Generalization of solubility of aromatic substances in supercritical fluid media with the use of entropy method of similarity theory

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Abstract. The results of generalization of the solubility of aromatic hydrocarbons in supercritical carbon dioxide using the entropy method of similarity theory are presented. The subject of generalization was the experimental data of various authors on the solubility of 11 substances studied in the temperature range from 300 to 350 K (total 823 experimental points and 57 isotherms).

1. Introduction

Critical phenomena attract constant interest [1–3], but there are not yet fully investigated, and today new supercritical fluid (SCF) technologies succeed to their commercialization [4–6].

The extent and nature of the change in solubility of substances in SCF media, and in particular the abnormal nature of differential solubility variation, largely determine the feasibility, benefits and viability of the key processes of SCF technologies.

The main source of information on the solubility of substances in SCF media is still a time-consuming experiment in terms of methods, techniques and approaches [7]. At the same time, different researchers are developing mathematical models [8–15], designed not only to generalize the large amount of experimental data available to date, but also to predict the solubility of various substances with minimal involvement of experimental data. These models, in turn, can be in principle divided into two types.

The first type of model is based on various equations of state of real gas, such as the Peng–Robinson, Soave–Redlich–Kwong, van der Waals equations, and others [8–11]. The experience of the authors in calculations with the use of one of these models [16,17] shows that to obtain a correct description of solubility, a significant and not always available amount of experimental data is needed.

The second type includes empirical models [12–15], linking the solubility of a substance in a supercritical fluid solvent with the density of the fluid. These models represent equations in which the constants are determined on the basis of experimental solubility data and are highly exclusive. Furthermore, they do not provide qualitative information on the interaction of the soluble substance in solvent and are almost incapable of correctly predicting the behavior of the solubility.
The advantage of the models of the first group is their versatility and the ability to perform solubility calculations with known binary interaction parameters with high accuracy. However, if there is a need to generalize experimental data on solubility, especially for different substances, even if they belong to the same class, these models have to carry out a large amount of complex calculations. At the same time, the entropy method of similarity theory developed by A.G. Usmanov and presented in [18] copes well with the problem of generalization. However, the generalization is always a kind of averaging line that does not always adequately take into account the individual characteristics of the generalized experimental data. In this regard, the task of this work is to develop a generalized model of solubility description based on the entropy method of similarity theory.

2. Theoretical basis

The initial prerequisites for the development of the entropy method of the similarity theory were the need to generalize the experimental data on the thermal conductivity, viscosity, and diffusion of various substances [18].

The analysis of the similarity conditions for any process consists in clarifying the requirements for the invariance of the equations describing this process with respect to similar transformation of variables. Speaking of transfer processes, here the Fourier, Newton and Fick equations are not suitable for solving such a problem, since the form of the functions $\lambda = \lambda(t,p)$, $\eta = \eta(t,p)$ and $D = D(t,p,c)$ is not known in the general case. This circumstance makes us to look for other ways to analyze the similarity conditions of the transport processes, which will be considered below.

Transfer processes are states of nonequilibrium, therefore, in order to describe the state of the system in which these processes occur, we proposed to divide it into a number of macroscopic subsystems [18]. When the parameter gradients are not too large, the state of each such subsystem at any time can be characterized by a specific value of the state parameters $P$, $T$, $S$, etc.

At the same time, if the subsystem under consideration changes, its phase point moves, describing a certain trajectory. If the subsystem is part of a system in thermodynamic equilibrium, the trajectory of the phase point lies in a thin layer near the surface of the constant energy. In the case when the subsystem is part of a non-equilibrium system, the phase trajectory does not remain within this layer. This does not allow to write the equation of motion of the phase point in explicit form. However, since its movement occurs in a certain changing field of the probability distribution density, it is natural to assume that the relative velocity of the phase point is determined by the following dependence:

$$U_{Ps} = \varphi(\text{grad} \rho).$$ \hspace{1cm} (1)

where $\rho$ – is the probability density distribution.

Obviously, the dependence (1) applies equally to all molecular processes, since the authors of [18] have, in this respect, impose no restrictions.

The average relative velocity of the motion of the phase point, or, equivalently, the average relative velocity of the molecular process, will be:

$$\bar{U}_{rel} = \Phi \left( \frac{\Delta \rho}{l} \right) = \Phi \left( \frac{\rho_2 - \rho_1}{l} \right) = \Phi \left[ \frac{\rho_1}{l} \left( \frac{\rho_2 - \rho_1}{\rho_1} - 1 \right) \right].$$ \hspace{1cm} (2)

Or in other form,

$$\bar{U}_{rel} = \varphi \left( \frac{S_1 - S_2}{R} \right),$$ \hspace{1cm} (3)

where $S_1$, $S_2$ – molar entropy, J/(mol·K) in the temperature range from $T_0 = 273.15$ K to $T_1$ and $T_2$ respectfully, $R$ – universal gas constant, J/(mol·K).
Table 1. Initial systems [19].

| No. | Substance name   | System temperature range, K | Number of experimental points |
|-----|------------------|-------------------------------|-------------------------------|
| 1   | Fluoranthene     | 308 – 348                    | 45                            |
| 2   | Phenanthrene     | 308 – 333                    | 113                           |
| 3   | Pyrene           | 313 – 333                    | 93                            |
| 4   | Triphenylene     | 308 – 348                    | 44                            |
| 5   | Triphenylmethane | 308 – 328                    | 86                            |
| 6   | Naphthalene      | 308 – 318                    | 90                            |
| 7   | Acenaphthene     | 308 – 348                    | 45                            |
| 8   | Perylene         | 323 – 333                    | 19                            |
| 9   | Anthracene       | 308 – 333                    | 109                           |
| 10  | Biphenyl         | 308 – 328                    | 31                            |
| 11  | Fluorene         | 308 – 343                    | 148                           |

The latter is taken as a basis for the generalization of experimental data on molecular transport. In this equation, the speed $U_{rel}$ retains its previous meaning and on example of the different special cases of the transfer effect should be treated as relations heat flux $q/q_{∆S}$, flux of momentum $η/η_{∆S}ΔS$ and diffusion flux $ω/ω_{∆S}$. Generalizations of these values obtained on the basis of equation (3) are presented in [18].

3. Methodology
When choosing experimental systems, on the basis of which it was planned to generalize solubility, we focused on the work [13], also devoted to the description and generalization of solubility of aromatic compounds. The solubility data for the substances we selected were taken from the book [19]. Thus, at the initial stage of work, 11 substances were included in the calculations. For these substances, solubility data were found on 57 isotherms studied by different authors, representing a total of 823 experimental points presented in table 1. In graphical form, these isotherms are shown in figure 1. The graph shows that the spread of generalized data is 4 orders of magnitude – the minimum values are about $10^{-6}$, and the maximum – $10^{-2}$ mole fractions.

In the case of solubility, the authors of [20] proposed equation to generalize the experimental data on the solubility of mono-, di- and triethylene glycol in supercritical carbon dioxide, that we modified to extend its range of its application. It finally took the following form:

$$\ln \left( \frac{y_{∆μ}}{y_{∆S}∆μ_{∆S}} \cdot \frac{ρr}{T_r} \right) = ϕ_i \left( \frac{S_1 - S_2}{R} \right),$$  \hspace{1cm} (4)

where $y$ – solubility of the substance in the fluid; $∆μ$ – is the chemical potential of a supercritical fluid in the temperature range from $T_0 = 273.15$ K to experimental temperature $T_{exp}$, J/mol, acts as the driving force of the dissolution process; $y_{∆S}∆μ_{∆S}$ – scale factor; $T_r = \frac{T}{T_{cr}}$ – the ratio of the system temperature to the critical temperature of the solute; $ρr = ρ_i/ρ_{cr}$ – the ratio of the carbon dioxide density at the parameters $i^{th}$ the experimental point to the CO$_2$ density in the critical point.

One of the difficulties in the development of the model was that in order to determine the scale factor of $y_{∆S}∆μ_{∆S}$, it is necessary for each system to have experimental points in which the entropies $S_1$ and $S_2$ have the same value. In the absence of such data, the authors of the
method in [21] proposed to determine the scale factor by the equation, which for the developed model will take the following form:

$$y_k S \Delta \mu = \frac{y_k \Delta \mu_k}{S_1 - S_k},$$

where $y_k$ is the solubility value of the substance under study at the extreme point on the generalized system isotherm, mole fraction; $\Delta \mu_k$ is the chemical potential of the supercritical fluid at the parameters of the last point of the generalized system, J/mol; $S_k$ is the entropy of a pure supercritical fluid under the parameters of the last point of the generalized system, J/(mol·K).

As in [20], the chemical potential and entropy of pure carbon dioxide at the parameters of generalized systems were determined from the Altunin equation of state [22]. Since most of the generalized isotherms are in the range of 308–348 K, the initial entropy value $S_1 = 154.0385$ J/(mol·K), which is included in the entropy range of these systems. The scale flow was determined according to the equation (5).

Figure 2 shows the results of the final generalization of the solubility of aromatic compounds in supercritical carbon dioxide. The calculations allowed us to derive the following functional from the generalized dependence between $y \Delta \mu \rho r / T r y \Delta S \Delta \mu S$ and $(S_1 - S_2)/R$:

$$f(x) = 0.0141 x^6 - 0.0103 x^4 - 0.036 x^3 - 0.0529 x^2 + 1.8479 x + 2.1467,$$

where $x = (S_1 - S_2)/R$, and $f(x) = \ln \left( \frac{y \Delta \mu S \Delta \mu S \cdot \rho r}{y \Delta S} \right)$.

We see in figure 2, that with rare exception, all points with a relatively small error are described by the equation (6), which corresponds to the error of experiments of these systems. The inverse calculation of solubility in accordance with the equation (6) gives the standard deviation of the experimental data from the calculated values of 12.69%.
Figure 2. Results of final generalization of solubility of the systems under study. 1 – experimental data, 2 – correlation.

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