Thermophysical properties of the mixture of anthracene with supercritical propane-butane

Z I Zaripov, R R Nakipov, A R Gabitova, V F Khairutdinov and F M Gumerov
Kazan National Research Technological University, 68 Karla Marksa street, Kazan, 420015, Russia

E-mail: nakip88@yandex.ru

Abstract. The heat capacity at a constant pressure of the anthracene – supercritical propane-butane system was measured in the temperature range 343–473 K and pressures up to 19.6 MPa. The studies were carried out on the experimental setup that implements the method of scanning calorimetry. The combined expanded uncertainty of heat capacity measurements at a confidence level of 95% with a coverage factor of k = 2 is estimated at 2.8%. The results of measuring the heat capacity at a constant pressure of the mixture were used to calculate the enthalpy of the mixture.

1. Introduction
The current trend in the oil refining industry is the use of heavy oils. Due to the higher content of heteroatoms, asphaltenes and metals, as well as a larger number of non-separated hydrocarbons, it is more difficult to process heavy oils using traditional methods [1-3]. The solution to this problem is the introduction of a wide range of modern mining and processing technologies such as thermal steam [1-2], cold mining [3], using solvents and catalysts [4-7]. One of the promising, environmentally friendly methods for the extraction and processing of high viscosity oils and natural bitumen today is the use of supercritical fluid (SCF) technologies [8-10]. The main disadvantage of supercritical fluid technology is insufficient data on the thermophysical properties (specific heat, heat of dissolution, solubility) of the components used in the above-described processes in supercritical fluids. For the development and optimization of oil refining technological processes, knowledge of the phase behavior, thermal properties (density, viscosity and thermal conductivity) of both the oils themselves, the components of the fractions, and their mixtures with solvents is necessary. High viscosity oils are a dispersed medium in which asphaltenes are dispersed into hydrocarbons with a lower molecular weight. All this unstable dispersed medium is stabilized by polycyclic aromatic compounds and resins forming a solvate shell [11]. Under the influence of various factors (temperature, pressure), the medium undergoes various phase transformations (precipitation, dissolution) [12-14], which are accompanied by processes of heat generation or absorption.

A lot of research is being done in this direction; these are works on phase equilibria [17-18], compositions and properties [19-21]. Of particular interest are the thermal effects that accompany this process. Excessive thermodynamic functions, in particular the enthalpy of dissolution (mixing), can be obtained from data on heat capacity, phase equilibria [22-24] or calculated from equations of state [25, 26].

The main objectives of this study are obtaining new data and updating the existing database on the
thermodynamic properties of the anthracene-supercritical propane-butane system with the parameters of the process of oil extraction from oil sludge from deposits of the Republic of Tatarstan by supercritical propane-butane [27-29], first implemented by the authors. Anthracene - one of the polycyclic aromatic hydrocarbons that is part of oil sludge [11].

The components of this system (anthracene and propane-butane) were studied in detail in [30–46]. Measurements of mixing enthalpy are mainly concentrated on gas-liquid systems, SCF-liquid, such as \( \text{CO}_2\)-\( \text{H}_2\text{O} \) [47], \( \text{H}_2\text{S}-\text{H}_2\text{O} \) [18], \( \text{CO}_2 \) - aqueous solutions of methyl-diethanolamines [49]. Experimental studies of the enthalpy of dissolution in a gas – solid system are presented in [50–51], which presents the results of measuring the enthalpy of dissolution of caffeine, anthracene in supercritical carbon dioxide. For the system of interest, anthracene - supercritical propane-butane, there are no data on thermophysical properties, including the heat of dissolution.

### 2. Experimental part

Propane + butane gas mixture with a composition of 45.8 wt.% propane and 54.2 wt.% butane was provided by UralOrgSintez LLC (No. GOST 20448-90). Anthracene sample (CAS # Anthracene 120-12-7) provided by Acros Organics. The purity of anthracene was 99%. No further purification was undertaken. Table 1 lists the commercial sources, purity, water content and analysis method of the samples used.

| Chemical name | No. CAS | Water content (wt.%) | Purity (mac.%) | Commercial sources |
|---------------|---------|---------------------|---------------|-------------------|
| Anthracene    | 120-12-7 | ≤ 0,005%           | ≥ 99,0(GC)    | «Acros Organics»   |
| (propane) +54.2 wt. % (n-butane) | | | | OOO «UralOrgSynthesis» |

*aUncertainty in the concentration of the propane + butane mixture is 0.99% (propane) and 0.77% (n-butane).

Table 2 shows the recommended critical parameters of anthracene and propane-butane mixture.

| Chemical name | \( P_{cr} \) MPa | \( T_{cr} \), K | \( \omega \) | \( T_{mp} \) | \( T_{bp} \) |
|---------------|------------------|----------------|-----------------|--------------|---------------|
| Anthracene    | 3.17±0.10 [46]   | 894±9. [46]    | 0.402[46]       | 490.6[44]    | 613.9[44]     |
| 45.8 wt.% (propane) +54.2 wt. % (n-butane) | 4.3[41-43] | 394.25 [41-43] | | | |

The heat capacity of the anthracene – supercritical propane-butane system was measured on an experimental setup (figure. 1), created on the basis of a scanning (ITS-400) [52,53] calorimeter, with an computer-assisted acquisition system. The ranges of research parameters with a scanning calorimeter are shown in table 3.

| Name | Temperature range, T, K | Pressure range, \( P \), MPa |
|------|-------------------------|-----------------------------|
| Anthracene-supercritical propane-butane system | 343,15÷473,15 | 4,9÷19,6 |
Figure 1. Experimental setup flow sheet: 1 - measuring cell; 2 - heat capacity meter IT-s-400; 3 - dead-weight pressure-gauge tester; 4 - separation bellows assembly; 5 - vacuum pump; 6 - liquid pump; 7 - vessel with the test substance; 8 - analog-to-digital converter; 9 - personal computer.

The calculation formula of the method has the form:

\[
C_p(t) = \frac{C_p''(t)}{\rho} \cdot \frac{\tau_i(t) - \tau''_i(t)}{\tau_i(t) - \tau''_i(t)}.
\]  

where \(C_p(P, T)\), \(C_p''(P, T)\) – heat capacity at constant pressure of the test sample and the reference sample at the corresponding pressure \(P\) and temperature \(T\), J\(\cdot\)kg\(^{-1}\)\(\cdot\)K\(^{-1}\); \(m\) и \(m''\) are the masses of the test sample and the reference substance, kg; \(\tau_i\) и \(\tau''_i\) are the delay times of measuring thermocouples, respectively, for the test and reference samples, sec; \(\tau_0\) is the delay time of the measuring thermocouples of the empty measuring cell, sec.

The results of control measurements of the heat capacity of stearic acid (Chemically pure), anthracene at atmospheric pressure [51] and the heat capacity of n-butyl alcohol (\(n_{D20} = 1.3995\), \(\rho_{m25} = 809.5\) kg\(\cdot\)m\(^{-3}\)) at pressures of up to 30 MPa and comparisons with literature data showed deviations within the total measurement errors. Deviations in \(C_p\) of stearic acid to the melting temperature from the data [54] do not exceed 1-2%, and for n-butyl alcohol they do not exceed 2-3% from [54, 55]. The heat of the first-order phase transition from crystal to liquid, determined on the basis of the obtained heat capacity of stearic acid and anthracene, was 61.6 kJ\(\cdot\)mol\(^{-1}\)\(\cdot\)K\(^{-1}\) and 28.81 kJ\(\cdot\)mol\(^{-1}\)\(\cdot\)K\(^{-1}\), respectively. Deviations from the literature data for stearic acid are not more than 0.7%, for anthracene from [40] they do not exceed 2.1%.

The confidence intervals of the total measurement uncertainty (\(P = 0.95\)) of the specific heat do not exceed \(\pm 2.8\%\).

3. Results and discussion
The specific heat of anthracene in supercritical propane-butane was measured as a function of temperature and pressure in the range 343–473 K and pressures 4.9–19.6 MPa. The measured heat capacity values obtained in the work are shown in figure 2. Some selected experimental results for the specific heat for this system are shown in figure 2 and 3 depending on \(C_p\) from P and \(C_p\) from T.
Figure 2. The heat capacity at a constant pressure of the anthracene–supercritical propane-butane system as a function of pressure at various temperatures: 1 - T = 343.15 K; 2 - T = 363.15 K; 3 - T = 383.15 K; 4 - T = 393.15 K; 5 - T = 403.15 K; 6 - T = 423.15 K; 7 - T = 443.15 K; 8 - T = 473.15 K.

As can be seen from figure 2, the behavior of low isothermal curves depending on pressure is almost linear, while high isothermal curves are characterized by greater curvature, that is, they exhibit large deviations from linearity. The largest changes in the derivative are in the pressure of 4.9 MPa and temperature T = 393.15 K. With an increase in pressure above 9.8 MPa, the value of the derivative assumes an almost constant value. In the temperature range 343.15–393.15 K and pressures 4.9–7.84 MPa, the derivative increases, and then the sign changes with increasing temperature after 393.15 K. In addition, as can be seen from figure 3, at isobaric curve below 10 MPa, the temperature behavior of the Cp-T curves has a large curvature, and high isobaric curves above 10 MPa are almost linear. The maximum heat capacity falls on the parameters close to the critical parameters of the propane-butane mixture (table 2): P = 4.9 MPa and T = 393.15 K. In figure 3 for comparison, the temperature dependence of the specific heat of anthracene at atmospheric pressure is shown together with the data presented. The temperature dependence of the heat capacity of the anthracene–supercritical propane-butane system is identical to the propane-butane mixture. As an example, figure 4 shows the temperature dependences of the systems anthracene-supercritical propane-butane and propane-butane (figure 4).

As can be seen from this figure 4, with increasing temperature after reaching the maximum heat capacity, the derivative changes sign and after 430K the value of the derivative tends to zero. The temperature dependence of the heat capacity at higher isobaric curves is less pronounced (figure 3).
Figure 4. Heat capacity at constant pressure of the anthracene–supercritical propane-butane system as a function of temperature at a pressure of $P = 4.9$ MPa: 1-anthracene–supercritical propane-butane; 2-propane–butane.

Figure 5. The excess heat capacity at constant pressure of the anthracene–supercritical propane-butane system as a function of temperature at various pressures: 1-$P = 4.9$ MPa; 2-$P = 9.8$ MPa; 3-$P = 14.7$ MPa; 4-$P = 19.6$ MPa.

Figure 6. The enthalpy of the anthracene–supercritical propane-butane system as a function of temperature at various pressures: 1-$P = 4.9$ MPa; 2-$P = 9.8$ MPa; 3-$P = 14.7$ MPa; 4-$P = 19.6$ MPa.

Excessive thermodynamic properties $c_p^E$ and $\Delta H^E$ of the anthracene–supercritical propane-butane systems were obtained by calculation from the data on the heat capacity of the mixture.

To calculate the excess heat capacity of the binary system, the following formula was used:

$$c_p^E = C_p - \left( C_{antr} N_{antr} + C_{gas} N_{gas} \right)$$  \hspace{1cm} (2)

where $c_p^E$ - excess heat capacity of a mixture of anthracene and propane butane, $J\cdot mol^{-1}\cdot K^{-1}$; $C_p$ – heat capacity of the mixture, $J\cdot mol^{-1}\cdot K^{-1}$; $C_{antr}$ и $C_{gas}$ – heat capacity of anthracene and supercritical butane propane mixture, $J\cdot mol^{-1}\cdot K^{-1}$; $N_{antr}$ и $N_{gas}$ molar concentrations of anthracene and propane butane in a mixture. The values of $C_{antr}$ are taken from [38,40,51], and the heat capacity of the propane-butane mixture from [45].

The excess enthalpy of the anthracene - propane butane system is obtained from the equation:

$$\partial H^E = c_p^E \cdot \partial T$$  \hspace{1cm} (3)
where \( c_p^E \) - excess heat capacity of a mixture of anthracene and propane butane, J\cdot mol\(^{-1}\)\cdot K\(^{-1}\); \( H^E \) - excess enthalpy of a mixture of anthracene and propane butane, J\cdot mol\(^{-1}\).

The largest changes in the excess heat capacity of the mixture (figure 5) were noted for an isobaric curve of 4.9 MPa. In the temperature range 343-393K, there is a sharp increase of \( c_p^E \) from a negative value of -125 J\cdot mol\(^{-1}\)\cdot K\(^{-1}\) to +175 J\cdot mol\(^{-1}\)\cdot K\(^{-1}\). The greatest thermal effect (figure 6) occurs in the temperature range 383-403 K and a pressure of 4.9 MPa.

4. Conclusion
The studies of a mixture of anthracene and propane-butane in the temperature range 343.15 ÷ 473.15 K and pressures from 4.9 MPa to 19.6 MPa found that the extreme change in the heat capacity of the mixture only on the isobaric curve 4.9 MPa at a temperature of 393 K, close to the critical parameters of propane-butane mixture. The results of measurements and calculations showed the absence of an abnormal change in properties \( (c_p, c_p^E) \) on other isobaric curves in the entire temperature range studied. A negative thermal effect was obtained in the range of parameters \((T = 403 ÷ 443 K \text{ and pressures } P = 10 ÷ 20 MPa)\) for the extraction of hydrocarbons from oil sludge by supercritical propane-butane [27–29].

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