



Temperature and sodium chloride effects on the solubility of anthracene in water

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ARTICLE INFO

Article history:

Received 12 February 2010

Received in revised form 28 May 2010

Accepted 14 June 2010

Available online 19 June 2010

This paper is dedicated to Professor Fernando del Río (Universidad Autónoma Metropolitana-Iztapalapa, México) to commemorate his 70th birthday

Keywords:

Anthracene

Solubility

Sodium chloride

Solubility-temperature dependence

Sechenov parameter

Transfer thermodynamic properties

ABSTRACT

The solubility of anthracene was measured in pure water and in sodium chloride aqueous solution (salt concentration, $m/\text{mol} \cdot \text{kg}^{-1} = 0.1006, 0.5056, \text{ and } 0.6082$) at temperatures between (278 and 333) K. Solubility of anthracene in pure water agrees fairly well with values reported in earlier similar studies. Solubility of anthracene in sodium chloride aqueous solutions ranged from ($6 \cdot 10^{-8}$ to $143 \cdot 10^{-8}$) $\text{mol} \cdot \text{kg}^{-1}$. Sodium chloride had a salting-out effect on the solubility of anthracene. The salting-out coefficients did not vary significantly with temperature over the range studied. The average salting-out coefficient for anthracene was $0.256 \text{ kg} \cdot \text{mol}^{-1}$.

The standard molar Gibbs free energies, $\Delta_{\text{tr}}G^\circ$, enthalpies, $\Delta_{\text{tr}}H^\circ$, and entropies, $\Delta_{\text{tr}}S^\circ$, for the transfer of anthracene from pure water to sodium chloride aqueous solutions were also estimated. Most of the estimated $\Delta_{\text{tr}}G^\circ$ values were positive [(20 to 1230) $\text{J} \cdot \text{mol}^{-1}$]. The analysis of the thermodynamic parameters shows that the transfer of anthracene from pure water to sodium chloride aqueous solution is thermodynamically unfavorable, and that this unfavorable condition is caused by a decrease in entropy.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic compounds consisting of hydrogen and carbon arranged in the form of two or more fused benzene rings. They are primarily formed by incomplete combustion of organic matter during several industrial and natural processes [1].

PAHs are widely distributed in the environment and have been detected in sediments, soils, air, surface waters, animal and plant tissues, and food [2–11]. It is estimated that during 2004, the total global atmospheric emission of the 16 PAHs listed by the US EPA as priority pollutants, was 520 giga grams [1]. Since many PAHs have been identified as carcinogens or mutagens [12–16] there is an increasing concern regarding their environmental fate, their measurement, and their ultimate control [17].

From a global standpoint the largest emissions of PAHs are into the atmosphere [15]. Once in atmosphere PAHs can be adsorbed on to airborne particles and disperse regionally and intercontinentally through long-range atmospheric transport [1]. Airborne PAHs eventually enter surface waters due to precipitation of particles or to diffusion processes [15].

In order to develop accurate models that estimate the transfer and transformation of PAHs into marine systems, the solubility of these compounds under various temperature and salinity conditions needs to be known. The water solubility is a fundamental parameter in controlling both the extent to which aquatic biota are exposed to organic pollutant compounds and the potential distribution of these compounds throughout the hydrologic system [18–20]. Water solubilities are also parameters of thermodynamic interest to gain information on the nature of the highly non-ideal (water + hydrocarbon) systems [21,22].

The change in solubility of a nonelectrolyte in an aqueous solution, which results from the addition of an electrolyte, is known as the salting effect [23]. There can either be a decrease or an increase in solubility of the nonelectrolyte with increasing concentrations of added electrolyte. These phenomena are known as salting-out and salting-in, respectively [24,25–27]. Salting effect can depend on temperature [28,29]. Depending on the kinds of electrolyte and nonelectrolyte in the aqueous system, the salting effect could vary slightly [30–34] or significantly [27,29,35] with temperature.

Following our previous studies related to the solubility of PAHs in aqueous systems [36,37] in this work, we report results related to the effect of sodium chloride, NaCl, and temperature on the solubility of anthracene in aqueous solution. Solubility results were used to calculate properties such as standard molar Gibbs free energies, $\Delta_{\text{tr}}G^\circ$, enthalpies, $\Delta_{\text{tr}}H^\circ$, and entropies, $\Delta_{\text{tr}}S^\circ$, of transfer

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of anthracene from pure water to sodium chloride aqueous solution. The Sechenov parameters were also estimated.

2. Materials and methods

2.1. Materials

The source, the mole fraction purity x , and the relative molar mass M of the chemicals were as follows: anthracene (Chem Service, West Chester, PA; $x = 0.99$; $M = 178.2292$), methanol (J.T. Baker, Xalostoc, Mexico; HPLC grade, $x = 0.999$; $M = 32.0419$), sodium chloride (J.T. Baker, Xalostoc, México; $x = 0.99$; $M = 58.4425$), acetonitrile (Caledon Lab., Georgetown, ON, Canada; HPLC grade, $x = 0.998$; $M = 41.0520$), methylene chloride (Fermont, Monterrey, México; HPLC grade, $x = 0.999$; $M = 84.9320$). All these reagents were used without further purification. Water (electrical resistivity = $18 \text{ M}\Omega \cdot \text{cm}$; $M = 18.0153$) was purified by a Nanopure deionizer (Barnstead Thermolyne, Dubuque, IA). 100/120 mesh Chromosorb W-HP, was provided by Chromatography Research Supplies (Louisville, KY). Before use, Chromosorb W-HP was washed by Soxhlet extraction with acetonitrile and methanol. After washing, the solid support was dried overnight at 120°C and stored in a dessicator until used.

2.2. Method

The solubility of anthracene in aqueous solution was determined by the dynamic coupled column liquid chromatographic (DCCLC) technique developed by May *et al.* [38,39]. The experimental setup and method have been well described [36].

Saturated solutions of anthracene were generated by pumping the studied aqueous solution through a stainless steel generator column ($25 \text{ cm} \times 4.2 \text{ mm i.d.}$) packed with 100/120 mesh Chromosorb W-HP, coated with anthracene (0.4 g of PAH/100 g of solid support).

Before any measurement was taken, 1100 cm^3 of the studied aqueous solution was pumped through the generator column to equilibrate it. After equilibration a known amount of the aqueous phase was passed through the generator column and the dissolved anthracene was extracted using a stainless steel ($2.0 \text{ cm} \times 4.2 \text{ mm i.d.}$) extraction column packed with a $5\text{-}\mu\text{m}$ C18 bonded stationary phase (Spherisorb ODS-2; Waters Associates, Milford, MA.). The eluted aqueous sample was collected and carefully weighted.

Desorption of anthracene from the extraction column was carried out by a 0.7572:0.2428 (mass fraction) (acetonitrile + water) mixture. This mixture was also used during the chromatographic analysis step.

When anthracene was extracted from a NaCl aqueous solutions it was necessary, previous to the desorption step, to eliminate the NaCl present in the extraction column, otherwise, the fritted disks at the ends of the column got blocked. Elimination of NaCl was carried out by passing 0.5 cm^3 of pure water (flow rate = $0.05 \text{ cm}^3 \cdot \text{min}^{-1}$) through the extraction column.

Analysis of anthracene was performed by reverse-phase liquid chromatography with fluorescence ($\lambda_{\text{EX}} = 402 \text{ nm}$, $\lambda_{\text{EM}} = 380 \text{ nm}$) and ultraviolet (235 nm) detection. The wavelengths used in the analyses do not correspond to any maximum in the fluorescence or UV spectra of anthracene [40,41]; however, the attained sensitivity was appropriate for quantifying the PAH. A $12.5 \text{ cm} \times 4.6 \text{ mm i.d.}$ analytical column, packed with a $5\text{-}\mu\text{m}$ polymeric bonded phase (EnviroSepTM-PP; Phenomenex, Torrance, CA), was used in all the chromatographic analyses.

The molality of the studied sodium chloride aqueous solutions was $m/\text{mol} \cdot \text{kg}^{-1} = (0.1006 \pm 0.0002)$, (0.5056 ± 0.0009) , and (0.6082 ± 0.0011) .

Temperature determinations were carried out with a standard platinum resistance thermometer calibrated to the ITS-90 [42]. The uncertainty in the temperature measurements was 0.01 K .

Quantification of anthracene in the saturated aqueous solutions was carried out through an unweighted 7 point calibration. Only fresh solutions were used during the calibration process.

To reduce the uncertainty during the quantification of anthracene the calibration curve was constructed in a narrow concentration interval ($3.1 \mu\text{g} \cdot \text{cm}^{-3}$ to $12.7 \mu\text{g} \cdot \text{cm}^{-3}$). In addition, the mass of the collected aqueous sample, at the studied temperatures, was varied in such a way that the size of the chromatographic signal used to quantify the anthracene was always located in a point close to the centroid of the regression line [43]. The mass of the collected aqueous samples varied from 0.6625 g to 16.1744 g .

The uncertainty during the quantification of anthracene was estimated using standard statistical techniques [36,43]. The uncertainty related to other steps of the experimental procedure was also determined and appropriately considered during the calculation of the uncertainty of the solubility values [44].

2.3. Accuracy of experimental determinations

The solubility of anthracene in water has been determined by several authors. Experimental determinations include studies at room temperature and atmospheric pressure [18,45–60], at moderated temperature and atmospheric pressure [31,39,61–65], and at high temperature or high pressure [66–70].

To evaluate the accuracy of experimental values determined in this work these values were compared with other experimental data previously reported.

The solubility of anthracene in water determined in this work is presented in table 1. The reported values are averages of typically three to five independent determinations. Uncertainty in the experimental values ranged from 1.4% to 2.5%. Values reported in $\text{mol} \cdot \text{L}^{-1}$ were calculated considering the density of the studied aqueous solution. Densities of NaCl aqueous solutions as a function of temperature and salt concentration were estimated through the method reported by Laliberté and Cooper [71]. The effect of the small amount of dissolved anthracene in the NaCl aqueous solutions was not considered during the density estimations.

Figure 1 presents a comparison between the solubility data determined in this work and other solubility values previously reported. As observed, despite the large number of solubility values reported, most of them are only in partial agreement. This discrepancy is mainly due to several factors that can adversely affect both the accuracy and the precision of the experimental determinations [38,39]. It has been established that the DCCLC technique circumvents many of these factors [39,64]. Hence, only those values determined with this technique [21,31,36,39,61,64,65] were used

TABLE 1
Solubility of anthracene in water as a function of temperature.

T/K	$S_{i,0} \cdot 10^8 / (\text{mol} \cdot \text{kg}^{-1})$	$S_{i,0} \cdot 10^8 / (\text{mol} \cdot \text{L}^{-1})$	$S_{i,0} \cdot 10^9 / x$
278.11	7.32 ± 0.18	7.32 ± 0.18	1.318 ± 0.032
288.13	13.22 ± 0.22	13.21 ± 0.22	2.381 ± 0.039
293.38	18.48 ± 0.31	18.44 ± 0.31	3.329 ± 0.056
298.24	25.05 ± 0.37	24.98 ± 0.36	4.513 ± 0.066
303.14	34.10 ± 0.49	33.95 ± 0.49	6.143 ± 0.089
308.25	48.03 ± 0.67	47.74 ± 0.67	8.65 ± 0.12
313.35	64.6 ± 1.0	64.1 ± 1.0	11.63 ± 0.18
318.26	86.5 ± 1.6	85.6 ± 1.5	15.58 ± 0.28
323.19	115.2 ± 2.8	113.9 ± 2.7	20.76 ± 0.50
333.34	217.9 ± 4.3	214.2 ± 4.2	39.25 ± 0.77

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