The equipment for measuring the solubility of granulated and liquid types of substances in a supercritical fluid

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Abstract. Improved device for the implementation of extraction processes using supercritical fluids (SCF), which allows to achieve a constant predetermined pressure in the cell and to eliminate multiple control of the SCF flow rate due to the installation of a chiller that provides increased heat transfer performance and minimal inertia of coolant temperature fluctuation. To assess the reliability of the results obtained at the facility, verification measurements of the solubility of anthracene in supercritical carbon dioxide (SC-CO₂) were carried out at T = 423 K and P = 10-20 MPa. The results are in good agreement with published data. The methodology for expressing measurement uncertainty is described in detail taking into account parameters that contribute to the uncertainty based on the calculation formula for calculating the solubility of anthracene and the measurement uncertainty of the specified parameters.

1. Introduction

The experimental data on the solubility of substances that deactivate the catalyst in supercritical carbon dioxide are an important component of the database, which is necessary at the stage of modeling the process of supercritical fluid extraction regeneration in order to solve the applied problem of hardware design and technology scaling. The solubility results of substances in supercritical carbon dioxide at various pressures and temperatures in the reference and periodic literature are extremely limited.

The results of numerous experimental works [1, 2] indicate that the solubility behavior of substances of various chemical nature in supercritical fluids is of a general nature. In [3], it was found that with approaching the critical point of a pure solvent, within the experimental error, we can talk about the universal behavior of the solubility of substances, both solid and liquid.

Despite the encouraging results obtained in the framework of the entropy method of similarity theory, the accumulation of reliable experimental data remains an urgent task. This is especially true for the region of state parameters that directly applies to the critical point of a pure solvent, where the selectivity of fluid extraction is maximum and energy costs tend to a minimum. The accuracy of the experiments and the reduction of the uncertainty of the results of measuring the solubility of substances in a supercritical fluid are greatly influenced by the apparatus design and the improvement of the technological process. To achieve the above, experimental plants are constantly being modernized by making changes both to the technology of the experiment and to the hardware design of the installation.
2. Materials and methods

The present work describes a device (figure 1) for measuring the solubility of granular and liquid types of substances in a supercritical fluid. It is the result of the improvement of the device for the implementation of extraction processes using supercritical fluids [4], the disadvantage of which is the need to constantly control the flow of supercritical fluid to maintain a given process pressure using a throttle valve, due to temperature fluctuations of the solvent supplied to the high pump pressure. The disadvantage was eliminated thanks to the installation of a chiller, which provides increased heat transfer performance and minimal inertia of the coolant temperature fluctuation, in contrast to a refrigeration unit based on a domestic refrigerator.

The device contains a high-pressure plunger pump 3, into which compressed gas (CO\textsubscript{2}) enters from cylinder 1 through a refrigeration unit 2. A Waters P50A high-pressure plunger pump 3 provides a fixed supply of solvent under pressure up to 60 MPa. For normal operation of the pump, it is necessary to supply liquid carbon dioxide to the suction circuit. Gas liquefaction occurs in the refrigerator 2 and directly in the pump and is provided by the circulation of refrigerant in the pump cooling jacket and the annulus of the refrigerator. The required refrigerant temperature (up to \(-15 \degree\) C) is supported by chiller 4 of the Thermo Scientific brand Accel 500 LC.

Co-solvent is supplied from tank 5 by a high-pressure plunger pump 6 of the LIQUPUMP 312/1 brand through a three-way valve 7 to the common line. Pump 6 allows you to adjust the supply of co-solvent in the range of 0.01-9.99 ml / min, thereby setting the required concentration (2-10\%) of the co-solvent in supercritical CO\textsubscript{2}.

Check valves are used to prevent the return of CO\textsubscript{2} and the co-solvent back to the pumps.

The extraction cell 8 is a pressure vessel, divided into two parts. In one part, the extraction of solids, in the other part, the extraction of liquid substances. The cell is installed in a heat exchanger 9, which is a thick-walled copper pipe, onto which a heating cable and a pipe are laid in special grooves in a spiral, where the preliminary heating of the solvent supplied for extraction takes place. This design provides the maximum reduction in temperature gradients inside the cell due to uniform
heating of the cell itself and preheating of the supplied solvent. The cell is equipped with two
temperature sensors, one of which is located directly on the cell body, the other on the heat exchanger.
The signals from the sensors are fed to an electronic meter-controller 10 of the 2TPM1 brand, which
maintains the temperature with an accuracy of ± 5 °C. The surface of the heat exchanger is covered
with thermal insulation.

The collections of the extract 11a, 11b, inside of which there are replaceable sleeves for the extract,
are placed in a thermostatic bath 12.

The PRV 41SS piston pressure reducing valve 14, which acts as a restrictor, maintains the
necessary constant pressure in the first extract collector, which allows fractionation of certain
components of the mixture.

The throttle valve 13 of the HIP 60-11HF2-V brand is designed to provide accurate control of SCF
flow at pressures up to 414 MPa and temperatures up to 505 K.

The gas meter 15 of the SGBM-1.6 brand allows you to control the flow rate of SCF that has
passed through the test sample.

3. Results and discussion

In order to verify the accuracy of the measured values and the reliability of the experimental
procedure, verification measurements of the solubility of anthracene in SC-CO$_2$ were carried out at
T = 423 K and P = 10 ÷ 20 MPa. Comparison of the results of the solubility of anthracene obtained in
this work and in [5, 6] showed the practical coincidence of the experimental data with the values
published in the literature, which indicates the operability of the proposed method and the reliability
of the results.

The scatter of values of the results of the solubility of anthracene in SC-CO$_2$ was determined
according to the method of expressing the measurement uncertainty GOST R 54500.3-2011 taking
into account the parameters that contribute to the uncertainty based on the calculation formula for
calculating the solubility of anthracene (1) and the measurement uncertainty of the specified
parameters.

Initial data:

- object of measurements - anthracene;
- the measured value is the solubility of anthracene at a temperature of 423 K and a pressure of
  10 MPa;
- unit of measurement - molar fractions;
- measurement technique - experimental computing;
- measurement method - weighted by the difference in mass of the source and final substance.

3.1 The mathematical model of measurement

The calculation formula for calculating the solubility of anthracene:

$$y = \frac{m_x}{M_x},$$

where $m_{CO_2}$ – the mass of solvent that was involved in the process; $m_x$ – mass of anthracene; $M_{CO_2}$,
$M_x$ molecular mass CO$_2$ test substance.

Solvent Weight:
\[ m_{CO_2} = V_{CO_2} \cdot \rho_{CO_2}, \]  

where \( V_{CO_2} \) – volume of carbon dioxide that was involved in the process, \( m^3 \); \( \rho_{CO_2} \) – density \( CO_2 \) under n.c, \( g/m^3 \).

### 3.2 Analysis of input variables contributing to uncertainty

#### 3.2.1. Mass of anthracene \( (m_x) \), carbon dioxide \( (m_{CO_2}) \) and volume of carbon dioxide

The indicated parameters contributing to the uncertainty are related to the estimation of uncertainty by type A and type B.

The estimation of standard uncertainty (standard deviation of the mean value) reflects the inaccuracy of the mathematical expectation, which is based on repeated observations (type A estimation).

The mathematical expectation of the above parameters \( (m_x, m_{CO_2}, V_{CO_2}) \) is obtained from many observations under the same conditions and is determined as the arithmetic mean of the observation values:

\[
\bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i
\]

where \( x_i \) is the general expression of the parameters of the extractant masses, carbon masses and carbon volumes in each case, respectively; \( n \) is the number of observations (in our case, \( n = 5 \)).

The sample variance of observations estimates the variance of the probability distribution above the specified parameters and is calculated by the formula:

\[
u^2(x) = \frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2
\]

The sample standard deviation characterizing the scatter of values relative to the mathematical expectation is defined as:

\[
u(x) = \sqrt{\nu^2(x)} = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} (x_i - \bar{x})^2}
\]

The standard deviation of the average value, reflecting the inaccuracy of the determination of mathematical expectation, is determined by the formula:

\[
u(\bar{x}) = \frac{\nu(x)}{\sqrt{n}}
\]

The standard uncertainty estimate is related to the instrument readings (type B) and was estimated based on information about the readability of the following measuring instruments: laboratory balance VLT 150-P with the largest weighing limit of 150 g and readability \( (d) = 0.001 \) g; gas meter SGMB-1,6 with discrete readout \( (d) = 0.001 \) g.

Assuming a rectangular probability distribution of discreteness values within \( \pm d/2 \), and taking into account double weighing (before and after the experiment) for the weights, the standard uncertainty \( \nu(x) \) is calculated by the formula:

\[
u(x) = \sqrt{c \left( \frac{d}{2\sqrt{3}} \right)^2}
\]

where \( c \) is the number of measurements \( (c = 2 \) for the balance, \( c = 1 \) for the gas meter).
3.2.2. Molar mass of anthracene ($M_a$) and carbon dioxide ($M_{CO2}$). The standard uncertainty in the measurements of the molar mass of anthracene $u(M_a)$ and carbon dioxide $u(M_{CO2})$, g/mol (type B estimate), is determined based on the uncertainty of the last digit ($\Delta$) of the atomic mass of carbon, hydrogen and oxygen (taken from the atomic mass tables IUPAC [8]), as well as the number of atoms ($n_C$, $n_H$, $n_O$) of these elements in the molecules of anthracene and carbon dioxide. Assuming a rectangular probability distribution of the atomic masses of the elements, the standard uncertainty in the measurements of the molar mass of anthracene $u(M_a)$ and carbon dioxide $u(M_{CO2})$, g/mol, is determined by the formulas:

$$u(M_a) = \sqrt{\left(\frac{n_C \Delta A}{\sqrt{3}}\right)^2 + \left(\frac{n_H \Delta A}{\sqrt{3}}\right)^2}$$ (8)

$$u(M_{CO2}) = \sqrt{\left(\frac{n_C \Delta A}{\sqrt{3}}\right)^2 + \left(\frac{n_O \Delta A}{\sqrt{3}}\right)^2}$$ (9)

3.3 Correlation analysis
All input quantities are considered uncorrelated.

3.4 Total Standard Uncertainty
The total standard uncertainty of the measurements of the solubility of anthracene is determined in accordance with the law of propagation of uncertainties by summing the relative standard uncertainties of all the influencing quantities included in the measurement functions (1) and (2), according to the formula:

$$u_r(y) = \sqrt{\sum_{i=1}^{N} \left(\frac{\partial y}{\partial x_i} u_r(x_i)\right)^2}$$ (10)

The values of the relative standard uncertainties of the influencing quantities are calculated as the ratio of the standard uncertainty of the influencing quantity to the value of the estimation of the influencing quantity.

3.5 Results of calculation of standard and total standard uncertainty
Table 1 presents the results of the assessment of the standard and total standard uncertainty of measurements of the solubility of anthracene at $T = 423$ K, $P = 10$ MPa.

3.6 Extended uncertainty
The expanded uncertainty $U(y)$ of the measurements of the solubility of anthracene in pure supercritical carbon dioxide is the product of the total standard uncertainty $u_r(y)$ by the coverage coefficient $k$, which is assumed to be two at a confidence level of approximately 95% under the assumption of a normal probability distribution of the measured quantity:

$$U_p(y) = u_r k = 0.0000033 \cdot 2 = 0.0000066 \text{ mol.frac.}$$ (11)

3.7 Measurement result
The solubility of anthracene at $T = 423$ K, $P = 10$ MPa, in mole fractions, in pure supercritical carbon dioxide is $y = 0.0000804 \pm 0.0000066$ mol.frac.
**Table 1.** Evaluation results of the standard and total standard uncertainty of anthracene solubility measurements at \( T = 423 \text{ K} \), \( P = 10 \text{ MPa} \).

| Value, \( x_i \) | Unit | Valuation Values | Standard uncertainty | Total Standard Uncertainty |
|-----------------|------|------------------|----------------------|---------------------------|
| \( m_a \) | g | 0.026 | 0.000711805 | 0.027 |
| | | 0.028 | 0.000711805 | 0.025 |
| | | 86.12 | 0.000711805 | 80.0 |
| \( m_{CO_2} \) | g | 0.0405 | 1.789453548 | 0.83 |
| | | 0.0436 | 0.769 | 86.12 |
| | | 0.0405 | 0.0436 | 0.0420 |
| | | 0.0405 | 0.0389 | 0.0436 |
| \( V_{CO_2} \) | m³ | 0.00950491 | 0.0420 | 0.0405 |
| | | 0.00950491 | 0.0436 | 0.0389 |
| \( M_a \) | g/mol | 0.00557735 | 178.01 | 0.0000804 |
| \( M_{CO_2} \) | g/mol | 0.00647894 | 44.01 | 0.0000804 |
| \( \rho_{CO_2} \) | g/m³ | 0.01008163 | 1976 | 0.0000804 |
| \( y \) | mol.frac. | 0.0000330 | 0.0000804 |

The SCFE process was supported at specified parameters by pressure and temperature control and measuring devices. The temperature was measured using a chromel-copel thermocouple with an error of \( \Delta T = \pm 0.02 \text{ K} \). The pressure was measured using an exemplary pressure gauge in the range of 0-60 MPa with an accuracy class of 0.15. The absolute error of the pressure readings was \( \Delta P = 0.0015 \times 60 = 0.09 \text{ MPa} \).

The standard uncertainty of measurements of temperature \( u_c(T) \) and pressure \( u_c(P) \), g. was estimated on the basis of information on the limits of the permissible error \( \Delta T \) and \( \Delta P \), and the discreteness of the readout of the device \( d = 0.1 \text{ K} \) (MPa) established in the technical documentation. Assuming a rectangular probability distribution of the values of the error and discreteness the standard uncertainty is calculated by the formula:

\[
\begin{align*}
  u_c(T(P)) &= \sqrt{\left(\frac{\Delta T}{\sqrt{3}}\right)^2 + \left(\frac{d}{2\sqrt{3}}\right)^2} \\
  &\quad (12)
\end{align*}
\]

The expanded measurement uncertainty of the temperature and pressure parameters \( U_r(T(P)) \) is the product of the total standard uncertainty \( u_c(T(P)) \) by the coverage coefficient \( k \) which is assumed to be two at a confidence level of approximately 95% under the assumption of a normal probability distribution measured value:

- for temperature \( U_r(T) = u_c k = 0.03109 \times 2 = 0.0623 \text{ K} \);
• for pressure $U_p(T) = u_k = 0.05944 \cdot 2 = 0.1189K$.

4. Conclusion
An improved device is described that allows the measurement of the solubility of substances using supercritical fluids. Verification measurements of the solubility of anthracene in supercritical carbon dioxide are in good agreement with published data which confirms the reliability of the results. The value of the confidence level for the results of measuring the solubility of anthracene, calculated through the extended uncertainty, is within the acceptable error values.

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