Study of the solubility of antracene in pure and modified supercritical carbon dioxide

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Abstract. In the framework of the supercritical fluid extraction regeneration of catalysts, an original experimental device was created for measuring the solubility of substances in pure and modified supercritical carbon dioxide, protected by a RF patent for a useful model. To prevent entrainment during the implementation of the process of extraction of substances in the solid state, a special vessel with a microporous membrane was used in the extraction cell. The solubility of anthracene in pure supercritical carbon dioxide was studied with 423, 435, 448 K isotherms in the pressure range from 9.6 to 22 MPa. It is established that an increase in temperature and pressure contribute to an increase in the solubility of anthracene. In order to increase the dissolving ability of SC-CO$_2$, a search for modifiers of various nature (acetone, hexane, ethanol) was conducted. It is revealed that hexane and ethanol are more effective modifiers. In this regard, the effect of the concentration of these modifiers on the dissolving ability was investigated. The content in the solvent 2% of the mass. hexane and ethanol have a maximum effect than their other concentration. The solubility of anthracene in SC-CO$_2$ modified with hexane and ethanol was studied at a 435 K isotherm in the pressure range 10-20 MPa. The use of modifiers made it possible to increase the solubility of anthracene using ethanol and hexanan by 56% and 76%, respectively. The solubility of anthracene in pure supercritical carbon dioxide is described using the Peng-Robinson equation of state and three adjustable parameters. To describe the solubility of anthracene in a modified SC-CO$_2$, only one adjustable parameter was used. In addition, the descriptions of the solubility of anthracene in pure SC-CO$_2$ obtained experimentally in this work and in the works of other authors are presented. The obtained dependences of the parameters of the binary interaction on temperature make it possible to interpolate the values of solubility on the basis of existing experimental data.

1. Introduction

Recently, searches are underway for new methods for regenerating catalysts that are implemented in non-aggressive, inert media with minimal energy consumption. Such methods include supercritical fluid extraction (SCFE) regeneration, which is one of the promising innovative scientific and technological areas. SCF technologies are based on using a rather wide range of substances as supercritical extractants. The supercritical carbon dioxide (SC-CO2) is the most popular and widely demanded [1]. The main problem of the SCFE process is the insufficient knowledge of the solubility of compounds that deactivate the catalyst in SCF media of appropriate chemical nature. Therefore, for the last 2-3 decades, the solubility of substances in SCF solvents has been the subject of intensive research. The results of the analysis of the composition of the compounds (coke) which deactivate the
catalyst show that the characteristics of coke deposits on the catalysts depend on the formation conditions and can vary widely in chemical composition, structure, dispersion and distribution on the catalytic surface [2]. Among the products of coke deposits can be distinguished naphthalene, anthracene and others. In this connection, anthracene was chosen as the object of the solubility study.

2. Materials and methods
The solubility measurements were carried out by the dynamic method on the original experimental device protected by the RF patent [3]. Figure 1 shows a schematic diagram of this device.

![Figure 1. A device for measuring the solubility of substances in SC-CO$_2$: 1 – balloon; 2 – gas pre-cooling vessel; 3, 6 – high pressure pumps; 4 – recirculation chiller; 5 – vessel for co-solvent; 7 – three-way valve; 8 – extraction cell; 9 – heat exchanger; 10 – electronic measuring and controlling device; 11a, b – extract collectors; 12 – capacity for heating extracts collectors; 13 – throttle valve; 14 - reducing valve; 15 – gas meter.](image)

The device contains a gas cylinder 1, two high-pressure plunger pumps 3, 6, which supply the solvent and co-solvent, respectively, to the extraction cell 8, heated by a heat exchanger 9, gas pre-cooling vessel 2, where gas is liquefied due to the circulation of a refrigerant which is cooled by recirculation chiller 4, two extract collectors 11a, 11b, inside of which are replaceable sleeves for the extract, placed in a thermostatic bath 12. The desired temperature in the bath and in the cell is maintained by an electronic measuring and controlling device 10. The required flow rate of SCF passing through the test substance is regulated by a high pressure valve 13 using a gas meter 15. The pressure in the first extract collector after the high-pressure valve is maintained by the reducing valve 14 is lower than in cell 9, but higher than the critical value. Pumps are prevented from returning gas and co-solvent by reverse action valves.

To prevent carry-over during the implementation of the process of extraction of substances in the solid state, and, namely, in the form of powder in the cell is used a special vessel with a microporous membrane, designed to download the test substance.

Studies have been conducted using pure and modified by additive solvent (extractant). In this work, anthracene (C$_{14}$H$_{10}$) of the analytical grade brand was used, carbon dioxide with 99.8% by volume - CO$_2$ content was used as a solvent, hexane and ethanol with the content of the analytical grade with less than 99.5%.

3. Results and discussion
To assess the reliability of the data obtained and the operability of the experimental procedure at the facility, we carried out test measurements of the anthracene solubility at $T = 423.15$ K and $P = 10$-20 MPa (figure 3). The obtained results of anthracene solubility agree well with the data of other authors [4], [5].
Experimental measurements of the solubility of anthracene in pure SC-CO₂ were carried out at isotherms of 423, 435, 448 K in the pressure range of 9.6–22 MPa.

In addition, using the Peng-Robinson equation of state, the solubility of anthracene is described [6, 7]. As the initial equation used equation:

\[
\frac{\partial \ln \gamma_k}{\partial p} = \frac{V_m^k}{RT} \left( 1 - \frac{1}{p} \frac{\partial \ln \phi_k}{\partial p} \right),
\]

where \( \gamma_k \) – is the mole fraction of the dissolved component \( k \) in the supercritical solvent, \( V_m^k \) – is the molar volume, \( p \) – is the pressure, \( \phi_k \) – is the volatility coefficient.

As a result of integrating equation (1) in the interval from \( p_0 \) to \( p \), we obtain:

\[
\ln \gamma_k = \ln \gamma_0 + \frac{V_m^k}{RT} \left( p - p_0 \right) - \ln \frac{p}{p_0} - \ln \frac{\phi_k}{\phi_0} ,
\]

where \( \gamma_k = \gamma_k(p_0), \phi_k^0 = \phi_k(p_0) \). Many sources \( p_0 \) equation parameter is not taken into account, leading to additional errors in connection with this equation to determine the fugacity coefficient \( \ln \phi_k \) we solved considering \( p_0 \), which made it possible to minimize the mean square error.

The fugacity coefficient of the component \( k \) at \( T \), \( V \approx \text{const} \):

\[
\ln \phi_k = \int_{\nu_0}^{\infty} \left[ \frac{\partial n_z}{\partial n_k}_{T,V} - 1 \right] \frac{dV_M}{V_M} - \ln z
\]

where \( n = \sum_k n_k \) – the total number of moles, \( n_k \) – is the number of moles of component \( k \), \( V_M = V/n \) – molar volume, \( z \) – compressibility factor, calculated by the equation of state.

The compressibility factor is determined according to the Peng-Robinson state equation:

\[
a = \sum_{i,j} \sigma_{ij} a_{ij} \left( \frac{b}{b_{ij}} \right)^{\beta_{ij}} y_i y_j, \quad b = \sum_{i,j} \gamma_i \gamma_j b_{ij} \sqrt{y_i y_j}
\]

where \( a_{ij} = a_{ji}, b_{ij} = b_{ji} \) are coefficients that depend on temperature and parameters \( T_{xp} \) and \( P_{xp} \) of the mixture components, \( \sigma_{ij} = \sigma_{ji}, \sigma_j = 1, \gamma_i = \gamma_j, \gamma_j = 1, \beta_{ij} = \beta_{ji}, \beta_{ij} = 1 \) – are the parameters of the binary interaction, \( x_i = n_i/n \) – is the mole fraction of component \( i \) in the mixture.
In the literature sources presented a different number of binary interaction parameters is given, more often the adjusting parameter $\beta_{ij}$ or the parameters $\sigma_{ij}, \beta_{ij}$ or $\gamma_{ij}$. In our case, three fitting parameters were used, namely, $\beta_{ij}, \sigma_{ij}$ and $\gamma_{ij}$ [6].

In accordance with the choice of the number of fitting coefficients $\sigma_{ij}, \beta_{ij}$ and $\gamma_{ij}$, the following mixing rules were obtained:

- if $\sigma_{ij} = 1 \forall i, j$ and $\beta_{ij}, \gamma_{ij}$ then mixing rule is the following:
  \[ a = \sum_{i, j} a_{i, j} \left( \frac{b}{b_{i, j}} \right)^{\beta_{ij}} y_i y_j, \quad b = \sum_i b_{i, j} y_i \]  
  \( (4) \)

- if $\beta_{ij} = 0 \forall i, j$, the following mixing rule is possible:
  \[ a = \sum_{i, j} \sigma_{i, j} a_{i, j} \left( \frac{b}{b_{i, j}} \right)^{\gamma_{ij}} y_i y_j, \quad b = \sum_i b_{i, j} y_i \]  
  \( (5) \)

The calculation of the fitting parameters of the binary interaction for the listed mixing rules was made taking into account the best rms approximation to the experimental results.

In the case of obtaining the results of experiments at a constant temperature and different pressures $T_s, s = 0, \ldots, n$, the parameters of the binary interaction $\sigma_{ij}, \beta_{ij}, \gamma_{ij}$ are determined on the basis of [8]:

\[ \Delta = \min_{\sigma, \gamma, \beta} \sqrt{\frac{1}{n} \sum_{s=0}^{n} \left( \frac{\bar{y}_k - y_k(p_s)}{\bar{y}'_k} \right)^2}, \]  
\( (7) \)

where $y_k(p_s)$ is calculated by substituting the corresponding $p_s$ and $\bar{y}'_k$ values into the right-hand side of expression (2).

Comparison of experimental measurement values and descriptions of anthracene solubility, presented in figure 3, shows that mean square deviation of the description results from the experimental data in the investigated pressure range on the isotherms 423, 435, 448 K does not exceed 6.48%.

An increase in pressure and temperature have a positive effect on the dissolving ability of SC-CO$_2$.

In order to increase the dissolving power of supercritical carbon dioxide, a search for co-solvents of various nature (acetone, ethanol, hexane, etc.) was conducted [9]. Studies have shown that hexane and ethanol are more effective modifiers. In this regard, the influence of the concentration of these cosolvents on the dissolving ability was analyzed. The content in the solvent 2% of the mass. hexane or ethanol had a maximum effect than their other concentration. The results of anthracene solubility in SC-CO$_2$ modified with hexane and ethanol are clearly presented in figure. 4. The table shows the results of experimental measurements and descriptions of the solubility of anthracene in SC-CO$_2$ modified with hexane and
ethanol. To describe the solubility of anthracene in modified SC-CO$_2$, the Peng-Robinson equation of state was also used, but with only one adjustable parameter $\beta_{ij}$ (4).

![Graph](image1)

**Figure 3.** Experimental and calculated anthracene solubility values in SC-CO$_2$ (points - experiment, lines - description).

**Figure 4.** Anthracene solubility in hexane modified (1), ethanol (2) and pure (3) supercritical carbon dioxide at $T = 435$ K.

**Table.** Experimental data and description of anthracene solubility in SC-CO$_2$, modified with hexane and ethanol, at $T = 435$ K.

| $p$, MPa | SC-CO$_2$+ethanol $\times 10^6$, molar fraction | SC-CO$_2$+hexane $\times 10^6$, molar fraction |
|----------|-----------------------------------------------|---------------------------------------------|
| 10       | 296                                           | 10.1                                        |
| 13       | 396                                           | 12.8                                        |
| 20       | 772                                           | 16                                          |

Modification of SC-CO$_2$ had a positive effect on the solubility of anthracene. So with the maximum research pressure (20 MPa) using ethanol and hexane as a co-solvent, the solubility of anthracene increased by 56% and 76%, respectively.

In addition, a description of the solubility values of anthracene in pure SC-CO$_2$, obtained experimentally in this work and in the works of other authors [10], [4], using the Peng-Robinson equation and three adjustable parameters (parameter $\gamma = 0.05$). The values of the binary interaction parameters and their temperature dependence are presented in figures 5 and 6.

![Graph](image2)

**Figure 5.** Temperature dependence of the parameter binary interaction $\sigma$ by results descriptions: 1 – data [10], 2 – data [4], 3 – data [3].

![Graph](image3)

**Figure 6.** Temperature dependence of the parameter binary interactions $\beta$ by results descriptions: 1 – data [10], 2 – data [4], 3 – data of
of the present work. the present work.

4. Conclusion
The obtained dependences of the parameters of the binary interaction on temperature make it possible to interpolate the solubility values on the basis of the existing experimental data.

The value of the confidence interval of the results of measuring the solubility of anthracene in pure SC-CO$_2$ was determined in accordance with the recommendations on the expression of measurement uncertainty, the scope of which includes conducting basic and applied research and development in science and technology. The value of the confidence level for the results of measuring the solubility of anthracene, calculated using the expanded uncertainty, is in the range from $\pm 1.75\%$ to $\pm 8.23\%$.

To measure the solubility of anthracene in pure and modified supercritical carbon dioxide, an original experimental device has been created that is protected by a Russian patent for a useful model.

New data were obtained on the solubility of anthracene in pure supercritical carbon dioxide at 423, 435, 448 isotherms in the pressure range 9.6-22 MPa. It has been established that an increase in temperature, pressure and the addition of modifiers of various nature have a positive effect on the dissolving ability of SC-CO$_2$. The solubility of anthracene in SC-CO$_2$ modified with hexane and ethanol was measured at an isotherm of 435 K in the pressure range 10–20 MPa. The use of modifiers made it possible to increase the solubility of anthracene using ethanol and hexane by 56% and 76%, respectively.

A description of the anthracene solubility in pure supercritical carbon dioxide and in modified SC-CO$_2$ is given using the Peng-Robinson equation of state. The temperature dependence of the parameters of the binary interaction is obtained, which makes it possible to interpolate the solubility values on the basis of the existing experimental data.

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