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Highly efficient supercritical fluid extraction process: solubility and pseudosolubility

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The results of an experimental study on the solubility of acetone in carbon dioxide are presented. The study was conducted along the critical isopleth with a critical concentration of the binary mixture components beyond the binodal curve using a dynamic measurement method. The pressure ranges in which the solubility exhibits regular behavior in one case and singular behavior in another have been identified. For the first time, in the asymptotic vicinity of the critical point as it is approached, the fact of an anomalous increase in solubility has been established. The prerequisites and conditions for the swelling of the component intended for extraction, which formed the basis for new concepts about the mechanism of supercritical fluid extractive separation as applied to type I–II phase behavior systems, are discussed. For the first time, an explanation of the concept of pseudosolubility is provided. According to this concept, the designated characteristic simultaneously combines, on one hand, the indicators of the target component's extraction into the extractant phase within the traditional understanding of solubility, and on the other hand, the possibility of transferring macroscopic volumes of the extractable component to the separator. This transfer is caused by its swelling in the extractor due to the dissolution of the supercritical fluid solvent into it. Experimental data on the pseudo-solubility of acetone in carbon dioxide at supercritical isobars are presented. At pressures near its critical value, the pseudosolubility significantly exceeds the values of the equilibrium solubility by multiple times.

Keywords: extraction, supercritical fluid state, type of phase behavior, regime of complete miscibility, solubility, pseudosolubility.

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Introduction

In the 1980s, the number of laboratory, pilot and commercial applications of the supercritical fluid extraction process was evaluated as near 80 % of the total cases compared with all other supercritical fluid (SCF) techniques (SCF drying, SCF dispersion and impregnation, chemical reactions in SCF and, finally, SCF chromatography). The situation hasn't changed significantly since that time. However, the long-standing stable interest in the SCF extraction (SCFE) process hasn't turned into a level of understanding that could be estimated as adequately full.

The available knowledge regarding the solubility of SCF-extracted substances in physically and chemically different extractants being the key attribute of the efficiency of the SCFE process of interest is mainly represented in the form of tabular data. In this case, focus can be made on a handbook of solubility in supercritical carbon dioxide SC CO_2) [1] that is probably the best one in terms of the quality of provided experimental data, data systematization and structuring, coverage of sources of information and scope of information. Moreover, note that more than 99 % of the handbook content is devoted to Type V–VII phase behavior binary solute — solvent systems according to Konynenburg's [2] and Williams' [3] classification. Less than 1 % falls on solubility data calculated using the liquid branch of the binodal for Type I–II phase behavior systems that by default correspond to a binary mixture's subcritical state. Type V phase behavior is characterized by the liquid-phase state of solute and the discontinuous critical curve of the binary mixture, while Type VI and VII phase behaviors refer to systems with a solid-state solute. For Type V–VII phase behavior systems, investigations of solubility in supercritical carbon dioxide in vast majority of cases use a dynamic method widely described in the literature, including, for example, [4]. The scheme of dynamic method for measuring solubility in SCF solvents is completely identical to the SCF extraction process concept.

In those 1980s (1985), a well-grounded representation was patented [5] where the SCFE process for a solute's liquid-phase state is only feasible for systems with a continuous critical curve (TypeI–II phase behaviors), whereas for binary systems, whose critical lines are discontinuous (Type V phase behavior), the subcritical fluid (SbCF) extraction process is recommended. It was found, in particular, that in this case an additional liquid-vapor equilibrium region may occur on the phase diagram near the critical temperature of a pure solvent. Capabilities of this region may be used to reduce considerably the operating pressure during extraction, energy and materials consumption of process equipment. According to the authors of patent [5], efficiency of extraction in the SbCF state region is not lower compared with the SCFE process for Type V phase behavior systems.

It means that a thermodynamic basis of the SCF extraction process for Type V phase behavior systems is available in the form of the solubility data and handbook, but the process itself turns out to be not very cost-efficient. Then, as for the high-demand SCF extraction process as applicable to Type I–II phase behavior systems (high-efficiency SCFE process), there is no any knowledge of solubility at all. This is, frankly, an incredible situation, but it does exist.

Determination of the flow rate variation range for a solvent going through a measuring cell is one of the key preliminary procedures employed to implement the dynamic method for measuring solubility in SCF solvents, where the concentration variations of a substance dissolved in a solvent evaluated for the same pressures and temperatures are within the limits defined by the absolute solubility measurement error (conditional plateau).

The magnitude of the solubility of interest is defined by intermolecular interactions applicable to the corresponding physical and chemical nature of the solute and solvent, and by thermodynamic conditions of the dissolution process. It can be easily assumed that in the extreme case true values of the solvent's dissolving power and desired solubility will be properly determined only when there are the largest possible phase contact area for two participants of the process and the resulting solvent saturation with the solute. For example, supply of the SCF solvent into the measuring cell, that is filled with the solute to any extent, only via a single hole in the bottom leads to the highly probable presence of „dead" (noncontact) zones for binary mixture components and to an absolutely conservative value of solubility. Whilst a fine mesh in the bottom of the same measuring cell and small-sized glass balls within the solute provide a larger phase contact area bringing the system much closer to the thermodynamic equilibrium state and providing a more correct solubility measurement. But a more effective alternative still exists.

And before we start discussing this alternative, mention should be made of some familiar definitions. It is understood that miscibility and solubility are not synonyms. Miscible substances are referred to as two components that may mix with each other in any proportion without forming two separate phases. Whilst selected proportions define partial miscibility. When components separate to form a phase interface, then this refers to immiscible substances. When passing from Type I phase behavior to Type VII for binary systems according to Konynenburg's [2] and Williams' [3] classification, miscibility of components steadily decreases. Solubility, for example, of component A is defined as a capability to form real solutions in solvent B up to a particular concentration.

The SCF region of Type I–II binary system (outside the binodal with critical component ratio in the mixture), that is often referred to as an infinite miscibility region, has no phase interface. But the fact is that in this case, when the system passes from the liquid-vapor two-phase equilibrium region to the single-phase supercritical fluid state region, a perfect method for mixing components, that is notionally called a „thermodynamic" method by the authors of this work, occurs naturally and acts to provide the above-mentioned largest possible phase contact area. Is it right in this case to rely only on the SCF extraction process capabilities for Type V phase behavior systems, when it is possible to perform the process in the infinite miscibility region only through a variation of the extractant's physical and chemical nature together with the type of system phase behavior to get in return a many-fold higher efficiency of that very extraction process. For example, for disposal of highly hydrocarbon-loaded molybdenum-containing aqueous runoff [6] and wooden railway sleepers [7], this transition made it possible to increase the SCFE process efficiency by a factor of ~ 8 and ~ 4, respectively. Displacement agent extractivity with respect to extremely high viscosity index oil produced by the tertiary recovery method at the Ashalchinskoye field under the same assumptions increased $\sim$ 10-fold [8]. Gels made from aqueous solutions by traditional evaporation that are widely used commercially have extremely low quality. SCF drying process involving CO_2 comes across limited mutual solubility and miscibility of carbon dioxide and water (Type V phase behavior). But step-by-step water substitution to complete substitution, for example, by ethanol or acetone and the high-eficiency SC CO_2 extraction process (CO_2-ethanol and CO_2-acetone exhibit Type I–II phase behaviors) provide commercial-scale production of high quality aerogels [9,10].

But one have to find out whether it is only the infinite miscibility that causes the above-mentioned many-fold increases in the SCF extraction process efficiency when passing to Type I–II phase behavior systems. Key questions of solubility in the infinite miscibility region and SCF extraction mechanism applicable to Type I–II phase behavior systems have been only raised and remain to be solved.

The authors will focus on at least two features or physical signs that distinguish significantly Type I–II and V phase behavior binary systems. The first case deals with clustering as a whole represented by solvation complexes in a regular behavior region and by density fluctuations in asymptotic proximity to critical points (singular behavior region) of Type I–II phase behavior binary systems. The latter simply don't occur for Type V systems due to the absence of critical points on the phase equilibrium diagram. The second physical manifestation that has a different, but also significant effect on solubility study results and SCFE process efficiency indicators, is in considerable differences in the presence of a highly volatile component on the liquid branches of phases equilibrium diagrams of Type I–II and V phase behavior binary systems.

The foregoing arguments initiate deep understanding, search for and formation of other concepts of the origin of the driving force behind the high-efficiency SCF extraction process (for TypeI–II phase behavior systems) that was first called pseudo solubility in [6]. Numerical values of pseudo solubility have been never an object of study, but the facts of many-fold increase in the SCF extraction process efficiency implemented outside the binodal are most suggestive and make the problem of pseudo solubility extremely important. It is this problem that has been elevated to the target priority by the authors of this work:

1. Theoretical analysis

1.1. Second-order phase transitions

Phase transition in the critical liquid-vapor equilibrium point is classified as second-order phase transitions due to the absence of jumps of first-order derivatives of the thermodynamic potential (specific volume and specific entropy) and, consequently, of phase transition heat, but to the presence of jumps of second-order derivatives of the same thermodynamic potential (isobaric heat capacity, isothermal compressibility, thermal expansion coefficient). Critical mixing point of a two-component solution is also classified as second-order phase transitions. Second-order phase transitions further include a very wide range of phase transitions that look unlike at first sight, in particular: Curie point of ferromagnetic and ferroelectric materials, Neel point of antiferromagnetic materials, liquid helium transition to superfluid state, superconductivity of some metals and alloys in certain temperature conditions, alloy ordering and, finally, sudden change of crystal symmetry combining simultaneously the signs of the first-order and second-order phase transitions [11].

1.2. Density fluctuations

Anomalous light scattering (critical opalescence near critical liquid-vapor equilibrium points of a pure substance, on the one hand, and binary solution mixing points, on the other hand) and neutron scattering near the Curie point of ferromagnetic materials were detected experimentally in some systems within the above-mentioned phase transitions and quite long ago [12–14]. This is the evidence that there are order parameter or density fluctuations, for example, in a near-critical state fluid, and the size of these fluctuations grows when approaching the critical point. In M.A.Anisimov's figurative words [15], substance in this state is similar to a „gas of droplets". Anomalous growth exceeding the above-mentioned density fluctuations and enhancement of interaction between the fluctuations when approaching the critical point from higher temperatures $(T > T_c)$ is predetermined by the prospect of disordered phase transformation into the ordered phase when passing to the subcritical $(T < T_c)$ two-phase equilibrium region. Disordered and ordered phases near the critical point are little different [11]. On the approach to the critical point, correlation radius of density fluctuations grows without limits and in fact defines the size of those „doplets", and, in a strong fluctuation region, exceeds any dimensions characterizing interparticle forces in a substance. For example, study [16] devoted to determination of the isothermal compressibility γ and correlation length r_c of CO_2 in asymptotic proximity to the critical point $(0.023\,\mathrm{K} < T - T_c < 10.0\,\mathrm{K})$ as part of light and X-ray radiation scattering experiments provided the findings, according to which the correlation length on the critical isochor for boundaries above the given temperature range is 60.94 nm and 1.303 nm, respectively, with a direct molecular interaction radius of just 0.15 nm. It would appear reasonable in this case that it is the fluctuation ensemble behavior, rather than the interatomic interaction pattern, that defines the desired system properties and characteristics [11].

1.3. Second-order phase transition isomorphism

Comprehensiveness of critical fluctuations, equivalence of some simple models describing different phase transitions suggest more generally that they are isomorphic [17]. In particular, second-order phase transitions may be classified as isomorphic, if thermodynamic potentials of various systems with properly chosen (isomorphic) variables have the same functional relation to the temperature and order parameter [15].

1.4. Solvation complexes or clusters and solubility in SCF media

In the search for a molecular mechanism applicable to mixtures in a supercritical fluid state, there is a hypothesis of solvent molecule accumulation around solute molecules with formation of so-called solvation complexes or clusters. Numerous experimental and theoretical studies, including [18–26], provided convincing proof of their existence. In this context, it is logical to assume that an increase in solvation level strongly pronounced in immediate proximity to the critical point (large-scale density fluctuations) will define a higher dissolving power of the supercritical fluid solvent/extractant and, consequently, a higher efficiency, for example, of the SCF extraction process or Type I–II phase behavior systems.

Adhering to the principle of isomorphism of second-order phase transitions and classifying the SCF state regions of pure substances and Type I–II phase behavior solute — solvent/extractant binary systems as isomorphic, it may be reasonably suggested that such important thermodynamic property as solubility may fall, though for the first time, into anomalous property variation regions in this binary system case. Consequently, this property in the most general terms shall have components defined by the mechanisms of both regular and singular behavior subregions. For pure substances, an anomalous property variation subregion in a near-critical state region $(T > T_c)$ is defined by the following temperature variation range $T = T_c\,(1.0 - 1.1)$ and density variation range $\rho = \rho_c\,(0.7 - 1.3)$, where T_c and ρ_c are the critical substance temperature and density, respectively [9].

Turning back to the studies of solvation complexes and clusters applicable to mixtures in a supercritical fluid state, some of them are summarized below. Work [20] describes experimental solubility data for a wide range of substances in supercritical carbon dioxide (SC CO_2), and an equation was derived from laws of contiguity (solvation) where it is the solvent density that is the driving factor of solubility. Moreover, experimental solubility data analysis using this equation is also used to determine the degree of association of solvation complexes (number of solvent molecules around a solute molecule). According to Chrastil's paper [20], solvation complexes are generally nonstoichiometric and degree of association is non-integral, accordingly. Capabilities of his equation are compared with the experimental solubility data. Good agreement was found. Nevertheless, the author [20] limits usability of the equation by solubility values lower than 100−200 g/l of the solute. The degree of association of systems studied in the temperature range of 40 °C−80 °C and at pressures up to 250 atm varied within 1.463−12.095. In the context of [20], the statement made in [23] may be also given, according to which an increase in the supercritical fluid solvent density increases the size of cluster formed around a solute molecule. However, in both cases the aspects of clustering with focus on the region of asymptotic proximity to the critical point were not addressed.

A method of integral equations for distribution functions was used in [25] to examine clustering, in particular, in the vicinity of the critical point. According to the findings, when approaching the critical point, correlations of the solvent molecule fluctuations around the solute molecules become increasingly long-range and the fluctuations themselves become larger. Calculations using the molecular dynamics method [24] show that clusters maintain their structural integrity during a quite long time, are typical of solvation structures in the vicinity of the critical point and are responsible for anomalous thermodynamic property behavior of systems in the given state region.

Based on the fact that the preferred version of a solute-solvent system is still Type I−II phase behavior mixture with an infinite miscibility region, then an increase in the solvation complex sizes and, therefore, in solubility [20,23] with an increase in the SCF solvent density due to pressure rise is observed during motion in the opposite direction from the critical point (for example, along the isoline of the constant concentration of the highly volatile component in the mixture $C_c = \text{const}$ corresponding to the concentration in phase interface disappearance conditions). This is actually an example of a typical behavior of binary mixtures exposed to pressure even regardless of whether there is a critical point on the phase diagram or not [27]. Consequently, this pattern may be reasonably regarded as a sign of regular behavior relating to binary system properties such as solvation complex/cluster size or substance solubility in the SCF solvent in the above-mentioned conditions (Figure 1).

In [24,25], focus is primarily made on clustering in immediate vicinity to the critical point. Even when the binary system is treated as an infinitely dilute solution and focus is made on the phase diagram of the pure substance, then we can move to the critical point, for example, as is common for the evaluation of critical indices, on the critical isochor. This means that the density remains unchanged, the temperature decreases and the pressure decreases too. Understanding that such motion is accompanied by an increase in the correlation radius and development of large-scale density fluctuations, we acknowledge another anomalous clustering incentive or mechanism with a clearly pronounced singular shade inherent in second-order phase transitions.

As mentioned above, such system behavior when approaching the critical point from higher temperatures $(T > T_c)$ is predetermined by the prospect of disordered phase transformation into the ordered phase in transition to the subcritical $(T < T_c)$ two-phase equilibrium region. Note that disordered and ordered phases near the critical point are little different [11]. When using the phase diagram for Type I−II phase behavior system, motion to the critical point along isoline $C_c = \text{const}$ is followed by a decrease in both pressure and density (Figure 1). It means that the mechanism and patterns of the singular behavior region [24,25] differ fundamentally from those inherent in the regular behavior regions [20,23].

1.5. Low-volatile component swelling in the supercritical fluid extraction process

Highly volatile component (solvent/extractant) concentration on the liquid branch, for example „$P - x, z$“ of the phase equilibrium diagram is another essential, yet not addressed before, difference of binary systems with continuous and discontinuous critical curves that can considerably affect the comparison of binary system capabilities involved in the SCF extraction process. Highly volatile component concentrations for Type I−II and V phase behavior binary systems directly or indirectly related to aqueous runoff from „Nizhnekamskneftekhim“ and „Kazanorgsintez“ are given below (Table 1).

Chemical theory describes the dissolution process, including also gases in liquid, as formation of an unstable compound mixture with a variable composition accompanied by a thermal effect and system volume variation. Prior to discussing the important topic of volume variation, note that the nature of solute and solvent exerts the highest influence on gas solubility in liquids. The magnitude of this solubility depends both on the gas pressure above the liquid and the phase contact area. With few exceptions, gas solubility in liquids decreases during heating.

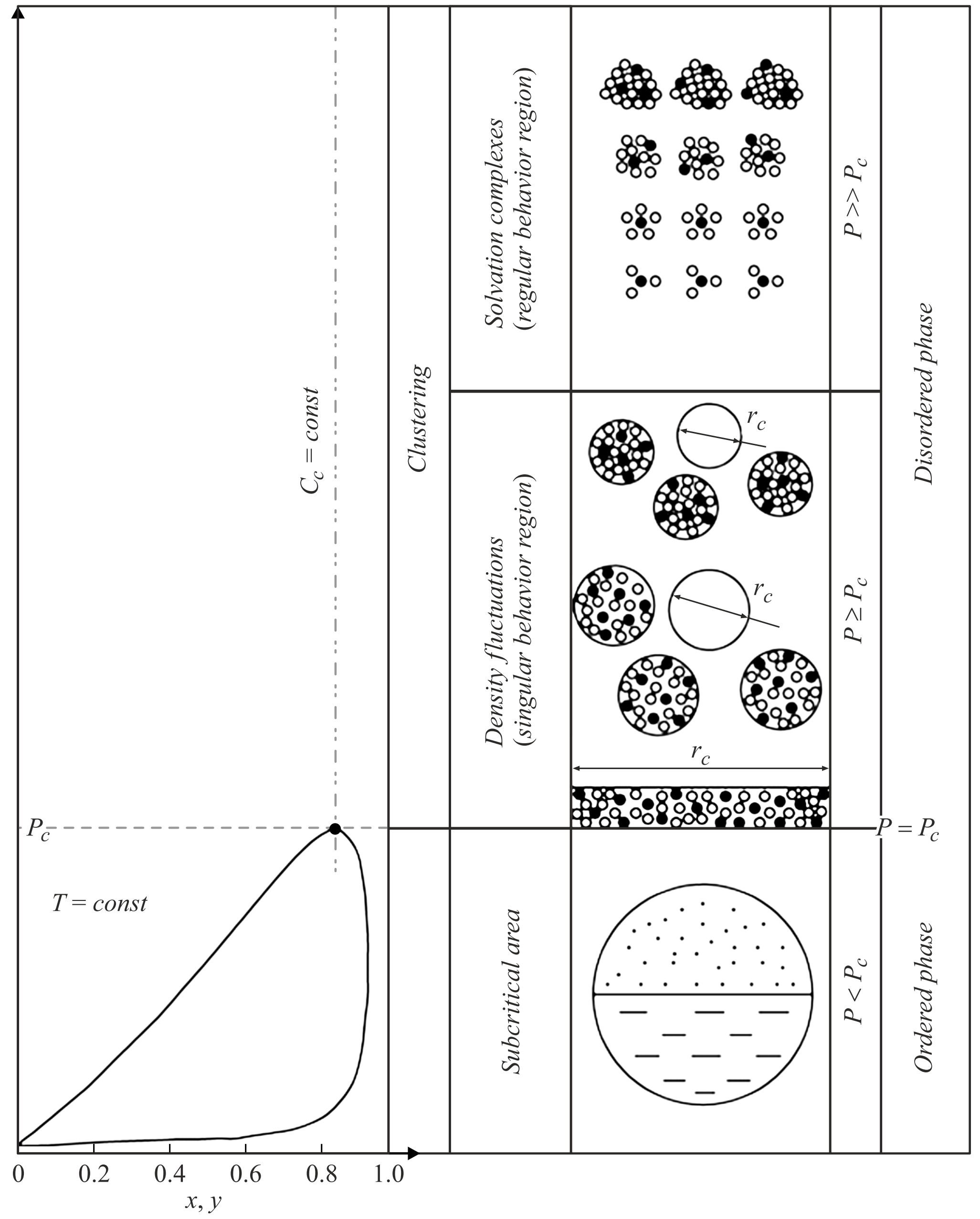

Figure 1. Schematic diagram of clustering in Type I–II phase behavior binary mixture in the SCF state region when moving to the critical point along isoline C_c = const from a higher pressure region. P_c — critical pressure:

Considering that the gas dissolved in the liquid shall occupy some volume in this liquid, a concept of „free volume“ $V - b$ introduced by Van der Waals comes to mind immediately. While the molar volume V of liquid obviously depends on the state parameters, then for the volume occupied by liquid molecules b, it should be only noted that it has a status of constant in the equation of Van der Waals state that qualitatively correctly describes the vapor-liquid equilibrium and defines the critical point parameters.

For the purpose of this work, the volume of low-volatile component molecules of binary mixtures (Table 2) was calculated using the quantum chemical method and „Gaussian 09“ program that implements the DFT method with the B3LYP density functional and the 6−311++g(df, p) basis set.

Even though the values in Table 2 will vary depending on the state variables, including the temperature and pressure, the informative value of the conceptual and comparative plan will not be lost. A few examples of the above-mentioned variations are given below. And, in particular, for acetone in conditions of one of the experiments ($t = 40\,^{\circ}$C, $P = 10$ MPa) that will be described in the Experimental section, $V - b$ will be as high as 9.953 cm^3/mol. In [37], the

Table 1. Concentration of a highly volatile component of some binary systems on liquid branch „$P-x, z$" of the phase equilibrium diagram

System	T, K	P, MPa	$x_{\max}$, mole fr.	Reference
I–II types of phase behavior				
CO_2 — acetophenone	313.15 328.15 348.15	81.0 115.0 165.0	0.803 0.806 0.888	[28]
CO_2 — styrene	328 333 343 353	100 108 130 137	0.97 0.95 0.92 0.90	[29]
CO_2 — 1-phenylethanol	303.15 313.15 323.15	91 126 161	0.89 0.91 0.90	[30]
CO_2 — toluene	323.0 343.0	86.6 114.74	0.883 0.9217	[31] [32]
CO_2 — acetone	291.15 298.16 303.13 308.15 313.13	52.7 58.2 62.7 71.7 73.9	0.910 0.935 0.9197 0.9336 0.9083	[33]
CO_2 — *n*-decane	319.0 344.3	89.77 127.4	0.986 0.924	[32]
CO_2 — Ethanol	291.15 298.17 303.12 308.11 313.14	54.5 61.3 66.3 71.7 79.2	0.8301 0.8302 0.8280 0.8257 0.8208	[33]
V type of phase behavior				
CO_2 — phenol	373.15 423.15	107 115	0.26 0.22	[34]
CO_2 — 2-phenylethanol	313.1 323.1	224.0 244.1	0.559 0.618	[35]
CO_2 — propylene glycol	398.2 423.2 453.2	300 300 300	~ 0.18 ~ 0.18 ~ 0.18	[36]

free volume of liquids at various pressures was evaluated by hypersound data and it was found that the volume of microcavities between molecules in liquid decreases as the pressure and molecular weight increase.

Without full analysis of data listed in Tables 1 and 2, though this data will be used again to discuss the experimental data, focus will be made only on the variables of the acetone and binary system consisting of acetone and carbon dioxide that are the objects of study in this work. And, in particular, concurrent review of the highly volatile component concentration on the liquid branch of binodal (0.91–0.93) and the free volume (8.88 cm^3/mol), which is the smallest compared with those for other liquids (Table 2), indicates that, at such high x_{CO2} and the smallest $V-b$, acetone with carbon dioxide dissolved in it will greatly increase in volume or swell. With proper combination of the low-volatile component volume in the extractor, extractor design and dimensions, and when a headpiece is available in the extractor, a condition may be achieved where the equilibrium solubility of acetone in SC CO_2 in this case will be significantly supplemented by the volumetric carry-over of the target component saturated with carbon dioxide into a separator resulting from the above-mentioned swelling. This is actually the main premise of a mechanism for increasing the SCF extraction process efficiency, which hasn't been discussed before and, therefore, is unknown, relevant to

Table 2. Free volume of the low-volatile component of binary mixtures from Table 1 at $t = 25\,^\circ$C and $P = 0.1$ MPa

Low-volatile component	μ, g/mol	ρ, g/cm^3	V, cm^3/mol	b, cm^3/mol	$V-b$, cm^3/mol
Acetophenone$C_6H_5COCH_3$	120.40	1.0281	116.890	97.272	19.618
Styrene $C_6H_5CHCH_2$	104.15	0.906	114.956	105.413	9.543
1-Phenylethanol$C_6H_5CH(OH)CH_3$	122.17	1.017	120.128	86.943	33.185
Toluene$C_6H_5CH_3$	92.14	0.86694	106.282	77.017	29.265
AcetoneCH_3COCH_3	58.08	0.7899	73.528	64.647	8.88
n-Decane$C_{10}H_{22}$	142.29	0.730	194.918	150.824	44.094
Ethanol C_2H_5OH	46.069	0.78945	58.356	45.756	12.60
PhenolC_6H_5OH	94.11	1.07	87.953	74.876	13.077
2-Phenylethanol$C_6H_5CH_2CH_2(OH)$	122.17	1.017	120.128	112.684	7.444
Propylene glycol$CH_2(OH)CH(OH)CH_3$	76.09	1.0363	73.425	56.923	16.502

Note. V is the molar volume of liquid; b is the volume of liquid molecules (per Van der Waals); $V-b$ free volume of liquid.

Type I–II phase behavior systems. When looking at the properties of Type V phase behavior systems (Table 1) and low-volatile components of these systems (Table 2), it is easy to understand that the above-mentioned swelling will be negligible there, which is proved conclusively in the experiment.

An example of successful implementation of this mechanism, though not fully understood, is commercial SCF drying of aerogels where it is acetone that is often removed by supercritical carbon dioxide from a highly porous matrix at the last stage [9]. Processes that employ this mechanism as an element of some general approach may also include displacement of tertiary oil by compressed gases, oil extraction from grain sees using the SCF extraction process and some other processes where the target component is saturated with compressed gas, swells, leaves the solid-phase matrix „volumetrically" and, thus, enhances the efficiency of these processes significantly. However, focus shall be also made on an important aspect of such statement, which still preferably includes the tasks where the target component to be removed from the feed stock is represented significantly. For example, during SCF drying of aerogels, a solid-phase matrix filler to be SCF extracted is 100 % represented by acetone (in particular case).

And, finally, clarification of the SCF extraction mechanism for Type I–II phase behavior systems may also explain the essence of such property as pseudo solubility that was first introduced by the authors of this work in [6]. According to the foregoing, the pseudo solubility combines an equilibrium component in the form of traditional solubility and a non-equilibrium component attributed to the volumetric carry-over of the target component into the extractor. Consequently, it is a good practice to qualify the pseudo solubility as a non-equilibrium characteristic (process variable) that, in particular, also defines the SCF extraction process efficiency for Type I–II phase behavior systems.

2. Experimental

2.1. Materials and methods

Investigation of solubility acetone and pseudo solubility of acetophenone (AP), ethylbenzene (EB), 1-phenylethanol (1-MPC) and propylene glycol in supercritical carbon dioxide used:

— high grade or premium grade carbon dioxide with at least 99.5 % of CO_2;

— acetone, AR, with at least 99.85 % of the base substance;

— acetophenone (methyl-phenyl ketone) with at least 93 % of the base substance;

— ethylbenzene with at least 93 % of the base substance;

— 1-phenylethanol (Methylbenzyl alcohol; 1-methyl phenyl carbinol), AR, with at least 98 % of base substance;

— propylene glycol (1,2-propanediol), AR, with at least 98 % of the base substance.

Phase equilibrium and state of the CO_2-acetone system in asymptotic proximity to the thermodynamic critical point were examined using an experimental system with a high-pressure optical cell (Figure 2).

2.2. Experimental test procedure

Pre-washed cell 1 is „dried" using a vacuum pump to remove solvent vapor and atmospheric air. Then the cell is heated to the set temperature using a thermostating system consisting of the TPM202 temperature sensor and controller, and an electric heater. The cell is covered with heat insulation on the outside to minimize heat loss. After reaching the set temperature conditions, the cell is filled

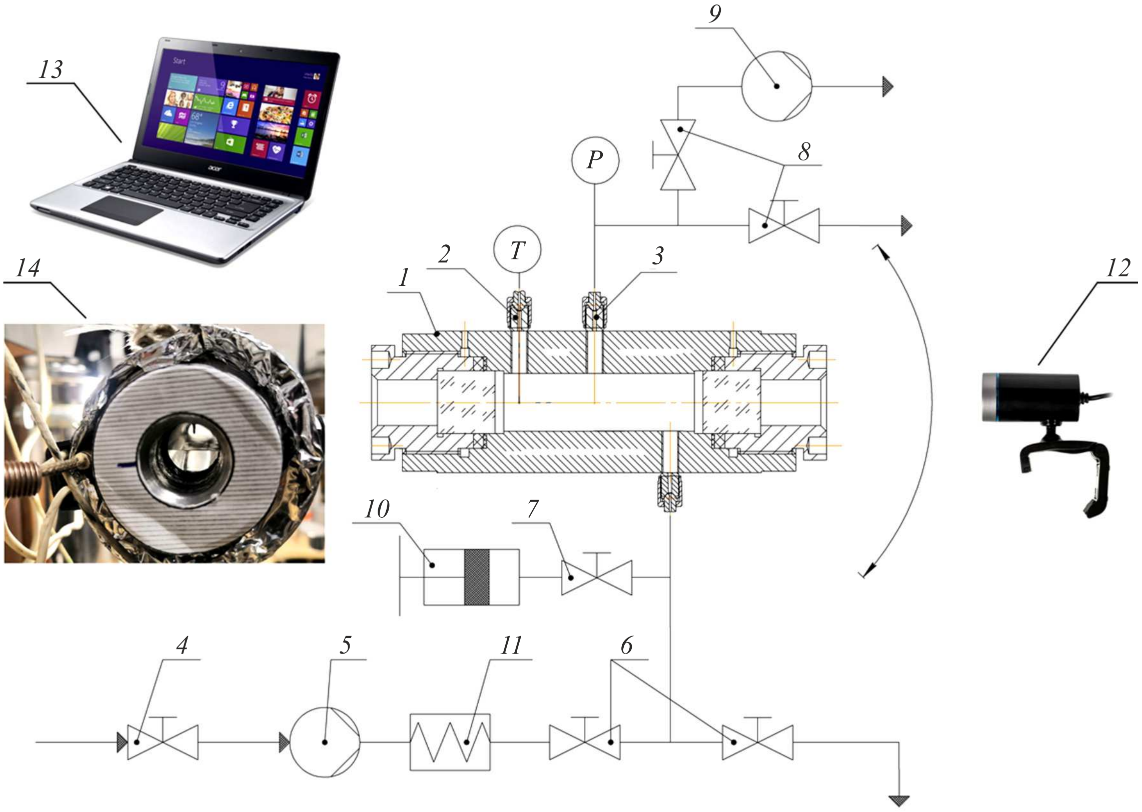

Figure 2. Diagram of the experimental system for testing phase equilibrium in binary systems using a high-pressure optical cell: *1* — optical cell; *2* — temperature sensor (thermocouple); *3* — pressure sensor; *4* — gas supply valve; *5* — high pressure pump; *6, 7, 8* — valves; *9* — vacuum pump; *10* — syringe pump; *11* — heat exchanger; *12* — video camera; *13* — laptop; *14* — optical cell image segment.

with a low-volatile liquid-phase component (acetone) of the anticipated binary mixture using a syringe pump. The final liquid-phase component amount in the cell is measured by the weight method. After achieving thermal equilibrium, a highly volatile component(CO_2) is supplied using pump *5*. The component is supplied until acetone (in this case) saturation with carbon dioxide is reached. Gas supply is accompanied with intense stirring of the cell content by rotating the cell at ±45° with respect to the sight glass horizon. After reaching the saturation state and set pressure, the system is held within 30 min.

Achievement of saturation in the thermodynamic cell is verified by one or two control tests by means of test sampling or by the absence of pressure in the optical cell. When the optical cell equilibrium state has been achieved, sample stirring is stopped. The phase equilibrium achievement process is monitored by the video system consisting of an external camera and PC display unit. A screen data recording program also actuates simultaneous temperature and pressure recording in the high-pressure optical cell. A reference disk with evenly spaced horizontal lines is placed around the cell's sight glass on the clamping cap nut for observation and quantitative estimation of the phase interface displacement behavior. Optical cell design allows test sampling of both liquid and gas phases.

Sampling and analysis are performed as follows: before sampling, the sampler is weighed using an electronic balance within ± 0.001 g; then the sampler is connected to the corresponding line of the optical cell, where a half turn microvalve provides quick sampling; the sampler is cooled to separate the sample into gas and liquid phases, and then the highly volatile component is released slowly. Solute carry-over during gas release is prevented by placing a trap at the sampler outlet. Due to a limited effective volume of the optical cell, the initial equilibrium concentration varies significantly after sampling, therefore the sample analysis may be repeated only after repeating the equilibrium state achievement procedure.

Solubility and pseudo solubility of acetone in supercritical CO_2 (in the infinite miscibility region outside the binodal) were investigated using an experimental system (Figure 3, *a*) that employed the dynamic measurement method. Solubility and pseudo solubility of acetone in supercritical CO_2 (in the infinite miscibility region outside the binodal) were investigated using an experimental system (Figure 1, *a*) that employed the dynamic measurement method.

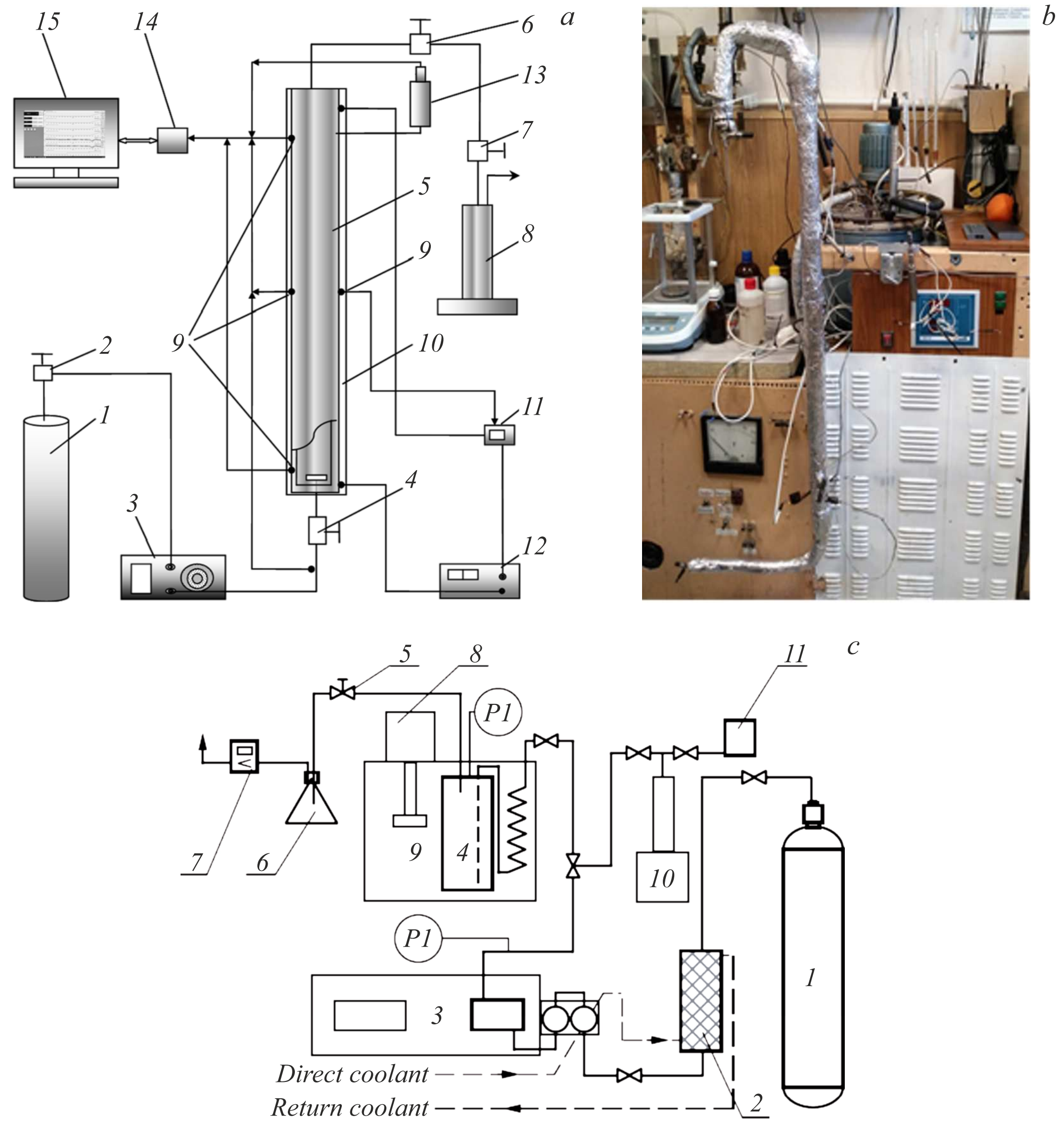

Figure 3. Diagram of the experimental system for testing solubility in SCF solvents (*a*), appearance of the setup (*b*) and extraction system diagram (*c*). *a* — *1* — gas cylinder; *2* — gas valve; *3* — liquid pump; *4* — cell inlet valve; *5* — solubility cell; *6* — outlet valve; *7* — control valve; *8* — separator; *9* — temperature sensor (thermocouple); *10* — heater; *11* — temperature controller; *12* — power supply; *13* — strain-gauge pressure transducer; *14* — ADC; *15* — PC. *c* — *1* — CO_2 cylinder; *2* — heat exchanger; *3* — CO_2 plunger pump *4* — extraction cell; *5* — throttling device; *6* — extract collecting tank; *7* — gas flow meter; *8* — heater; *9* — thermostat; *10* — co-solvent pump; *11* — co-solvent tank.

The experimental system (Figure 3,*a*) is used to study solubility of substances in supercritical fluids in the temperature range of 300–373 K and pressure range of 8–25 MPa. The system includes a pressurization and pressure maintenance system, temperature control and maintenance system, measurement cell and extract weight measuring and recording system. The pressurization and pressure maintenance system consists of 101 CO_2 cylinder *1* and Supercritical 24 high pressure pump *3* to keep the liquid CO_2 flow rate within 0.01–24 ml/min in the pressure range of 0–10000 psi (689.48 bar). The temperature control and maintenance system consists of electric heater *10*, THA (chromel-alumel) thermocouple and TRM-1 meter-controller. The extract weight measuring and recording system includes OKB Vesta electronic self-recording laboratory balance (measuring accuracy 0.001 g) and PC *15*.

2.3. Experimental test procedure

Pre-washed cell *5* is „dried“ using a vacuum pump to remove solvent vapor and atmospheric air. A pre-calculated volume of the test liquid is filled using a metering unit into the measuring cell through output control valve *6* with closed valve *4*. A liquid-phase component amount in the cell is measured by the weight method. Solvent represented by carbon dioxide from cylinder *1* enters high pressure pump *3* where it is pre-compressed and then supplied in the SCF state into the solubility cell at a low rate of 0.8–1.0 ml/min and a pressure below the experimental pressure. Then, the thermostating system consisting of TRM-1 „Oven“ temperature sensor and controller *11* and electric heater *10*. Consequently, the cell is heated up to the set temperature.

The cell is heat insulated on the outside to minimize heat loss. After reaching the set temperature conditions, supercritical fluid solvent is pumped up to the target experimental pressure. Gas supply is accompanied by intense stirring of the cell content by rotating the cell at ±45° with respect to the sight glass horizon. After reaching the saturation state and set pressure, the system is held within 30 min. Achievement of equilibrium in the thermodynamic system is identified by the absence of cell pressure variation. When the cell equilibrium state has been achieved, sample stirring is stopped. Cell pressure is controlled using strain-gauge pressure transducer *13*. Temperature field uniformity is controlled by chromel-alumel thermocouples *9* with temperature recording from analog-to-digital converter on PC *15*. Then after opening valve *6* and outlet control valve *7*, the SCF solution is fed to separator *8* where gas and liquid phases are separated. Constant flow rate of the SCF solvent with solute is provided by fine adjustment capabilities of valve *7*. Separator *8* is placed on the platform of the electronic self-recording laboratory balance connected to PC. Weight variation kinetics data is used to set a time period, within which the equilibrium dissolution of acetone (in this case) in SC CO_2 is maintained. The final result for acetone extracted from the measuring cell is obtained after weighing the whole measuring cell on the „CAS CUX-4200H“ balance.

Principle of operation and measurement procedure for the system shown in Figure 3, *b* are described in detail in [38]. It should be only added that cylindrical extraction cell *4* made of stainless steel 12X18H10T has ID equal to 30 mm and a height of 195 mm that define the internal volume equal to 137.8 ml.

3. Findings and discussion

3.1. Solubility

Investigation of the acetone solubility in SC CO_2 in infinite miscibility conditions outside the binodal (isoline with the critical concentration of the binary mixture components) encompasses:

— review of the phase equilibrium diagram of the CO_2-acetone system to identify the experimental bench performance (Figure 2) and the relevant procedure by comparing the findings of this work with the literature data;

— measurement of phase equilibrium characteristics near the binodal vertex to refine the critical pressure as applicable to the chosen temperature;

— phase state evaluation for the absence of phase interface for conditions on the isoline with the critical concentration of mixture components, for which solubility is to be investigated.

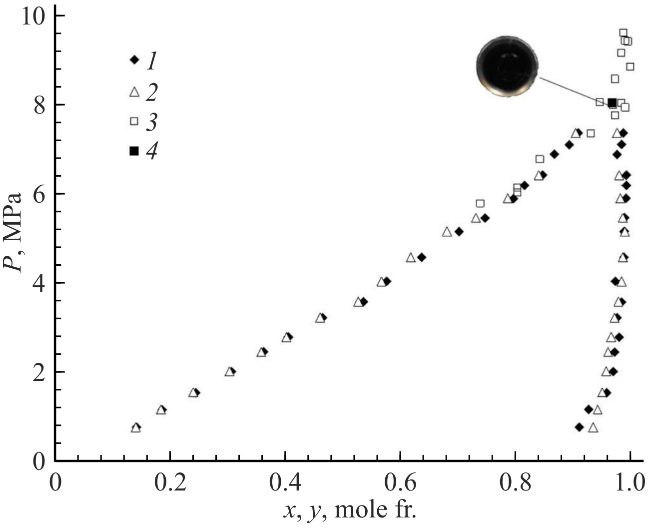

Figure 4. Phase equilibrium diagram of the CO_2-acetone binary system ($T = 313.15\,K$) supplemented by the measurements updating the critical point position and the absence of phase interface on the isoline with the critical concentration of mixture components (Table 3): *1* — [39]; *2* — [40]; *3* — this work; *4* — critical pressure $P_c = 8.048$ (this work).

Results of investigations performed for the above-mentioned sub-tasks are shown in Figure 4. When determining the critical point for the CO_2-acetone binary system, a critical opalescence phenomenon was observed and is shown in the figure as a dark shadow in the sight glass.

Estimation uncertainty of highly volatile component concentrations in the binary mixture on the liquid and vapor branches of the binodal is $\sim 0.1\,\%$ and up to $10.0\,\%$, respectively. Critical pressure based on the investigation is assumed equal to 8.048 MPa ($T = 313.15\,K$).

Preliminary investigations identified the solvent flow rate range (up to 0.3 ml/min) through the measuring cell using the dynamic measurement method that provides the equilibrium concentration of acetone in carbon dioxide in the experimental conditions.

Figure 5 shows the kinetics of acetone extraction by carbon dioxide in solubility conditions for one of conditions implemented in the SCF state region. The desired quantity is calculated exactly on the basis of the linear segment characteristics from this curve and solvent flow rate.

Figure 6 shows the data for acetone solubility in carbon dioxide calculated on the basis of the vapor branch characteristics of the binodal for the subcritical state region using the findings obtained by other authors, and the experimental data obtained by the authors of this work in the infinite miscibility region outside the binodal on the isoline of the critical acetone concentration in the mixture (Table 3). Due to an imperfection of the measurement bench, that very

Table 3. Acetone solubility in carbon dioxide in the infinite miscibility region of the SCF state

T, K	P, MPa	C_0, mol. fr.	y, mol. fr.	T, K	P, MPa	C_0,mol. fr.	y, mol. fr.
313.68	8.08	0.0273	0.075	314.13	10.75	0.0189	0.026
313.85	8.11	0.0299	0.059	313.60	11.02	0.0175	0.022
313.64	8.19	0.0287	0.051	313.87	12.86	0.0178	0.024
313.20	8.28	0.0259	0.039	313.44	12.89	0.0173	0.023
313.28	8.29	0.0283	0.037	313.66	13.00	0.0159	0.022
313.23	8.31	0.0273	0.041	313.28	13.11	0.0180	0.022
313.71	8.49	0.0262	0.034	313.74	13.67	0.0167	0.021
313.51	8.62	0.0252	0.033	313.52	13.73	0.0159	0.022
313.86	8.62	0.0227	0.034	313.36	14.76	0.0167	0.023
313.78	8.69	0.0228	0.027	313.35	14.83	0.0166	0.022
313.23	8.76	0.0210	0.026	313.73	14.89	0.0166	0.022
313.73	8.79	0.0218	0.026	313.74	16.59	0.0145	0.018
314.04	10.09	0.0206	0.022	313.57	16.62	0.0154	0.017
313.34	10.68	0.0185	0.023	313.82	16.67	0.0157	0.016

Note. C_0 is the initial concentration of acetone on CO_2.

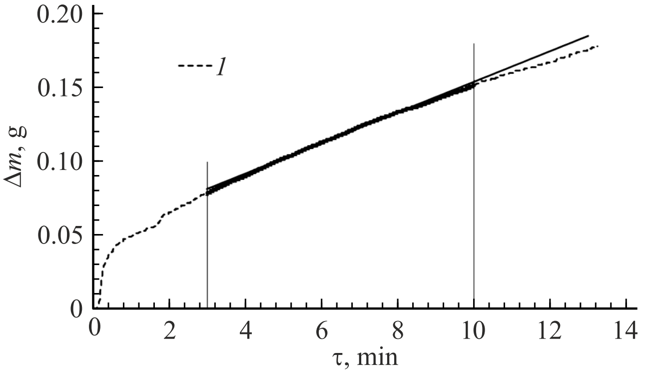

Figure 5. Kinetics of acetone extraction by carbon dioxide in solubility conditions at $T = 313.47$ K, $P = 14.77$ MPa and CO_2 flow rate equal to 0.3 ml/min: *1* — experimental curve; solid plump line —the calculated segment.

isoline couldn't have been strictly adhered to in the state variation range of interest.

The supercritical fluid state region $(P \geq P_c)$ of the studied mixture, by analogy with the theory of critical phenomena for pure substances [9,15], is represented by two important subregions: a regular behavior region $(P \geq\sim 10\,\text{MPa})$ and a region of asymptotic proximity to the critical point $(P_c \leq P \leq\sim 10\,\text{MPa})$, that combines contributions of both regular and singular behavior of the property of interest.

Within the same analogy with approaches implemented for single-component systems and assuming that the isoline of the critical binary mixture component concentrations in the infinite miscibility region may be treated as a nonstrict analogy of the critical isochor, the solubility behavior „y" in asymptotic proximity to the critical point is described by exponential function (*1*) with a common form[13–15] according to the results of this study (Figure 7).

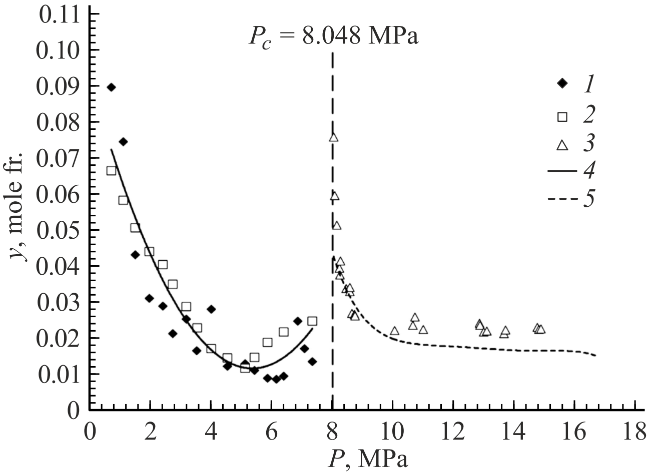

Figure 6. Acetone concentration in the carbon dioxide and acetone mixture on the vapor branch of the binodal and acetone solubility in carbon dioxide in the supercritical fluid state region at $T = 313.15$ K: *1* — [39]; *2* — [40]; *3* — (Table 3); *4* — averaging curve; *5* — C_0 (Table 3).

Experimental point scatter near the averaging curve is caused by temperature variation (assumed as permanent

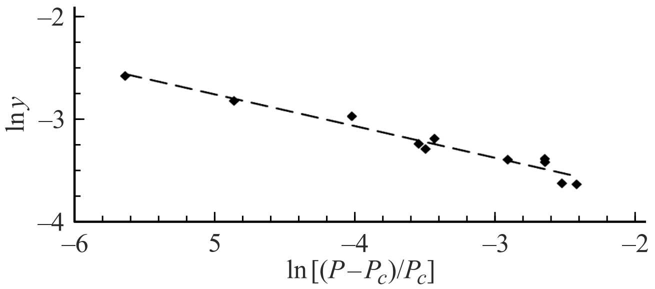

Figure 7. Solubility of acetone in carbon dioxide on the isoline of critical concentration C_c of the binary mixture components at $T \approx 313.15\,\mathrm{K}$ (Table 3).

for the entire point array) as well as by the experimental measurement error (uncertainty) for the desired solubility:

$$y_{Cc} = 0.0135\left(\frac{p-p_c}{p_c}\right)^{-0.308}. \qquad (1)$$

3.2. Pseudo solubility

High concentration of the highly volatile component of Type I–II phase behavior binary system on the liquid branch segment of the binodal adjacent to the critical point and high excess volumes of the same mixture in a quite narrow pressure range (up to $\sim 10-15\,\mathrm{bar}$) near the critical pressure value in the SCF state region show up as excess acetone swelling resulting from carbon dioxide dissolution in acetone.

It can be observed in the laboratory experiments using the high-pressure constant-volume optical cell that the phase interface moves with some speed to the ceiling of the cylindrical cell shell and then goes outside during acetone saturation with carbon dioxide when the initial acetone volumes in the high-pressure optical cell are significant ($\sim 30-50\,\%$). Finally, the solvent or extractant in similar cases, on the one hand, carries the target component to the separator on the basis of traditional solubility principle and, on the other hand, facilitates much greater transfer of the same acetone into the same separator according to a sort of „vapor lift" principle that is initially associated with swelling of the target feedstock component. As mentioned above, for Type V phase behavior systems featuring low concentration of the highly volatile component on the liquid branch of the phase equilibrium diagram and low excess mixture volumes in SCF extraction process conditions, the swelling effect is as low as possible and no „increase in the extractor's effective volume" is observed at all.

The effect of the above-mentioned factor on the key properties of the SCFE process efficiency will be demonstrated for Type V and I–II phase behavior systems with low-volatile components representing the aqueous runoff from „Nizhnekamskneftekhim" (Figure 8).

Results obtained for the CO_2-propylene glycol system (Figure 8, *a*) as a prototype of all other particular cases of Type V phase behavior systems clearly demonstrate that the dynamic method in this case makes it possible to get the equilibrium solubility that is only defined by the nature of the solute and solvent, and also by the thermodynamic conditions of dissolution. Whilst for Type I–II phase behavior systems (Figure 8, *b*), the dynamic method provides the equilibrium solubility that also depends in this case on the filling level of the measuring cell/extractor with the component to be extracted. Thus, this property attains a status of a process variable while demonstrating higher potential capabilities of the SCF extraction process for Type I–II phase behavior systems.

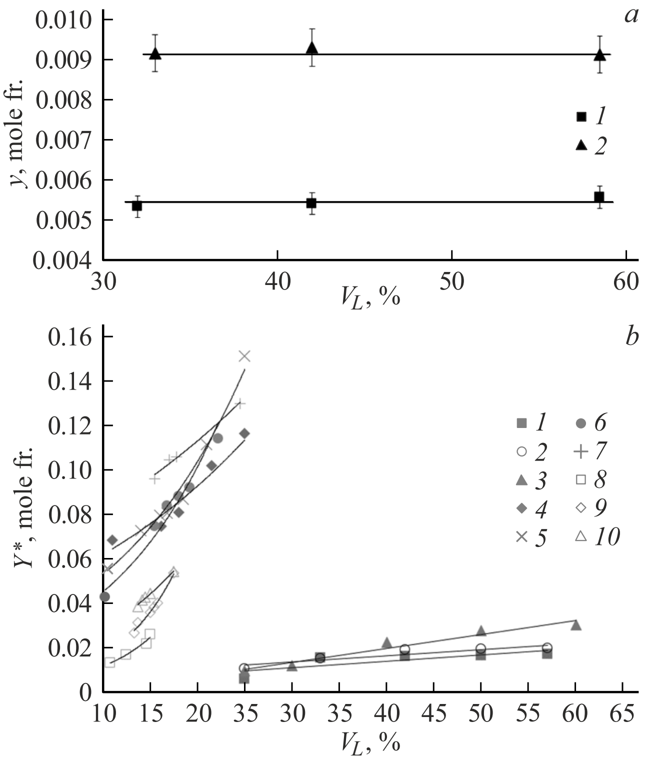

Figure 8. Solubility of propylene glycol (*a*) and pseudo solubility of methyl phenyl carbinol, acetophenone and ethylbenzene (*b*) in carbon dioxide as function of the filling level V_L of the extraction cell with the solute within the dynamic solubility method at $T = 318\,\mathrm{K}$: *a* — *1* — 15; *2* — 20 MPa; lines — least-square averaging; *b* — *1* — 12 (1-MPC); *2* — 15 (1-MPC); *3* — 20 (1-MPC); *4* — 10 (MPC); *5* — 12 (AP); *6* — 15 (AP); *7* — 20 (AP); *8* — 15 (EB); *9* — 24 (EB); *10* — 30 MPa (EB); lines — least-square averaging.

Figure 9 shows the kinetics of acetone extraction by carbon dioxide in pseudo solubility conditions for one of conditions implemented in the SCF state region. The desired quantity is calculated exactly on the basis of the „linear" segment (time range from 0 min to 50 min) characteristics from this curve and the solvent flow rate. A wavy shape of this segment is attributed to the feature of the macrotransfer mechanism employed in the device.

Table 4. „Pseudo solubility“ of acetone in carbon dioxide in the SCF state region

T, K	P, MPa	V_L, %	V_E, ml/mol	Y^*, mol. fr.
313.59	8.97	15.12	−34.27	0.076
313.96	12.68	14.82	−2.75	0.029
313.99	14.64	14.55	−1.64	0.027
313.71	16.69	13.70	−1.54	0.038
Mean filling level 14.55 %				
314.15	8.67	22.86	−49.37	0.293
314.13	12.38	21.80	−5.97	0.087
313.51	14.12	21.45	−1.33	0.019
314.01	16.25	21.03	−0.67	0.013
Mean filling level 21.79 %				
313.43	8.92	32.29	−26.42	0.450
313.48	12.85	29.45	−4.59	0.070
313.31	14.74	29.08	−1.60	0.028
313.53	16.71	28.86	−1.33	0.032
Mean filling level 29.13 %				
313.49	9.15	35.34	−24.99	0.302
313.49	12.62	34.72	−5.86	0.104
313.44	14.49	34.20	−1.68	0.027
313.60	14.49	34.23	−2.27	0.040
Mean filling level 34.62 %				

Note. V_E is the excess mixture volume (exceeding the ideal solvent volume) according to „REFPROP“ version 10.0. NIST (USA). 2018 [41].

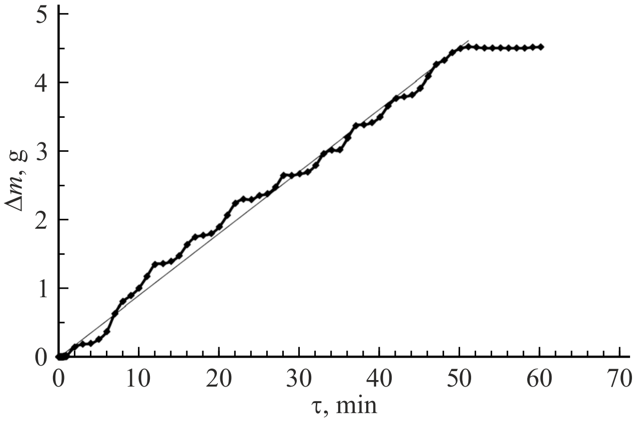

Figure 9. Kinetics of acetone extraction by supercritical CO_2 in the pseudo solubility conditions: $T = 313.0$ K, $P = 14.7$ MPa, CO flow rate $_2 = 1.0$ ml/min, acetone filling level of the extraction cell $V_L = 39$ % (extractor: $d_{in} = 10$ mm, $h = 1.273$ m).

Table 4 and Figure 10 show the measured solubility data (Y^*) for acetone in carbon dioxide in the supercritical fluid state region.

Note the excess mixture volumes with distinguished values in immediate proximity to the thermodynamic critical point of the binary mixture in the SCF state region.

Comparison of results in Tables 3 and 4 indicates that pseudo solubilities in certain thermodynamic conditions of dissolution are many times higher than the equilibrium solubility (Figure 6, 10, *a*) defining the higher efficiency of the supercritical fluid extraction process implemented using a mechanism that involves significant swelling of the solute in the extractor volume.

While for widely used Type V phase behavior systems, the dissolving power of the SCF solvent/extractant and, consequently, the SCFE process efficiency increase only with pressure growth, then for Type I–II phase behavior systems, the pseudo solubility effect, on the contrary, decreases with pressure growth and shows up only in a narrow region of lower pressures near the critical pressure for the binary system (Figure 10, *b*). Thus, there is another important energy efficiency factor of the SCFE process for Type I–II phase behavior systems due to lower specific quantity of metal in the process equipment and lower energetics of power units.

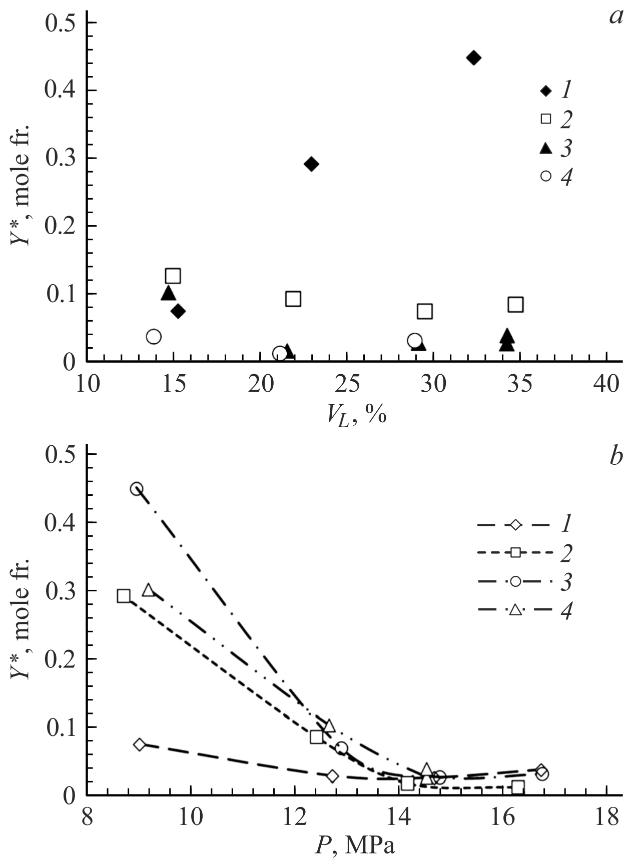

Figure 10. Pseudo solubility of acetone in carbon dioxide in the SCF state region as function of V_L of the extraction cell (*a*) and as function of pressure for various extraction cell filling levels (*b*) at $T \approx 313.7$ K: *a* — *1* — 8.85; *2* — 12.63; *3* — 14.5; *4* — 16.55 MPa (Table 4); *b* — *1* — 14.55 %; *2* — 21.79 %; *3* — 29.13 %; *4* — 34.62 % (Table 4).

Conclusion

An anomalous solubility behavior of the low-volatile components in a supercritical fluid solvent was first detected in asymptotic proximity to the critical point by using TypeI–II phase behavior CO_2-acetone binary system in the infinite miscibility conditions outside the binodal as an example. And, in particular, a multiple increase in the equilibrium concentration of acetone (in this case) in carbon dioxide is observed in a narrow pressure range when approaching the critical point on the isoline with the critical concentration of mixture components. However, the list of factors defining the increased efficiency of supercritical fluid extraction processes implemented for Type I–II phase behavior systems goes well beyond. The authors of the work have found that in the SCF conditions for the given binary mixture $(T, P \geq P_c)$ in a particular low-volatile component concentration variation range in the region where the critical concentration was exceeded, excess swelling of acetone (in this case) resulting from CO_2 dissolution in it might facilitate the occurrence of conditions where the extractor's effective volume was exceeded and, consequently, spontaneous movement of gross SCF solution volumes into the separator. However, note that for Type V phase behavior systems, these conditions are not observed at all due to low concentration of the low-volatile component on the liquid branch of the phase equilibrium and the absence of significant solution swelling in the SCF state region conditions.

Integral effect induced by the factors listed above was the basis introducing a new term called pseudo solubility. While the traditional solubility as a key equilibrium characteristic for binary systems is a property, the pseudo solubility is not the case, being just a SCFE process efficiency characteristic (a process variable) for Type I–II phase behavior systems. Much higher pseudo solubilities compared with the traditional solubility unambiguously suggest that the SCF extraction process is preferable for Type I–II phase behavior systems.

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Conflict of interest

The authors declare no conflict of interest.

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