Solubility of Anthracene in C1–C3 Alcohols from (298.2 to 333.2) K and Their Mixtures with 2-Propanone at 298.2 K

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The anthracene solubility in methanol, ethanol, 1-propanol, and 2-propanol from (298.2 to 333.2 K) and also in binary solvent mixtures of 2-propanone + C1–C3 alcohols at 298.2 K was reported. The van’t Hoff equation was used for correlation of the solubility data in monosolvents at different temperatures. The solubility of anthracene in mixed solvents was predicted using previously developed quantitative structure–property relationships (QSPR) that required knowledge of the solubility data in monosolvents. The overall mean percentage deviation of the correlated solubilities in monosolvents at different temperatures was 4.8 %. The corresponding value for solubility prediction methods in solvent mixtures varied from (8.5 to 11.9) %. Using ab initio prediction methods, the overall mean percentage deviations varied from (14.7 to 15.8) %.

Introduction

Solubility is an important consideration in many chemical and pharmaceutical applications, including crystallization, separation, decontamination, liquid extraction, and drug formulation design. Solubility data of anthracene are essential in the petroleum industry and in environmental decontamination. In many instances, the solubility in a neat solvent is not sufficient for the desired application. Temperature alteration and solvent mixing are the common methods to enhance the solubility of lowly soluble compounds. However, there is a significant lack of solubility data for many solutes; therefore, efforts have been devoted to developing predictive mathematical models that require a minimum number of experimental input values.1

Experimental solubility data of anthracene in a number of binary and ternary solvent mixtures have been reported in alcohols, ethers, alkenes, esters, and aromatic compounds by Acree and co-workers. Recently, the anthracene solubility in ternary solvent mixtures of 2,2,4-trimethylpentane + 2-propanone + alcohols2 and quaternary solvent mixtures of 2,2,4-trimethylpentane + 2-propanone + methanol + alcohols was reported.3 Experimental anthracene solubilities in binary ketone + alcohol solvent mixtures have not been reported to date.

A numerical method was developed employing the Jouyban–Acree model, the Abraham solute parameters, and the Abraham solvent coefficients. This combination enables one to predict the solubility of a solute in nonaqueous solvent mixtures employing the experimental and/or computed solubility data in monosolvents. The basic Jouyban–Acree model is4

\[
\ln C_m^{\text{Sat}} = x_1 \ln C_1^{\text{Sat}} + x_2 \ln C_2^{\text{Sat}} + x_1 x_2 \sum_{i=0}^{2} J_i(x_1 - x_2)^i
\]

where \(C_m^{\text{Sat}}\) is the molar solubility of the solute in the binary solvent mixtures; \(x_1\) and \(x_2\) are the mole fractions of solvents 1 and 2 in the absence of the solute; \(C_1^{\text{Sat}}\) and \(C_2^{\text{Sat}}\) denote the molar solubility of the solute in neat solvents 1 and 2; and \(J_i\) is the solvent–solvent and solute–solvent interaction terms. In a previous work, quantitative structure–property relationship (QSPR) models were proposed to calculate the numerical values of the \(J_i\) terms using Abraham’s water-to-solvent and gas-to-solvent coefficients of the solvents and Abraham’s parameters of the solutes.5 These parameters (both solute and solvent parameters) are used as the representative descriptors for possible interactions between solvents 1 and 2 and the solute in the solution.

The purposes of the present study are to report the experimental solubility data of anthracene in methanol, ethanol, 1-propanol, and 2-propanol at different temperatures and in the binary mixtures of acetone and C1–C3 alcohols at 298.2 K. The experimental results are used to assess the applicability of previously reported QSPR models for predicting the solubility of solutes in binary solvent mixtures.

Experimental Method

Materials. Anthracene (purity 0.96 in mass fraction) was purchased from Fluka, and it was recrystallized several times from 2-propanone and ethyl acetate to yield a purified sample having a melting point of 488 K. Its purity was checked by a thin layer chromatography method,6 and also the measured solubilities in a number of monosolvents were compared with the corresponding data from the literature. Methanol (0.995 in mass fraction), ethanol (0.999 in mass fraction), 2-propanol (0.995 in mass fraction), and 2-propanone (0.995 in mass fraction).
323.2 mol of the solid was placed into each of the monosolvents and at (298.2, 303.2, 313.2, 323.2, and 333.2) K. An excess amount of methanol, ethanol, 1-propanol, and 2-propanol was measured (i.e., $0.0000$) respectively. Calculated standard deviations of independent monosolvents at different temperatures and mixtures of solvents, solubilities being reproducible to within $2.3\%$ and $2.4\%$ in fraction) were purchased from Scharlau Chemie (Spain) and 1-propanol ($0.995$ in mass fraction) from Merck (Germany).

**Apparatus and Procedures.** The solubility of anthracene in methanol, ethanol, 1-propanol, and 2-propanol was measured at $(298.2, 303.2, 313.2, 323.2, and 333.2)$ K. An excess amount of the solid was placed into each of the monosolvents and incubated in ovens at $(298.2 \pm 0.2, 303.2 \pm 0.2, 313.2 \pm 0.4, 323.2 \pm 0.4, and 333.2 \pm 0.6)$ K (Behdad, Tehran, Iran) at least for five days. The binary solvent mixtures were prepared by mixing the appropriate volumes of the solvents, and then the mole fractions of the solvents were computed from the densities of the neat solvents. The solvent composition could be calculated to $0.001$ mole fraction. The solubility of anthracene in mixed solvents was determined by equilibrating an excess amount of the solid with the binary solvent mixtures using a shaker (Behdad, Tehran, Iran) placed in an incubator equipped with a temperature controlling system at $298.2 \pm 0.2$ K (Nabziran, Tabriz, Iran). Attainment of the equilibrium was verified by measurements at different times after $72$ h. The solutions were filtered using hydrophobic Durapore filters (0.45 $\mu$m, Millipore, Ireland) and then diluted with 2-propanone for spectrophotometric analysis at $357$ nm with a UV–vis spectrophotometer (Beckman DU-650, Fullerton, USA). The calibration graph is shown in Figure 1. Concentrations of the dilute solutions were determined from a UV absorbance calibration graph with the molar absorptivities of anthracene ranging from $667 \epsilon/(L \cdot mol^{-1} \cdot cm^{-1})$ to $713 \epsilon/(L \cdot mol^{-1} \cdot cm^{-1})$ for the anthracene concentrations ranging from $(0.0004$ to $0.0021)$ mol·L$^{-1}$. Each experimental data point is an average of at least three independent measurements with the measured mol·L$^{-1}$ solubilities being reproducible to within $2.3\%$ and $2.4\%$ in monosolvents at different temperatures and mixtures of solvents, respectively. Calculated standard deviations of independent solubility measurements for each data point ranged from $\sigma_{n-1} = 0.0000$ (i.e., $< 0.00005$) to $\sigma_{n-1} = 0.0001$ mol·L$^{-1}$ and $\sigma_{n-1} = 0.0001$ to $\sigma_{n-1} = 0.0032$ mol·L$^{-1}$ in monosolvents at different temperatures and in solvent mixtures at $298.2$ K, respectively. Densities of the saturated solutions were measured using a 5 mL pycnometer with the uncertainty of $0.0001$ g·cm$^{-3}$.

**Computational Methods**

For correlation of experimental solubility data in monosolvents at different temperatures, the van’t Hoff equation is used:

$$\ln C_{\text{Sat}}^T = \frac{a}{T} + b$$  \hspace{1cm} (2)

where $C_{\text{Sat}}^T$ is the saturated molar solubility at temperature $T$, and $a$ and $b$ are the model constants calculated using a least-squares method.

The $J_i$ terms of the Jouyban–Acree model were computed using eqs $2s$ to $4s$ (Supporting Information, SI) and then used to predict the anthracene solubility data in binary solvent mixtures using eq 1, employing experimental solubilities of anthracene in monosolvents. This numerical analysis was called method I. The same computations were carried out employing eqs $5s$ to $7s$ (SI). The latter computation method is referred to as numerical method II. To further reduce the experimental data requirement in the prediction process, it is possible to use the Abraham solvation models to predict the solubilities of anthracene in the monosolvents, that is, $C_{\text{Sat}}^\text{A}$ and $C_{\text{Sat}}^\text{W}$. The Abraham model for the water-to-solvent process is

$$\log\left(\frac{C_S}{C_W}\right) = c + e\cdot E + s\cdot S + a\cdot A + b\cdot B + v\cdot V$$  \hspace{1cm} (3)

and for the gas-to-solvent process

$$\log\left(\frac{C_S}{C_G}\right) = c + e\cdot E + s\cdot S + a\cdot A + b\cdot B + l\cdot L$$  \hspace{1cm} (4)

where $c$, $e$, $s$, $a$, $b$, $v$, and $l$ are the model constants (i.e., the Abraham solvent coefficients), $E$, $S$, $A$, $B$, $V$, and $L$ are the Abraham solute parameters, $C_S$ (the same term as $C_{\text{Sat}}^\text{A}$ and $C_{\text{Sat}}^\text{W}$ from this work) and $C_W$ are the solubility in the organic solvent and water (in mol·L$^{-1}$), respectively, and $C_G$ is the gas phase concentration of the solute.\(^8\) The basic Abraham model involves two different transfer processes, one for solute transfer between two condensed phases (such as water-to-organic solvent) and a separate equation for solute transfer to a condensed phase from the gas phase. The originating phase for the solute transfer process is essentially a reference point, and one can use the correlation to predict the solute properties in the final phase, provided that the solute properties in the originating phase are known. Equation 3 requires the aqueous solubility of the solute ($C_W$), and eq 4 requires the $C_G$ value. Both equations have been used to correlate and to estimate the solubility of crystalline solutes in organic solvents.\(^8\)–\(^11\) The numerical values of the solute’s Abraham experimental parameters for anthracene are: $\log C_W = -6.430$, $E = 2.290$, $S = 1.340$, $A = 0.000$, $B = 0.280$, $V = 1.454$, and $L = 7.568$.\(^8\) The log $C_G = -9.460$ was taken from a published paper by Acree and Abraham.\(^8\) The predicted $C_{\text{Sat}}^\text{A}$ and $C_{\text{Sat}}^\text{W}$ from eq 3 and $J_i$ terms computed using eqs $2s$ to $4s$ (SI) were used to predict the $C_{\text{Sat}}^\text{A}$, and this numerical method was called method III. A similar numerical analysis employing eqs $5s$ to $7s$ (SI) and eq 4 was called method IV.

All calculated $C_{\text{Sat}}^\text{A}$ solubilities were compared with the corresponding experimental values, and the mean percentage deviation (MPD) was calculated as an accuracy criterion by

$$\text{MPD} = \frac{100}{N} \sum \left| \frac{(C_{\text{Sat}}^\text{A})_{\text{calculated}} - (C_{\text{Sat}}^\text{A})_{\text{experimental}}}{(C_{\text{Sat}}^\text{A})_{\text{experimental}}} \right|$$  \hspace{1cm} (5)
Table 1. Experimental (expt.) and Correlated (cor) Molar Solubilities* of Anthracene in Methanol, Ethanol, 1-Propanol, and 2-Propanol Solvent Mixtures, at (298.2 to 333.2) K, a and b Values (± Standard Errors) of Equation 2, and the Mean Percentage Deviation (MPD)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>ρ (g/cm³)</th>
<th>C²Sat/mol·L⁻¹</th>
<th>expt.</th>
<th>cor</th>
<th>100-deviationb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>298.2</td>
<td>0.7883</td>
<td>0.00633</td>
<td>0.00646</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>303.2</td>
<td>0.7842</td>
<td>0.0073</td>
<td>0.00733</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>313.2</td>
<td>0.7793</td>
<td>0.0085</td>
<td>0.0093</td>
<td>9.7</td>
<td></td>
</tr>
<tr>
<td>323.2</td>
<td>0.7761</td>
<td>0.0114</td>
<td>0.0117</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>333.2</td>
<td>0.7704</td>
<td>0.0144</td>
<td>0.0145</td>
<td>0.8</td>
<td></td>
</tr>
</tbody>
</table>

| 1-Propanol |
| 298.2 | 0.7844 | 0.0008 | 0.00085 | 2.1 |
| 303.2 | 0.7824 | 0.0094 | 0.0109 | 8.6 |
| 313.2 | 0.7761 | 0.0115 | 0.0114 | 12.5 |
| 323.2 | 0.7732 | 0.0139 | 0.0199 | 3.1 |
| 333.2 | 0.7684 | 0.0265 | 0.0269 | 1.7 |

| 2-Propanol |
| 298.2 | 0.7813 | 0.0056 | 0.0054 | 3.0 |
| 303.2 | 0.7975 | 0.0101 | 0.0104 | 2.6 |
| 313.2 | 0.7922 | 0.0143 | 0.0153 | 7.3 |
| 323.2 | 0.7875 | 0.0229 | 0.0222 | 3.3 |
| 333.2 | 0.7834 | 0.0326 | 0.0313 | 4.0 |
| a Calculated as: |
| ln C²Sat = 2310/298.2 + 2.7 = -5.0465 → C²Sat = 0.0064 |
| b Deviation is calculated as: |
| 100-deviation = 100 * | ln(C²Sat) | 0.00631 | 0.0063 |
| 0.00303 |

Figure 2. Logarithm of the solubility of anthracene (∼ln C²Sat) in methanol; •, ethanol; ▲, 1-propanol; ■, 2-propanol; and their related calculated solubility data: - -, methanol; thick –, ethanol; – – –, 1-propanol; thin —, 2-propanol, using eq 2.

Results and Discussion

Table 1 gives the experimental molar solubilities of anthracene in methanol, ethanol, 1-propanol, and 2-propanol at the five temperatures studied, measured densities of the saturated solutions, the back-calculation of solubilities based on equation 2, and the equation coefficients. Equation 2 was found to describe the observed solubilities to within an overall MPD of 4.8 %. Figure 2 compares the experimental and back-calculated solubilities at the five temperatures studied.

The experimental and predicted solubilities of anthracene using methods I to IV are tabulated in Table 2, along with the densities of the saturated solutions. Our measured anthracene solubilities in 2-propanone (0.053 mol·L⁻¹), methanol (0.007 mol·L⁻¹), ethanol (0.009 mol·L⁻¹), 1-propanol (0.009 mol·L⁻¹), and 2-propanol (0.006 mol·L⁻¹) at 298.2 K were in good agreement with published literature values for anthracene dissolved in 2-propanone (0.052 mol·L⁻¹), methanol (0.006 mol·L⁻¹), ethanol (0.008 mol·L⁻¹), 1-propanol (0.008 mol·L⁻¹), and 2-propanol (0.006 mol·L⁻¹).
Table 3. Numerical Values of the Mean Percentage Deviation (MPD) for the Predicted Solubilities of Anthracene in 2-Propanone (1) + Alcohols (2) Using Various Numerical Methods and Their Overall Values

<table>
<thead>
<tr>
<th>solvent</th>
<th>method I</th>
<th>method II</th>
<th>method III</th>
<th>method IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-propanol</td>
<td>16.2</td>
<td>13.4</td>
<td>14.3</td>
<td>29.4</td>
</tr>
<tr>
<td>2-propanol</td>
<td>5.3</td>
<td>5.4</td>
<td>20.3</td>
<td>11.7</td>
</tr>
<tr>
<td>ethanol</td>
<td>14.2</td>
<td>10.9</td>
<td>18.5</td>
<td>13.0</td>
</tr>
<tr>
<td>methanol</td>
<td>12.0</td>
<td>4.3</td>
<td>9.9</td>
<td>4.6</td>
</tr>
<tr>
<td>overall MPD</td>
<td>11.9</td>
<td>8.5</td>
<td>15.8</td>
<td>14.7</td>
</tr>
</tbody>
</table>

The solubility of anthracene in binary solvent mixtures was predicted using numerical methods I to IV. The predicted solubilities were compared with the corresponding experimental data, and the computed MPD values are listed in Table 3. Method II has the best prediction capability by employing the solubility data in monosolvents, and its overall MPD (8.5 %) is significantly less than that of method I (11.9 %). There is no significant difference between overall MPDs of methods III and IV. Both are ab initio prediction methods, and to improve the prediction capability of these methods, more accurate solubility prediction tools for monosolvents are required.

In conclusion, the experimental solubility is reported for anthracene in four monosolvents at several different temperatures, along with the solubility of anthracene in binary mixtures containing methanol, ethanol, 1-propanol, and 2-propanol with 2-propanone at 298.2 K. The measured solubility data can be used in the chemical or petrochemical industries. The applicability of previously developed models to predict the solubility of anthracene is shown. The careful review of the overall MPDs showed that eq 2, the developed QSPR, and Abraham models can be used for anthracene solubility prediction in studied alcohols at different temperatures and binary solvent mixtures of 2-propanone + alcohols. These computations can be used for solubility predictions of anthracene in the chemical industry.

Supporting Information Available:
Details of the QSPR equations used in this work along with the required input data are included in a Word file. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited