibrium with water that was distilled and further treated with a Milli-Q water purification system.

The hexafluorobenzene aqueous solubility was also studied in salt solutions of NaCl ≥99.5% pure from R. P. Normapur and NaNO₃ ≥99.0% pure from Riedel-de Haën AG; both salts were used without further purification.

The dichloromethane (CH₂Cl₂) used for the organic extraction was ≥99.5% pure and was acquired from Carlo Erba Reagents. The internal standard chosen to perform the quantitative analysis was heptane ≥99.0% pure from R. P. Normapur, Prolabo. The solvent and the internal standard were also used without further purification.

Experimental Procedure. The experimental method consisted of maintaining the two phases stirred for 11 h to reach equilibrium, followed by 6 h of rest at the desired temperature. These periods ensured the saturation of the aqueous phase by the organic phase without the organic phase in suspension in the aqueous phase, in the equilibrium cell used.

The organic and the aqueous phases were kept in equilibrium at each studied temperature in a double-jacketed glass cell thermostated by means of a water bath. The cell had an exterior needle in contact with the water phase for sampling.

The temperature was determined before each extraction with a copper–constantan thermocouple, inserted into the body of the cell. This thermocouple was previously calibrated against a 25-Ω platinum resistance thermometer (±0.001 K, IPTS 68) and a Leeds and Northrup bridge (±10⁻⁴ Ω). The estimation of the uncertainty given by the thermocouple inside the equilibrium cell is 0.02 K for the temperature range 200 < T/K < 460.

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Table 1. Experimental Solubilities (x) of Ethylbenzene in Water and Respective Deviations from the Correlation by Equation 1

T/K	$10^{-5}(x \pm \sigma^a)$	$\delta_i^b/\%$
280.25	3.02 ± 0.07	0.157
290.09	2.95 ± 0.07	0.321
299.90	3.07 ± 0.07	0.126
309.71	3.25 ± 0.02	0.075
319.65	3.59 ± 0.02	0.271
329.89	3.99 ± 0.02	0.149
339.80	4.61 ± 0.04	0.002

^a Standard deviation. ^b $\delta_i = 100(x_i - x_{\text{calcd},i})/x_i$.

The liquid–liquid extraction was performed taking samples of 10 mL of the aqueous phase by immersing the needle in dichloromethane to reduce the loss of the organic compound by volatilization at the desired temperature. For temperatures higher than 303 K, the dichloromethane was submerged in ice to avoid evaporation. The sample was then vigorously shaken for 10 min to reach a complete extraction of the solute for analysis in the organic solvent. This time was optimized until no further variations were found in the solute quantitative analysis.

A previous addition to the extraction solvent of a known quantity of an internal standard was used to cancel volumetric errors in the gas chromatography analysis.

Gas Chromatography Analysis. The quantitative analysis was performed by gas chromatography (GC) in an HP model 5890 series II with a flame ionization detector (FID). Coupled to the GC was an HP model 3396 series II integrator. Chromatographic separations were accomplished with a 50-m HP Pona column (0.2-mm i.d. and 0.5- μm film thickness). The split injection mode was used.

Standard solutions were prepared gravimetrically over the range in which the actual analysis would be conducted, and all of the standards were immediately analyzed to establish calibration curves. Furthermore, a “monitoring solution” containing the analytes in the concentration range of the standard was also prepared. This solution was periodically analyzed to control the stability of the GC system.

At least three independent extractions were made with four minimum chromatographic analyses for each temperature and solution. Results and respective deviations are presented.

Results and Discussion

(Ethylbenzene + Water) System. Ethylbenzene was used to validate the experimental method because it

Table 2. Parameters for the Correlation of the Solubility (x) of Ethylbenzene in Water and of Hexafluorobenzene in Several Aqueous Salt Solutions Using Equation 1

ethylbenzene	A	B	C	solubility minimum	
				T/K	$10^{-5}x$
this work	-229.607	9454.4	32.9078	287.30	2.97
Heidman et al. ⁷	-185.170	7348.6	26.3453	279.0	2.82

hexafluorobenzene	A	B	C	T/K	$10^{-5}x$
pure water	-263.084	11898.3	37.4671	317.57	5.66
NaNO_3 $5.9 \times 10^{-2} \text{ mol}\cdot\text{kg}^{-1}$	-283.555	12878.6	40.4804	318.09	5.51
NaCl $8.6 \times 10^{-2} \text{ mol}\cdot\text{kg}^{-1}$	-266.480	12055.2	37.9631	317.59	5.40
NaCl $8.6 \times 10^{-1} \text{ mol}\cdot\text{kg}^{-1}$	-296.639	13385.8	42.4053	315.63	3.70

presents a water solubility on the same order of magnitude as that of hexafluorobenzene, and reliable solubility data from different authors was available.^{7–20} Table 1 presents the experimental measured solubilities for the (ethylbenzene + water) system at several temperatures. A comparison between the measured and literature data is presented in Figure 1. The good agreement between the literature and the experimental values measured here shows the reliability of the technique used.^{7,21}

The hydrocarbon presents a minimum in solubility corresponding to a zero enthalpy of solution, being that this behavior is similar in this respect to that of an ideal solution but otherwise being vastly different as exhibited by the almost complete immiscibility. From the obtained experimental data, the solubility minimum was located at around 287.30 K. As expected, after the minimum, increasing the temperature increases the solubility of ethylbenzene in water.

The correlation of data for the solubility of hydrocarbons in water can be carried out with eq 1 as proposed by Heidman et al.:⁷

$$\ln x = A + \frac{B}{T/K} + C \ln \left(\frac{T}{K} \right) \quad (1)$$

where x is the mole fraction solubility of the hydrocarbon in water, T is the temperature, and A , B , and C are the constants characteristic of each compound.

Data solubilities presented in Table 1 were correlated using eq 1 as shown in Figure 1. The standard deviation between each experimental solubility data point and the respective correlation value is presented in Table 1. Parameters A , B , and C were fit to the experimental solubility data and are presented in Table 2. This Table also shows the comparison with the Heidman et al.⁷ correlation for the solubility of ethylbenzene in water and

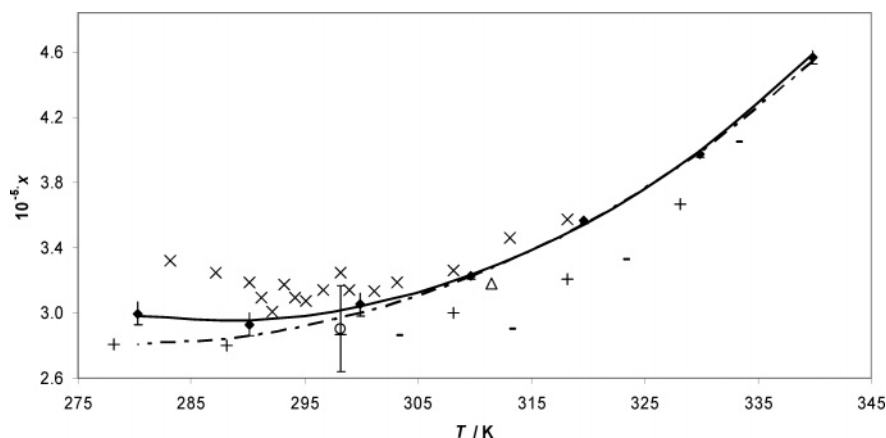


Figure 1. Mole fraction solubility (x) of ethylbenzene in water: \blacklozenge , this work; \triangle , Heidman et al.;⁷ $+$, Dohányosová et al.;⁸ \times , Owens et al.;⁹ $-$, Chen and Wagner;¹⁰ \circ , average data at 298.15 K from several authors.^{11–20} The solid and the dashed lines represent the correlation of data from this work using eq 1 and the correlation proposed by Heidman et al.,⁷ respectively.

the temperature corresponding to the minimum in solubility. Our correlation was performed in the temperature range of (280 to 340) K, and the correlation of Heidman et al.⁷ was carried out at especially high temperatures, (310 to 568) K. These differences in the temperature study can explain the deviations between the two correlations, especially at the lower temperatures presented in Figure 1. The average absolute standard deviation (AAD) between the measured and calculated values for ethylbenzene-in-water solubility using the proposed correlation is 0.2%.

Thermodynamic Functions of Ethylbenzene Dissolution. The dissolution of a liquid into a liquid is associated with changes in thermodynamics functions, namely, the standard Gibbs energy ($\Delta_{\text{sol}}G^\circ$), standard enthalpy ($\Delta_{\text{sol}}H^\circ$), and standard entropy ($\Delta_{\text{sol}}S^\circ$) of solution, which can be calculated from experimental solubility data. These functions represent the changes that occur in the solute neighborhood during the dissolution process due to the process of transference of one solute molecule to an infinitely dilute state in the solvent at a given temperature T .²²

From the Gibbs–Helmholtz equation, assuming both the activity coefficient for water in the water phase and for the organic component in the organic phase are equal to 1, it is possible to obtain the following equation

$$\left(\frac{\partial \ln x_i}{\partial T}\right)_P \cong \frac{\Delta_{\text{sol}}H^\circ}{RT^2} \quad (2)$$

where the enthalpy of solution, $\Delta_{\text{sol}}H^\circ$, is the difference between the partial molar enthalpy of component i in solution, H_i , and the pure molar enthalpy, H_i° , at temperature T :

$$\Delta_{\text{sol}}H^\circ = H_i - H_i^\circ \quad (3)$$

It should be noted that the integration of eq 2, where $\Delta_{\text{sol}}H^\circ$ is a linear function of temperature, leads to eq 1 used for the correlation of experimental data.

The enthalpy of solution, $\Delta_{\text{sol}}H^\circ$, can be split into two contributions: an enthalpy of vaporization ($\Delta_{\text{vap}}H^\circ$) and an enthalpy of solvation ($\Delta_{\text{solv}}H^\circ$):

$$\Delta_{\text{sol}}H^\circ = \Delta_{\text{vap}}H^\circ + \Delta_{\text{solv}}H^\circ \quad (4)$$

The enthalpy of solvation is the result of an enthalpy of cavitation ($\Delta_{\text{cav}}H^\circ$) and a hydrophobic interaction between the organic and the aqueous phase ($\Delta_{\text{int}}H^\circ$):

$$\Delta_{\text{solv}}H^\circ = \Delta_{\text{cav}}H^\circ + \Delta_{\text{int}}H^\circ \quad (5)$$

The enthalpy of vaporization and the enthalpy of solvation cancel each other at the temperature at which the oil solubility goes through a minimum. It is possible to determine the enthalpy of solvation of a system by knowing the enthalpy of solution from experimental solubility data and using the enthalpy of vaporization.

The thermodynamic functions $\Delta_{\text{sol}}G^\circ$ and $\Delta_{\text{sol}}S^\circ$ may be calculated from the temperature dependence of the solubility according to the following equations:

$$\Delta_{\text{sol}}G^\circ = -RT(\ln x_i)_P \quad (6)$$

$$\Delta_{\text{sol}}S^\circ = R \left(\frac{\partial(\ln x_i)}{\partial(\ln T)} \right)_P \quad (7)$$

where R is the gas constant.

Table 3. Thermodynamic Properties of the Dissolution of Ethylbenzene in Water

T	$\Delta_{\text{sol}}H^\circ$	$\Delta_{\text{solv}}H^\circ$	$\Delta_{\text{sol}}G^\circ$	$\Delta_{\text{sol}}S^\circ$
K	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
280.25	-1.93	-45.2	24.3	-93.4
290.09	0.76	-41.9	25.2	-84.1
299.90	3.45	-38.7	25.9	-74.9
309.71	6.13	-35.4	26.6	-66.1
319.65	8.85	-32.2	27.2	-57.4
329.89	11.65	-28.8	27.8	-48.9
339.80	14.36	-25.5	28.2	-40.8

The values for the thermodynamic functions of the dissolution of ethylbenzene at each temperature are presented in Table 3. $\Delta_{\text{solv}}H^\circ$ was estimated from literature values of $\Delta_{\text{vap}}H^\circ$ at different temperatures.²³ In Figure 2, estimated enthalpies of solution from solubility measurements of ethylbenzene in water obtained in this work are compared with calorimetric measurements and with solubility results from other authors.^{7–9,24}

Gill et al.²⁴ measured the enthalpy of solution of ethylbenzene in water from (288 to 308) K. These data predict a minimum in solubility around 292 K. The minimum found in this work presents a deviation from the calorimetric value of 1.6%. The enthalpies of solution derived in this work are in excellent agreement with the calorimetric results of these authors. Furthermore, the enthalpies of solution calculated from the solubility values of this work are in good agreement with the other data reported in the literature.^{7–9,24}

(Hexafluorobenzene + Water) System. The solubility of hexafluorobenzene was measured in pure water and in three salt solutions: NaCl $8.6 \times 10^{-1} \text{ mol}\cdot\text{kg}^{-1}$ ($\sim 50 \text{ g}\cdot\text{L}^{-1}$), NaCl $8.6 \times 10^{-2} \text{ mol}\cdot\text{kg}^{-1}$ ($\sim 5 \text{ g}\cdot\text{L}^{-1}$), and NaNO₃ $5.9 \times 10^{-2} \text{ mol}\cdot\text{kg}^{-1}$ ($\sim 5 \text{ g}\cdot\text{L}^{-1}$). These aqueous salt solutions were chosen because they are the most common salts used in cell culture media. This extended study permits us to analyze the influence of the salt concentration and the cation/anion effect on the solubility of hexafluorobenzene in water.

Experimental values of solubility are reported in Table 4. There is a decrease in the solubility of hexafluorobenzene in the presence of electrolytes because of a salting-out effect.

The solubility of hexafluorobenzene in pure water is 1 order of magnitude smaller than the solubility of the corresponding hydrocarbon.^{15,20,25–27} This decrease in the solubility of perfluorocarbons when compared with that of

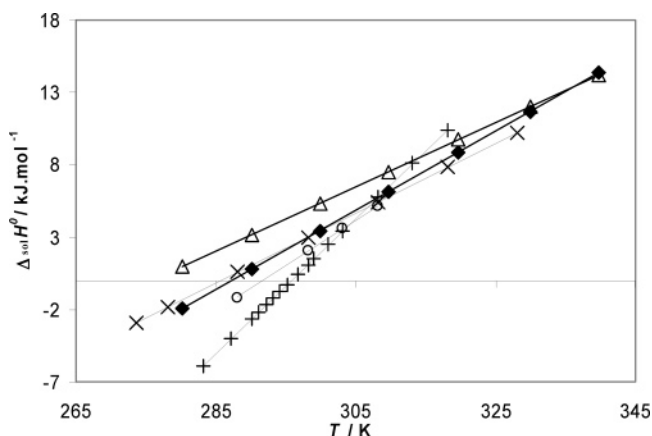
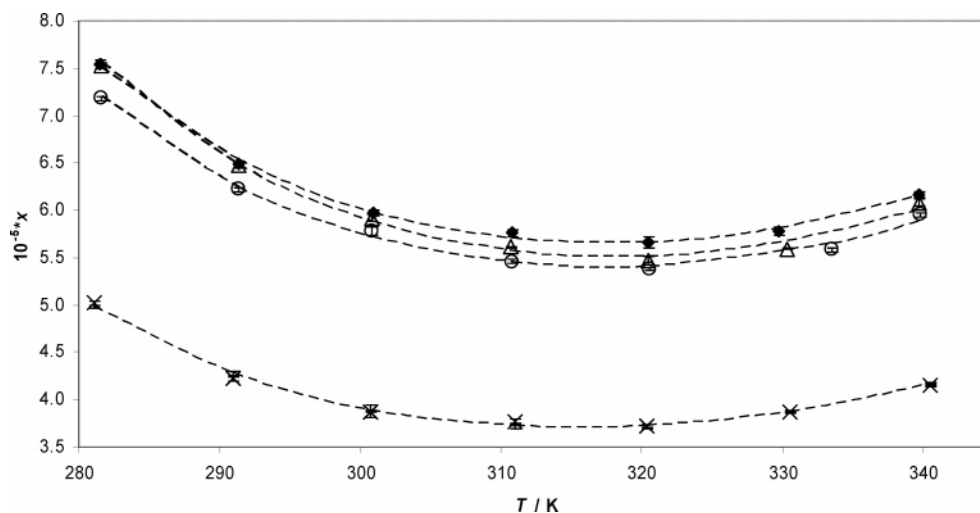


Figure 2. Enthalpy of solution of ethylbenzene in water: \blacklozenge , this work (solubility); \triangle , Heidman et al.⁷ (solubility); $+$, Owens et al.⁹ (solubility); \times , Dohányosová et al.⁸ (solubility); \circ , Gill et al.²³ (calorimetric).

Table 4. Experimental Solubility (x) of Hexafluorobenzene in Several Aqueous Salt Solutions

pure water		NaNO ₃ 5.9 × 10 ⁻¹ mol·kg ⁻¹		NaCl 8.6 × 10 ⁻² mol·kg ⁻¹		NaCl 8.6 × 10 ⁻¹ mol·kg ⁻¹	
<i>T</i> /K	10 ⁻⁵ ($x \pm \sigma^a$)	<i>T</i> /K	10 ⁻⁵ ($x \pm \sigma^a$)	<i>T</i> /K	10 ⁻⁵ ($x \pm \sigma^a$)	<i>T</i> /K	10 ⁻⁵ ($x \pm \sigma^a$)
281.46	7.54 ± 0.04	281.56	7.52 ± 0.03	281.56	7.18 ± 0.02	281.06	5.02 ± 0.02
291.36	6.48 ± 0.04	291.38	6.48 ± 0.02	291.38	6.22 ± 0.02	290.93	4.22 ± 0.02
300.97	5.97 ± 0.03	300.82	5.92 ± 0.03	300.85	5.78 ± 0.05	300.75	3.867 ± 0.003
310.82	5.76 ± 0.04	310.75	5.616 ± 0.007	310.77	5.46 ± 0.02	311.03	3.77 ± 0.02
320.51	5.67 ± 0.06	320.49	5.47 ± 0.05	320.56	5.38 ± 0.02	320.40	3.72 ± 0.02
329.77	5.78 ± 0.04	330.39	5.59 ± 0.01	333.51	5.58 ± 0.02	330.58	3.877 ± 0.005
339.76	6.16 ± 0.03	339.77	6.08 ± 0.04	339.80	5.95 ± 0.02	340.54	4.15 ± 0.01

^a Standard deviation.**Figure 3.** Mole fraction solubility (x) of hexafluorobenzene: \blacklozenge , in pure water; \triangle , in NaNO₃ 5.9 × 10⁻² mol·kg⁻¹ aqueous solution; \circ , in NaCl 8.6 × 10⁻² mol·kg⁻¹ aqueous solution; \times , in NaCl 8.6 × 10⁻¹ mol·kg⁻¹ aqueous solution. The dashed lines are correlations of experimental data using eq 1.**Table 5. Thermodynamic Properties of the Dissolution of Hexafluorobenzene in Pure Water, in NaNO₃ 5.9 × 10⁻² mol·kg⁻¹, in NaCl 8.6 × 10⁻² mol·kg⁻¹, and in NaCl 8.6 × 10⁻¹ mol·kg⁻¹ Aqueous Solution**

pure water					NaNO ₃ 5.9 × 10 ⁻² mol·kg ⁻¹				
<i>T</i>	$\Delta_{\text{sol}}H^0$	$\Delta_{\text{solv}}H^0$	$\Delta_{\text{sol}}G^0$	$\Delta_{\text{sol}}S^0$	<i>T</i>	$\Delta_{\text{sol}}H^0$	$\Delta_{\text{solv}}H^0$	$\Delta_{\text{sol}}G^0$	$\Delta_{\text{sol}}S^0$
K	kJ·mol ⁻¹	kJ·mol ⁻¹	kJ·mol ⁻¹	J·mol ⁻¹ ·K ⁻¹	K	kJ·mol ⁻¹	kJ·mol ⁻¹	kJ·mol ⁻¹	J·mol ⁻¹ ·K ⁻¹
281.46	-11.25	-48.1	22.2	-118.9	281.56	-12.31	-49.2	22.2	-122.7
291.36	-8.16	-44.3	23.4	-108.2	291.38	-9.01	-45.2	23.4	-111.1
300.97	-5.17	-40.7	24.3	-98.0	300.82	-5.83	-41.4	24.3	-100.3
310.82	-2.10	-36.9	25.2	-87.9	310.75	-2.49	-37.3	25.3	-89.4
320.51	0.92	-33.2	26.1	-78.4	320.49	0.79	-33.3	26.1	-79.1
329.77	3.80	-29.6	26.8	-69.6	330.39	4.12	-29.3	26.9	-69.0
339.76	6.91	-25.8	27.4	-60.3	339.77	7.28	-25.4	27.4	-59.3
NaCl 8.6 × 10 ⁻² mol·kg ⁻¹					NaCl 8.6 × 10 ⁻¹ mol·kg ⁻¹				
281.56	-11.36	-48.2	22.3	-119.7	281.06	-12.20	-49.1	23.1	-125.7
291.38	-8.26	-44.4	23.5	-108.9	290.93	-8.72	-44.9	24.4	-113.7
300.85	-5.27	-40.8	24.4	-98.7	300.75	-5.26	-40.8	25.4	-102.0
310.77	-2.14	-37.0	25.4	-88.5	311.03	-1.63	-36.4	26.3	-90.0
320.56	0.95	-33.2	26.2	-78.8	320.40	1.67	-32.6	27.2	-79.6
333.51	5.04	-28.1	27.2	-66.3	330.58	5.26	-28.1	27.9	-68.6
339.80	7.02	-25.7	25.5	-60.2	340.54	8.77	-23.9	28.6	-58.1

the corresponding hydrocarbon has already been verified by Bonifácio et al. for the gaseous *n*-perfluoroalkanes.²⁸

As shown in Figure 3, the solubility of hexafluorobenzene in pure water shows a minimum at approximately 317.57 K. This minimum occurs at a higher temperature than for the corresponding hydrocarbon, which is around 283.8 K.²⁶

In determining the enthalpies of solvation of the two compounds in pure water at 298.15 K, we have obtained -31.7 kJ·mol⁻¹ for benzene and -41.8 kJ·mol⁻¹ for the corresponding PFC.^{23,24} This indicates that the enthalpy of interaction ($\Delta_{\text{int}}H^0$) between the perfluorocarbon and the water is stronger than for the corresponding hydrocarbon; because perfluorobenzene is a larger molecule, it will have

a larger enthalpy of cavitation than benzene (eq 5). The stronger interaction between the organic and the aqueous phase explains why the minimum for perfluorobenzene is displaced toward higher temperatures. It was previously shown that the interactions between benzene and hexafluorobenzene with water are not the same kind. In fact, for the former the hydrogen atom of a water molecule interacts with the benzene plane (OH $\cdots\pi$ interaction), and for the perfluorobenzene the lone pair electrons of oxygen is situated over the face of the π system (O $\cdots\pi$ interaction).²⁹

Although the salts studied affect the solubility of hexafluorobenzene, the temperature dependence of the aromatic PFC solubility follows the same trend in pure water and

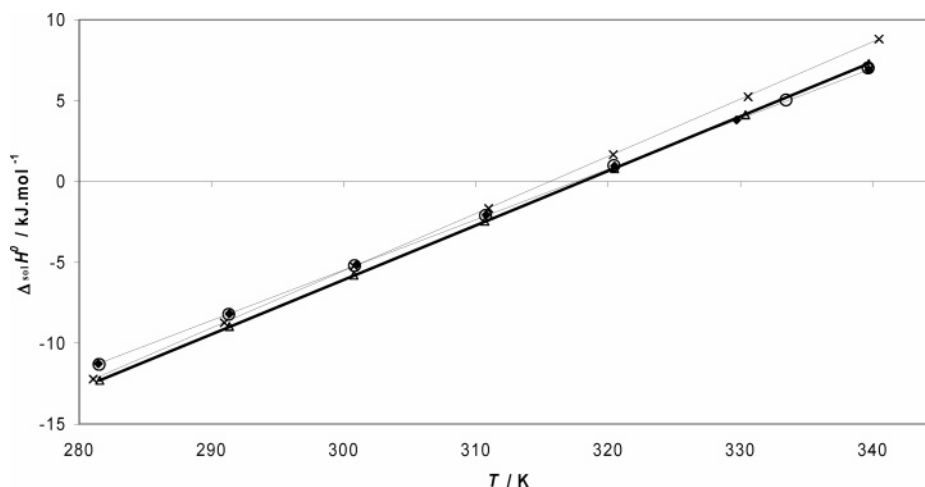


Figure 4. Enthalpy of solution of hexafluorobenzene: ◆, in pure water; △, in NaNO_3 $5.9 \times 10^{-2} \text{ mol}\cdot\text{kg}^{-1}$ aqueous solution; ○, in NaCl $8.6 \times 10^{-2} \text{ mol}\cdot\text{kg}^{-1}$ aqueous solution; ×, in NaCl $8.6 \times 10^{-1} \text{ mol}\cdot\text{kg}^{-1}$ aqueous solution.

in all of the aqueous salt solutions with the minimum present at around the same temperature as for pure water.

The NaCl salt solutions result in decreases in the hexafluorobenzene solubility of 4.3% and 52% for the less and the more concentrated solution, respectively. The addition of the NaNO_3 salt leads to a decrease of only 1.8% in the hexafluorobenzene solubility when compared to its value in pure water. The salting-out effect can be explained by hydration forces.³⁰ Ions, especially cations, like to form complexes with water (hydration), thereby leaving fewer free water molecules available for the dissolution of the solute.

The NaNO_3 and NaCl salts do not present the same Setschenow constant, meaning that the decrease in solubility is not proportional to the cation molality present in solution.³¹ This implies that the anion is also promoting a decrease in the hexafluorobenzene solubility in water, being that the anion Cl^- is a more preferable ion to complex with water than NO_3^- and thus having a stronger effect on the solubility.

Solubilities presented in Table 4 were correlated with eq 1 as shown in Figure 3 with an AAD smaller than 0.3%. Parameters A , B , and C are given in Table 2.

Thermodynamic Functions of Hexafluorobenzene Dissolution. The values of the thermodynamic functions, $\Delta_{\text{sol}}H^\circ$, $\Delta_{\text{sol}}H^\circ$, $\Delta_{\text{sol}}G^\circ$, and $\Delta_{\text{sol}}S^\circ$, of the hexafluorobenzene dissolution in the various aqueous solutions were calculated using eqs 2, 4, 6, and 7, respectively, and are reported in Table 5. The enthalpy of solution versus temperature, derived from experimental solubility data for each solution, is presented in Figure 4.

The estimated enthalpies of solution from solubility measurements of hexafluorobenzene in several aqueous solutions are similar to each other, with the major deviation for the more concentrated salt solution. For all of the studied cases, it was found that the enthalpy of solution is a linear function of temperature, thus giving a constant heat capacity of solution.

Conclusions

New data for the solubility of hexafluorobenzene in water and in aqueous salt solutions, in the temperature range between (280 and 340) K at atmospheric pressure, are presented.

The presence of electrolytes decreases the hexafluorobenzene solubility in water. The cation and anion influences in the aqueous solution phase equilibrium were verified.

The measured solubilities are very low, allowing for accurate enthalpies and entropies of solution to be calculated from the temperature dependence of the solubility. They show that the interaction between water and perfluorobenzene is stronger than that between water and benzene.

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