

Editor's Choice

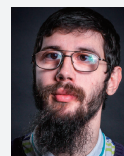
Experimental and Computational Study on the Solubility of Argon in Propan-2-ol at High Temperatures

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An experimental and computational study on the solubility of argon in propan-2-ol at high temperatures and pressures was performed. The following values of the Henry's law constant for the solution of argon in propan-2-ol were obtained: 58 ± 3 MPa at 480 K, 99 ± 3 MPa at 420 K, and 114 ± 2 MPa at 360 K.

Keywords: Argon solubility | Propan-2-ol | Henry's law constant

Studying phase equilibria and constructing phase diagrams is not only an important fundamental problem, but also an essential task for chemical engineering and technology.^{1,2} However, even for simple binary systems the process of collecting and systematising that type of thermophysical data is far from completion. Usually, both experimental and computational approaches are used to obtain the necessary information about the phase behavior of systems under consideration.

Noble gases have found wide application in medicine, environmental chemistry, and lighting. The solubility and phase behavior of noble gases in water and organic solvents was studied rather widely,³ however, for many systems the available information is not complete. The Henry's law constant for the solution of argon in propan-2-ol was previously reported only in a limited temperature range.^{4–7} This communication describes an experimental and computational study on the solubility of argon in propan-2-ol at high temperatures.

The experimental setup for the present gas solubility measurements⁸ is the same as employed in earlier studies. The following substances were used: argon (CAS number 7440-59-7) supplied by *Air Liquide* in a gas tank under a pressure of 30 MPa with a volume fraction of 99.9999% and propan-2-ol (CAS number 67-63-0) supplied by *Honeywell Riedel-de Haën* with a purity of >99.9%. The measuring cell was filled with argon and heated to about 20 K above the desired measuring temperature, and then the desired amount of propan-2-ol was added into it. When the mixture achieved a homogeneous state, the cell was slowly cooled down with the aim to reach the saturated liquid state.⁹ The experiments were carried out at the temperatures 360, 420, and 480 K. The density of argon and propan-2-ol as well as the saturated vapor pressure of pure propan-2-ol at these temperatures were calculated with equations of state.^{10,11} The experimental raw data together with the values used in the processing of them are presented in the Supporting Information. The resulting dependence of the phase equilibrium

pressure on the mole fraction of argon in liquid propan-2-ol at 360, 420, and 480 K is depicted in Figure 1.

As can be seen, the isotherms may be well approximated by straight lines. The slopes of these lines calculated with the least-squares technique were used to estimate the Henry's law constant at these temperatures; the estimated values together with their uncertainties are listed in Table 1.

Several approaches have been proposed in the literature¹³ to obtain the Henry's law constant on the basis of molecular simulation. The Henry's law constant is related to the residual chemical potential of argon in propan-2-ol at infinite dilution μ_{Ar}^{∞} .¹⁴ The molecular model for argon was developed in Ref. 15 and consists of a single Lennard–Jones site. The parameters ε and σ for argon were estimated to be the following: $\varepsilon_{\text{Ar}}/k_{\text{B}} = 116.79$ K, $\sigma_{\text{Ar}} = 3.3952 \times 10^{-10}$ m, where k_{B} is the Boltzmann constant. The molecular model for propan-2-ol consists of Lennard–Jones united atom sites for the two methyl, the methanetriyl, and the oxygen groups, accounting for repulsion and dispersion. Point charges were located on the methanetriyl and the oxygen Lennard–Jones sites, as well as on the nucleus position of the hydroxy hydrogen. The Coulombic interactions

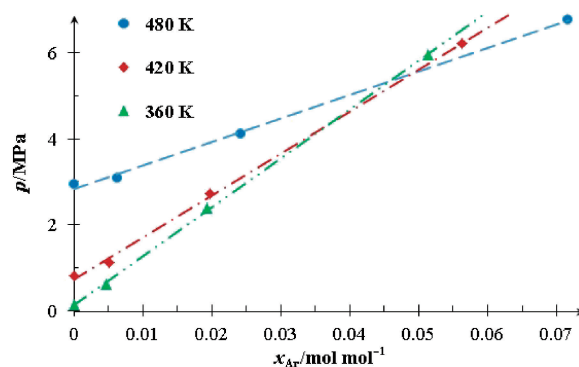


Figure 1. Experimental dependence of the phase equilibrium pressure over solutions of argon in propan-2-ol as a function of argon mole fraction at 360, 420, and 480 K.

Table 1. Experimental values of the Henry's law constant for the solution of argon in propan-2-ol at 360, 420, and 480 K¹²

T/K	480	420	360
$H_{\text{Ar}/2\text{-PrOH}}/\text{MPa}$	58 ± 3	99 ± 3	114 ± 2

Table 2. Henry's law constant for the solution of argon in propan-2-ol at various temperatures from molecular simulation¹⁹

T/K	$H_{\text{Ar}/2\text{-PrOH}}/\text{MPa}$
254.1	101.1 ± 0.9
279.6	114.6 ± 0.8
305.0	119.3 ± 0.5
330.4	118.1 ± 0.3
355.8	114.4 ± 0.3
381.2	106.4 ± 0.2
406.6	96.4 ± 0.2
432.0	84.4 ± 0.1
457.5	71.4 ± 0.1
482.9	57.4 ± 0.1

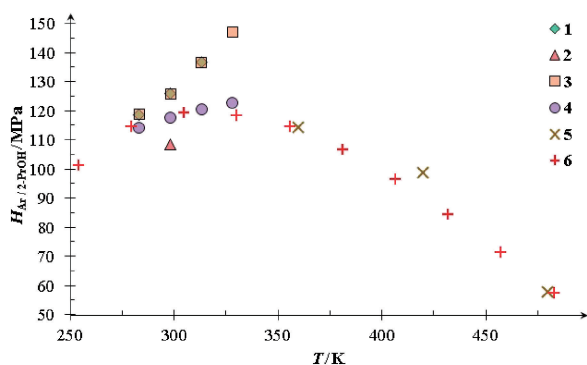


Figure 2. Henry's law constant for the solution of argon in propan-2-ol: 1, data from Ref. 4; 2, data from Ref. 5; 3, data from Ref. 6; 4, data from Ref. 7; 5, this work, experimental values; 6, this work, simulated values.

account for both polarity and hydrogen bonding. The interaction between unlike Lennard–Jones sites of two propan-2-ol molecules was defined by the Lorentz–Berthelot combining rule. To describe a binary mixture on the basis of pairwise additive potential models, the binary Lennard–Jones parameters σ_{AB} and ε_{AB} have to be determined. In this study a modified Lorentz–Berthelot rule was applied that has been discussed in detail elsewhere:¹⁶ $\sigma_{AB} = 0.5 \cdot (\sigma_A + \sigma_B)$, $\varepsilon_{AB} = \xi \cdot \sqrt{\varepsilon_A \cdot \varepsilon_B}$. The binary interaction parameter ξ can be adjusted to values of the Henry's law constant. During simulation, the mole fraction of argon in propan-2-ol is exactly zero, as required for infinite dilution because test particles for calculating μ_{Ar}^∞ are instantly removed after the potential energy calculation. Simulations were performed at temperatures ranging from 50% to 95% of the critical temperature of propan-2-ol and the according saturated liquid density and vapour pressure of pure propan-2-ol.¹⁷ The simulations were carried out using the software *ms2*¹⁸ on the “Hazel hen” machine at the High Performance Computing Centre in Stuttgart (hazelhen.hww.de). The state-independent parameter ξ was adjusted such that the differences between the simulation results, the present experimental values and the

literature data were minimal. It was found that for the solution of argon in propan-2-ol $\xi = 0.964$. The simulated values together with their statistical uncertainties are listed in Table 2. Figure 2 shows the good agreement between the simulated and experimental values of this work and literature data.

This work was supported by the Ministry of Education and Science of Russian Federation (state contract No. 10.723.2016/ДААД) and Deutscher Akademischer Austausch Dienst (grant No. 91547204).

Supporting Information is available on <http://dx.doi.org/10.1246/cl.170221>.

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- 19 The uncertainties relate to the particular molecular model, not to the real fluid.

Supporting Information

Chemistry Letters

Experimental and Computational Study on the Solubility of Argon in Propan-2-ol at High Temperatures

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(Received March 3, 2017; CL-170221; E-mail: npa@mail.uni-paderborn.de)

1. Experimental procedure

1.1. Experimental setup for studying the solubility of gases in liquids at high temperatures

The schematic of the experimental setup for the present gas solubility measurements¹ is shown in Fig. S1, and its appearance is depicted in Fig. S2.

The main part of the setup was a cylindrical high pressure equilibrium cell **A** made of V4a stainless steel, which had an internal volume of 14.85 ml. A magnetic stirrer was placed in the cell. To visually observe phase separation inside, two sapphire gauge-glasses **B** were mounted at the front and the back of the cylinder; a lamp was placed in front of the cylinder, and an endoscope **K** at its back. The image from the endoscope was transmitted to a television receiver through a SCART-SHVS adapter. The cell was constructed for temperatures up to 600 K and pressures up to 70 MPa. For this purpose, it was screwed together with eight expansion bolts and seven cup springs placed on each bolt. The cell was embedded in a copper cylinder **D** with electrical heating **C** so that the temperature can be controlled effectively and automatically. To avoid heat loss due to radiation, the cell was surrounded by an aluminum cylinder **E** with its own electrical heating. The whole setup was placed in a vacuum chamber **F** to reduce heat loss due to convection. Moreover, the vacuum atmosphere was useful to prohibit corrosion.

The cell was loaded via a three-way valve **V1** mounted at the top. A gas bottle **G** was connected to the left access (**V1a**) to load the gaseous component. The liquid component was loaded via a high pressure spindle press **H** which was linked to the right access (**V1b**). The press contained a scale that was calibrated with respect to the number of spindle turns from the starting position; a full passage of the press from the top to the bottom of the reservoir required 160.75 spindle turns. The high pressure pump was connected to a liquid reservoir **I** via valve **V3**. Valves **V2** and **V4** were subsidiary, whereas valve **V5** was used to purge the cell or to connect it to a vacuum pump **J**. The pressure transducers **P1** and **P2** were used to measure the pressure of the gaseous and the liquid components in the supply pipes during the loading process. The pressure in the cell was determined with the pressure transducer **P3**, which was possible even if valve **V4** was closed. The accuracy of all employed pressure transducers (model Super TJE, *Honeywell test & measurement*) was given as 0.1 % of their respective full measuring scale. The measuring scale was 20, 100 and 70 MPa for **P1**, **P2** and **P3**, respectively. For the temperature measurement, five calibrated platinum resistance thermometers with a basic resistance of 100 Ω (Pt100) were installed in the apparatus. Thereby, the temperature of the fluid in

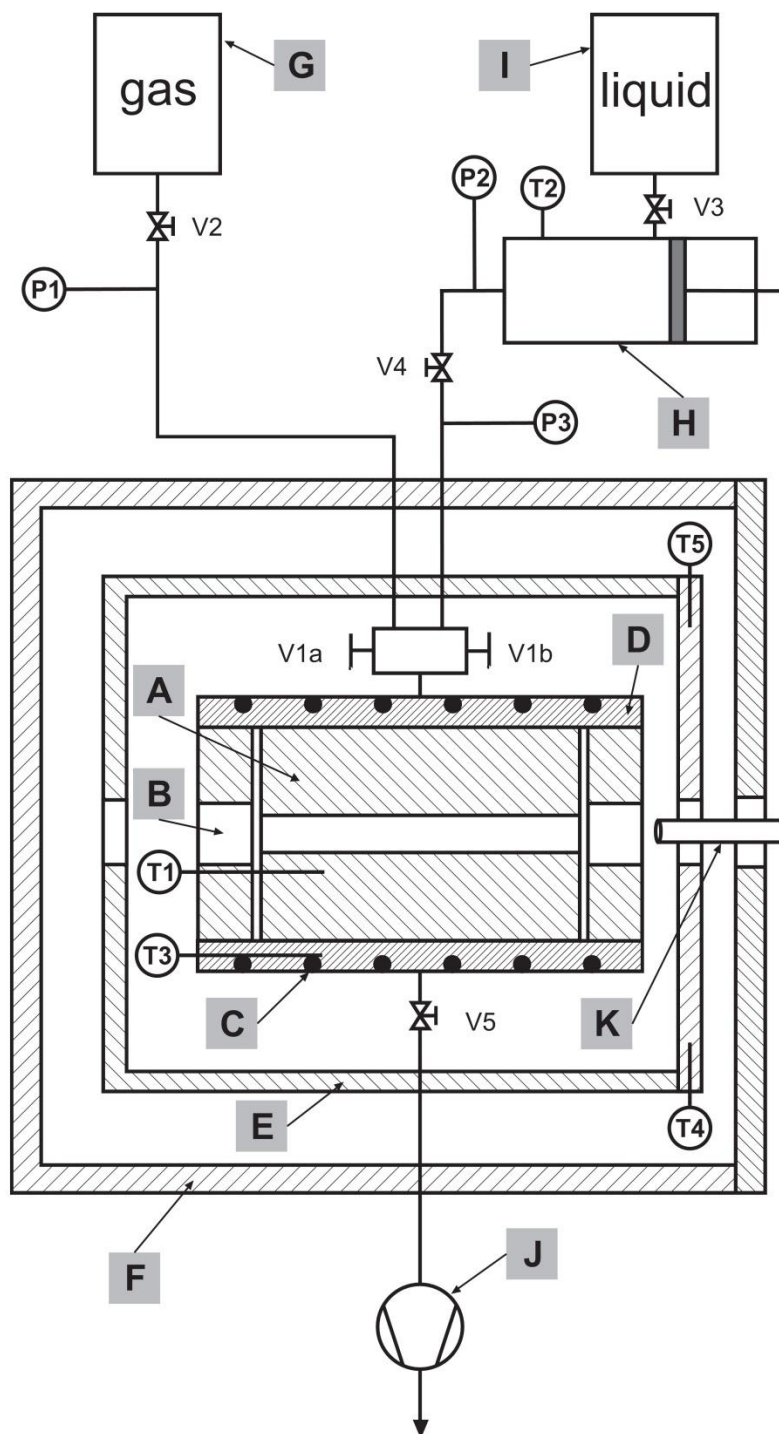


Fig. S1. Schematic of the experimental setup for the gas solubility measurements: **A** – high pressure equilibrium cell, **B** – gauge-glass, **C** – electric heater wire, **D** – copper cylinder, **E** – aluminum cylinder, **F** – vacuum chamber, **G** – gas reservoir, **H** – reservoir with the high-pressure spindle press, **I** – liquid reservoir, **J** – vacuum pump, **K** – endoscope, **V1**, **V2**, **V3**, **V4**, **V5** – valves, **T1**, **T2**, **T3**, **T4**, **T5** – platinum resistance thermometers, **P1**, **P2**, **P3** – pressure transducers.

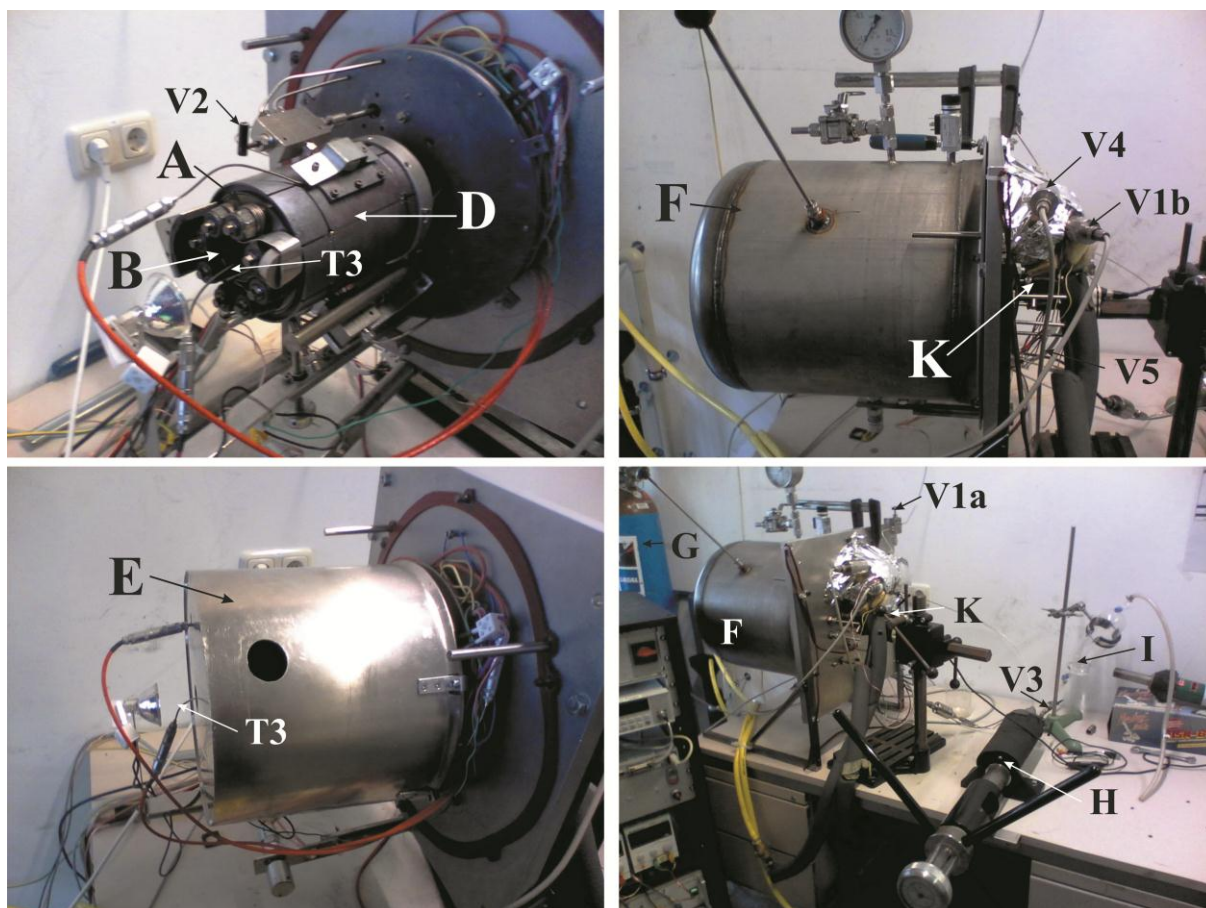


Fig. S2. Appearance of the experimental setup for gas solubility measurements. The labels are the same as in the Figure S1.

the cell and in the high pressure pump was measured with the Pt100 thermometers **T1** and **T2**, respectively. The temperature of the aluminum cylinder was determined with **T4**. The thermometers **T3** and **T5** were exclusively used to control the temperature of the cell and the aluminum cylinder, respectively. To calibrate the employed thermometers, a more precise platinum resistance thermometer with a basic resistance of 25 Ω was employed. The temperature measuring error was about ± 0.04 K. A dedicated software allowed for the continuous monitoring of the data from thermometers and pressure transducers and visualising it in text or graphic form.

1.2. Reagents

Argon (CAS number 7440-59-7) supplied by *Air Liquide* in a gas tank under a pressure of 30 MPa with a volume fraction of 99.9999% and propan-2-ol (CAS number 67-63-0) supplied by *Honeywell Riedel–de Haën* with a purity of > 99.9% were used.

1.3. Experimental procedure

Before loading the components of the studied mixture into the cell, the whole setup including the supply pipes was evacuated and thermostated at a temperature of 30 °C. Then, argon was filled into the cell **A** from the gas bottle **G** by opening valve **V1a** and the initial temperature (T_{Ar}) and pressure (p_{Ar}) of argon were noted after they took constant values. Next, propan-2-ol in the liquid reservoir **I** was degassed by vacuum over 10 minutes and was then added into the reservoir **H** by opening valve **V3**. Using the spindle press, a pressure close to 2.5 MPa was set in the reservoir, and initial values of the temperature (T_{2-PrOH}^1) and pressure (p_{2-PrOH}^1) of propan-2-ol were noted after they took constant values, together with the initial number of spindle turns z_1 . Cell **A** was heated up to a temperature that was about 20 K above the desired measuring temperature T_m , subsequently the desired amount of propan-2-ol was added into the cell with the spindle press by opening valve **V1b**. To achieve a homogeneous mixture, a magnetic stirrer was operated and the mixing process was visually inspected with endoscope **K**; it was completed when all gas bubbles disappeared. At this point, the mixture was in a homogeneous state (see Fig. S3a). In the next step, the cell was slowly cooled down towards the temperature T_m , with the aim to reach the saturated liquid state in the vicinity of T_m . In this case, the measured pressure p_m is the phase equilibrium pressure of the mixture with a specified liquid composition at T_m . However, usually saturation precisely at T_m could not be reached immediately with the present procedure. Therefore, several iterations were typically necessary. A typical thermal analysis curve that corresponds to this procedure is depicted in Fig. S4. From a homogeneous fluid state, the cell was slowly cooled down towards the desired measuring temperature T_m . During this cooling process, the pressure of the mixture was measured with the pressure transducer **P3** and plotted over time with the measurement program. At a certain temperature, the first small bubbles appeared (see Fig. S3b) and the slope of the pressure-time plot changed significantly (point p_1). At this temperature (point T_1), the mixture in the cell had reached the saturated liquid state. Because the cell temperature (T_1) was significantly above T_m when the first bubbles appeared, the amount of propan-2-ol in the cell was too small. In this case, more propan-2-ol was added into the cell with the spindle press. This procedure, namely adding more propan-2-ol into the cell, raising the cell temperature by about 20 K, waiting for equilibration and then cooling it down until bubbles appeared, was repeated several times (points p_2 through p_6 and T_2 through T_6) until the cell temperature was near the desired measuring temperature T_m when the mixture reached saturation. In the last step, the phase equilibrium pressure p_m at T_m was noted. After the end of the measurements, again, using the spindle press, a pressure close to 2.5 MPa was set in the reservoir **H** and final values of the temperature (T_{2-PrOH}^2) and pressure (p_{2-PrOH}^2) of propan-2-ol were noted after they took constant values, together with the final number of spindle turns z_2 .

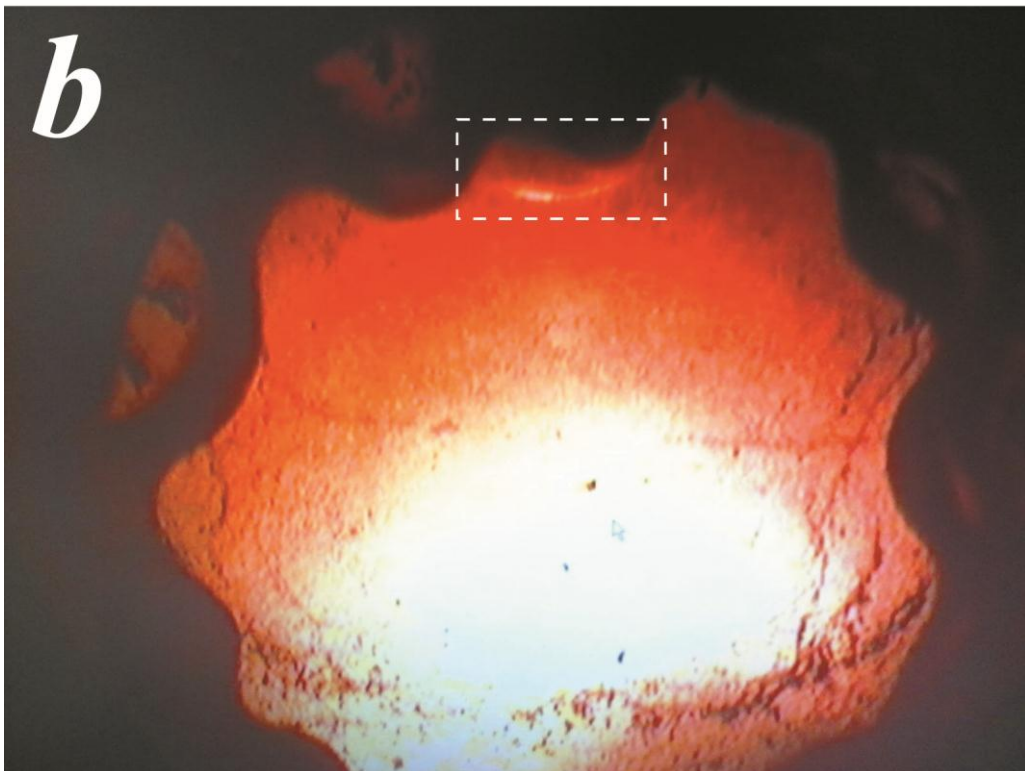
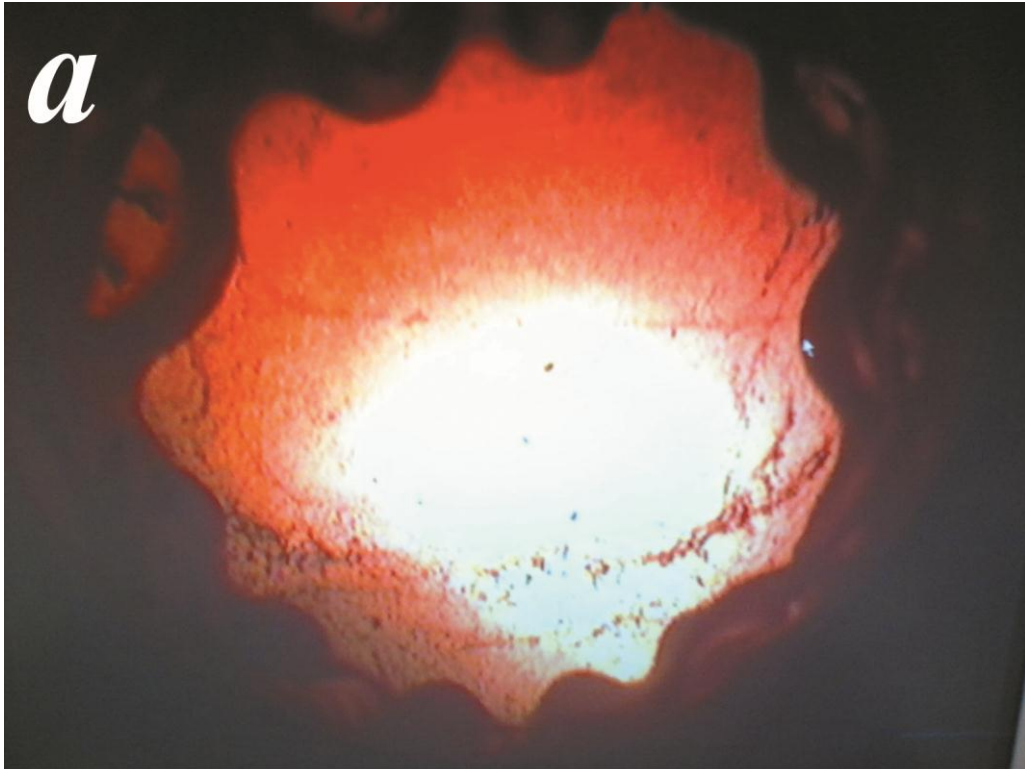


Fig. S3. Photographic pictures of the measuring cell: *a*) System in the homogeneous equilibrium state, *b*) Moment of the beginning of saturated vapour formation, where a bubble can be seen in the dashed box.

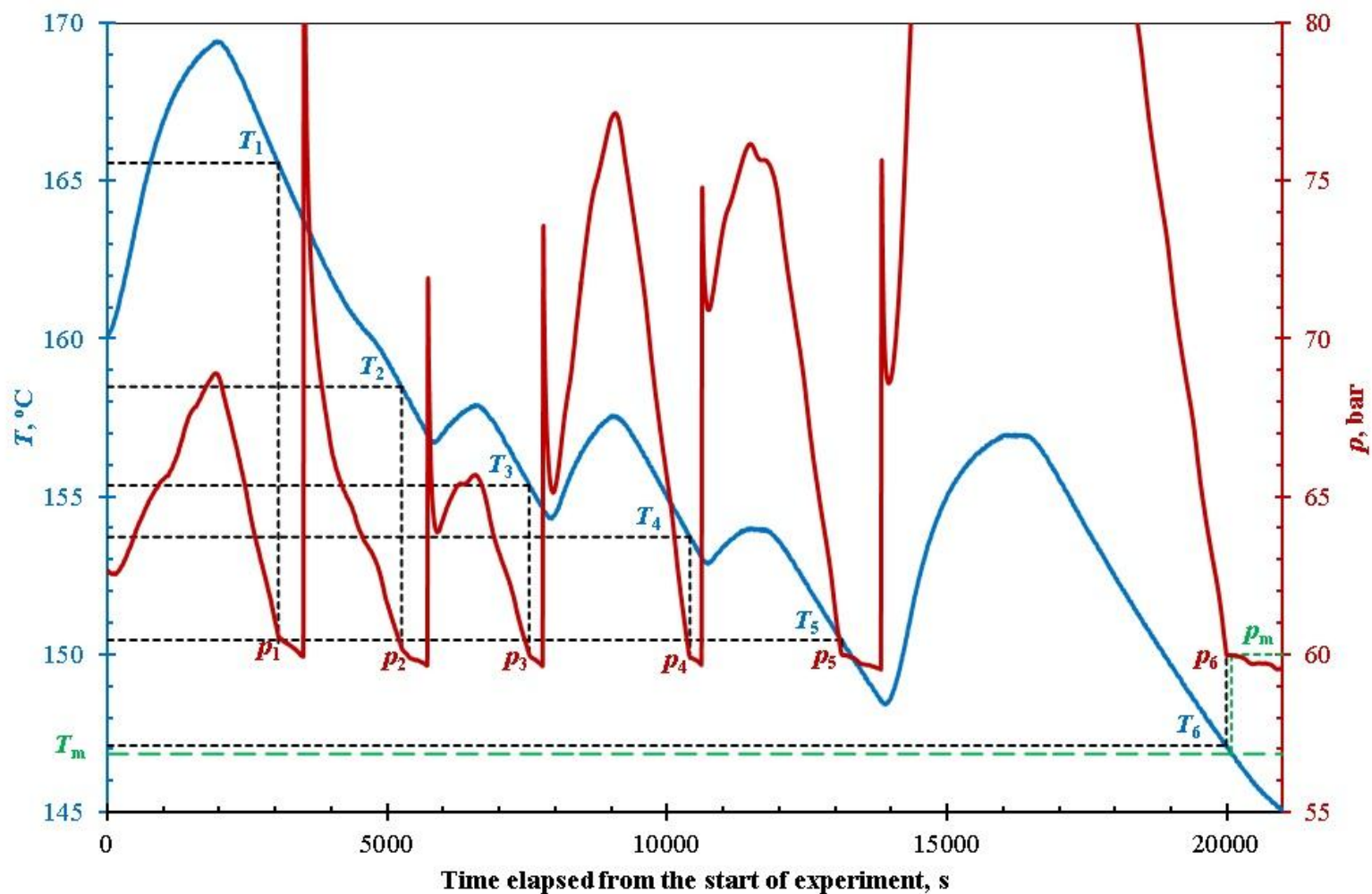


Fig. S4. Dependence of the system temperature and pressure on time elapsed from the start of experiment, depicting the procedure for the determination of the phase equilibrium pressure of argon + propan-2-ol mixture at the measuring temperature.

1.4. Processing of the experimental data

Using measured values of temperature T_{Ar} and pressure p_{Ar} of pure argon in the cell before the addition of propan-2-ol, the density of argon ρ_{Ar} was calculated according to the highly accurate reference equation of state proposed by Tegeler *et al.*² Since the cell volume was known $V' = 1.485 \cdot 10^{-5} \text{ m}^3$, the mass of argon in the cell was calculated by

$$m_{\text{Ar}} = \rho_{\text{Ar}} \cdot V',$$

which remained constant during the experiment.

Using the initial values of temperature $T_{2-\text{PrOH}}^1$ and pressure $p_{2-\text{PrOH}}^1$ of pure propan-2-ol in the reservoir **H**, the density of propan-2-ol in it before the start of the experiment $\rho_{2-\text{PrOH}}^1$ was calculated using the PC-SAFT equation of state,³ whose parameters for propan-2-ol were provided in Ref.^{4*} The volume occupied by propan-2-ol was calculated from the total volume of the reservoir **H** $V'' = 4.8 \cdot 10^{-5} \text{ m}^3$ and the number of spindle turns z_1

$$V_{2-\text{PrOH}}^1 = V'' \cdot \frac{160.75 - z_1}{160.75}.$$

Then, the initial mass of propan-2-ol in the reservoir **H** was calculated by

$$m_{2-\text{PrOH}}^1 = \rho_{2-\text{PrOH}}^1 \cdot V_{2-\text{PrOH}}^1.$$

In full analogy, using the data for $T_{2-\text{PrOH}}^2$ and $p_{2-\text{PrOH}}^2$, the density of propan-2-ol in the reservoir **H** after the experiment completion $\rho_{2-\text{PrOH}}^2$ was calculated, and then its volume

$$V_{2-\text{PrOH}}^2 = V'' \cdot \frac{160.75 - z_2}{160.75},$$

and mass

$$m_{2-\text{PrOH}}^2 = \rho_{2-\text{PrOH}}^2 \cdot V_{2-\text{PrOH}}^2.$$

The difference between the masses of propan-2-ol in the reservoir **H** at the beginning and the end of the experiment is the mass of propan-2-ol added into the measuring cell **A**

$$m_{2-\text{PrOH}} = m_{2-\text{PrOH}}^1 - m_{2-\text{PrOH}}^2.$$

With known masses of argon and propan-2-ol in the cell **A**, the mole fraction of argon in the equilibrium mixture is straightforward

$$x_{\text{Ar}} = \frac{m_{\text{Ar}} \cdot M_{2-\text{PrOH}}}{m_{2-\text{PrOH}} \cdot M_{\text{Ar}} + m_{\text{Ar}} \cdot m_{2-\text{PrOH}}},$$

where $M_{\text{Ar}} = 39.9481 \text{ g} \cdot \text{mol}^{-1}$ and $M_{2-\text{PrOH}} = 60.09502 \text{ g} \cdot \text{mol}^{-1}$ are the molar masses of argon and propan-2-ol, respectively.

According to Lewis' definition,⁵ the phase equilibrium pressure is the sum of the fugacities of argon and propan-2-ol

$$p_{\text{m}} = f_{\text{Ar}} + f_{2-\text{PrOH}}.$$

* Since this PC-SAFT equation of state is not of reference quality, its accuracy is discussed in Appendix 1.

For infinitely diluted solutions of argon in propan-2-ol, the fugacity of the solvent is determined by Raoult's law⁶

$$f_{2-\text{PrOH}} = p_{2-\text{PrOH}}^* \cdot x_{2-\text{PrOH}} = p_{2-\text{PrOH}}^* - p_{2-\text{PrOH}}^* \cdot x_{\text{Ar}},$$

and the fugacity of the solute by Henry's law⁷

$$f_{\text{Ar}} = H_{\text{Ar}/2-\text{PrOH}} \cdot x_{\text{Ar}}.$$

Thereby, the dependence of the experimentally determined phase equilibrium pressure p_m on argon mole fraction in the mixture x_{Ar} is a straight line with a slope equal to $H_{\text{Ar}/2-\text{PrOH}} - p_{2-\text{PrOH}}^*$ (see Fig. S5).

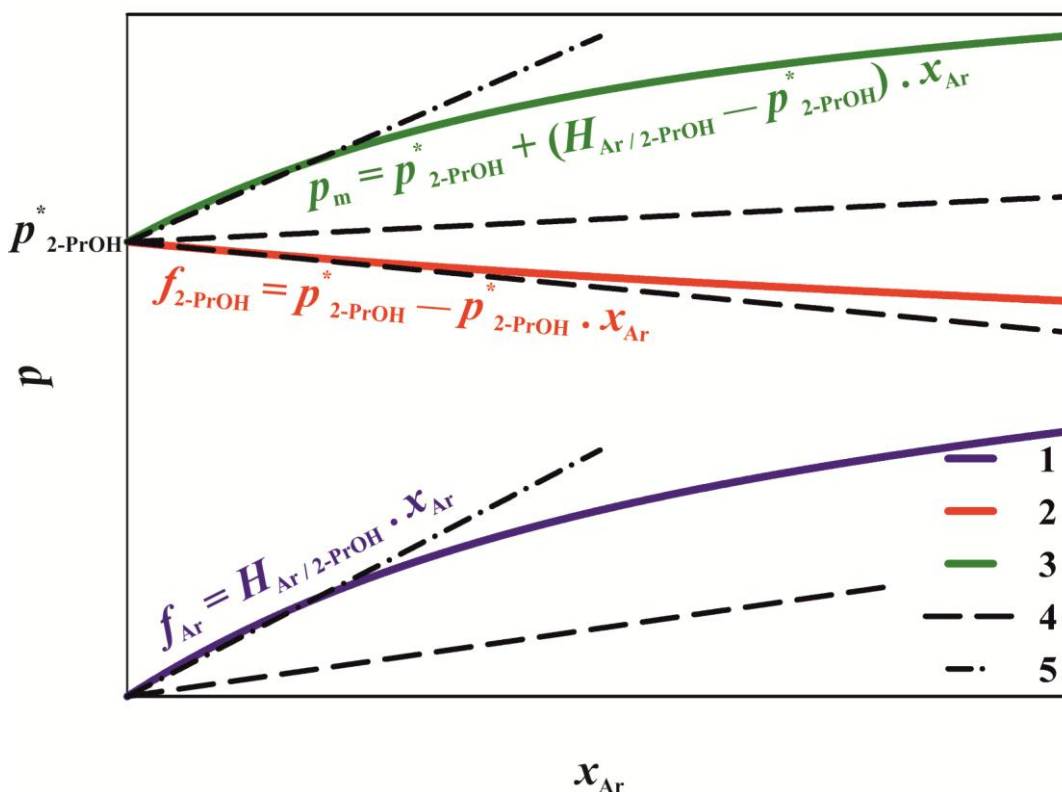


Fig. S5. Schematic on the dependence of the fugacity of argon and propan-2-ol, as well as the phase equilibrium pressure on the mole fraction of argon in the region of the infinitely diluted solutions: **1** – fugacity of argon, **2** – fugacity of propan-2-ol, **3** – phase equilibrium pressure, **4** – Raoult's law, **5** – Henry's law.

For each of the measuring temperatures T_m , a graph in the coordinates $p_m - x_{\text{Ar}}$ was plotted and its slope was calculated using the least squares technique.⁸ The saturated vapour pressure of propan-2-ol over pure propan-2-ol $p_{2-\text{PrOH}}^*$ was calculated according to the corresponding equation of state,⁴ and then the Henry's law constant was determined.

2. Molecular simulation

2.1. Molecular model for argon

The molecular model for argon was developed in Ref.⁹ and it consists of a single Lennard-Jones site. The parameters ε and σ for argon were estimated to be

$$\frac{\varepsilon_{\text{Ar}}}{k_{\text{B}}} = 116.79 \text{ K}, \sigma_{\text{Ar}} = 3.3952 \cdot 10^{-10} \text{ m},$$

where k_{B} is the Boltzmann constant.

2.2. Molecular model for propan-2-ol

The molecular model for propan-2-ol consists of Lennard-Jones united atom sites for the two methyl, the methanetriyl and the oxygen groups, accounting for repulsion and dispersion. Point charges are located on the methanetriyl and the oxygen Lennard-Jones sites, as well as on the nucleus position of the hydroxyl hydrogen. The coulombic interactions account for both polarity and hydrogen bonding. The potential energy u_{ij} between two propan-2-ol molecules i and j is given by

$$u_{ij}(r_{ijab}) = \sum_{a=1}^5 \sum_{b=1}^5 4\varepsilon_{ab} \cdot \left(\left(\frac{\sigma_{ab}}{r_{ijab}} \right)^{12} - \left(\frac{\sigma_{ab}}{r_{ijab}} \right)^6 \right) + \frac{q_{ia} \cdot q_{jb}}{4\pi \cdot \varepsilon_0 \cdot r_{ijab}},$$

where a is the site index of molecule i and b the site index of molecule j , respectively. The site-site distance between molecules i and j is denoted by r_{ijab} . σ_{ab} , ε_{ab} are the Lennard-Jones size and energy parameters, q_{ia} and q_{jb} are the point charges located at the sites a and b on the molecules i and j , respectively. Finally, ε_0 is the permittivity of vacuum. The interaction between unlike Lennard-Jones sites of two propan-2-ol molecules was defined by the Lorentz-Berthelot combining rule.¹⁰ The potential parameters are given in Table S1.

Table S1. Potential parameters of the molecular model for propan-2-ol.

Site	$\sigma_{aa} \cdot 10^{10}$, m	$\frac{\varepsilon_{aa}}{k_{\text{B}}}$, K	q_{ia} , elementary charges
S _{CH₃}	3.9052	106.05	0
S _{CH}	3.238312	20.2	0.309742
S _{OH}	3.153799	85.90353	-0.747203
S _H	0	0	0.437461

2.3. Molecular model for the binary mixture

To describe a binary mixture on the basis of pairwise additive potential models, two types of interactions between the molecules have to be specified. These are the interactions between like and between unlike molecules, where the like interactions are fully known from the pure substance models. The unlike

interactions can be separated into the electrostatic and the repulsive/dispersive contributions. While the former are straightforwardly known from the laws of electrostatics, for the repulsive and dispersive interactions between unlike molecules A and B, the Lennard-Jones parameters σ_{AB} and ε_{AB} have to be determined. In the present study, the modified Lorentz-Berthelot rule was applied that was discussed in detail elsewhere¹¹

$$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}, \quad \varepsilon_{AB} = \xi \cdot \sqrt{\varepsilon_A \cdot \varepsilon_B},$$

where ξ is a state independent binary interaction parameter that can be adjusted to known values of the Henry's law constant.

2.4. Calculation of the Henry's law constant

Several approaches have been proposed in the literature¹² to obtain the Henry's law constant on the basis of molecular models. The Henry's law constant is related to the residual chemical potential of argon in propan-2-ol at infinite dilution μ_{Ar}^∞ ¹³

$$H_{Ar/2-PrOH} = \rho_{2-PrOH} \cdot k_B \cdot T \cdot \exp \frac{\mu_{Ar}^\infty}{k_B \cdot T}.$$

In order to evaluate μ_{Ar}^∞ , Monte Carlo simulations applying Widom's test particle method¹⁴ were implemented. This is feasible due to the fact that the solute molecules are all smaller than propan-2-ol molecules and so acceptable statistics can be achieved. Therefore, test particles representing argon were inserted after each Monte Carlo cycle at random positions into the liquid propan-2-ol and the potential energy between the solute test particle and all solvent molecules ψ_{Ar} was explicitly calculated within the cut-off radius

$$\mu_{Ar}^\infty = \frac{k_B \cdot T \cdot \left\langle V \cdot \exp \frac{\psi_{Ar}}{k_B \cdot T} \right\rangle}{\langle V \rangle},$$

where V is the volume and the brackets represent the NpT ensemble average. The residual chemical potential at infinite dilution and, hence, the Henry's law constant is directly attributed to the unlike solvent-solute interaction and indirectly to the solvent-solvent interaction, which yields the configurations of the solvent molecules. Into these configurations, the test particles of argon are inserted. The mole fraction of argon in propan-2-ol was exactly zero, as required for infinite dilution, because the test particles were instantly removed after the potential energy calculation. Simulations were performed at specified temperature and the according saturated liquid density and vapour pressure of pure propan-2-ol.

2.5. Simulation details

In all simulations $N = 864$ molecules were used. In order to evaluate the Henry's law constant, Monte Carlo simulations were performed. After an equilibration of 20 000 cycles, 3 000 000 production cycles were carried out inserting $4 \cdot N$ test particles after each cycle.

The Lennard-Jones long range interactions beyond the cut-off radius were corrected employing angle averaging.¹⁵ The coulombic interactions were corrected using the reaction field method.¹⁶ The cut-off radius was $1.5 \cdot 10^{-9}$ m.

The simulations were carried out with the software *ms2*¹⁷ on the „Hazel hen“ machine of the high performance computing centre in Stuttgart (hazelhen.hww.de).

3. Results

The experimental data and together with the values calculated in processing these data are collected in Table S2. The saturated vapour pressure of pure propan-2-ol at the temperatures 360, 420 and 480 K, calculated according to the corresponding equation of state⁴ are presented in Table S3. Using these data, the dependence of the phase equilibrium pressure on the mole fraction of argon in liquid propan-2-ol at 360, 420 and 480 K was plotted, which is depicted in Figure S6. As can be seen, functions may well be approximated by straight lines. The slopes of these lines calculated with the least squares technique were used to estimate the Henry's law constant at these temperatures.

The parameter ξ was adjusted such that the differences between the deviations of the simulated values from the experimental results and available literature data were minimal. For the binary mixture argon + propan-2-ol $\xi = 0.964$ was found.

The values of Henry's law constant for the solution of argon in propan-2-ol at various temperatures from the literature, present experiments and simulations together with their statistical uncertainties are collected in Table S4. Figure S7 reveals the good agreement between the literature data and the results of the present work.

Table S3. Saturated vapour pressure of pure propan-2-ol at 360, 420 and 480 K calculated with the PC-SAFT equation of state.⁴

T , K	$p_{2\text{-PrOH}}^*$, MPa
360.00	0.1219
420.00	0.7943
480.00	2.9452

Table S2. Experimental results.

T_m , K	480.00			420.00			360.00		
T_{Ar} , K	303.139	303.178	303.070	303.139	303.178	303.070	303.139	303.150	303.070
p_{Ar} , MPa	1.8147	0.6152	0.1590	1.8147	0.6152	0.1590	1.8147	0.6560	0.1590
ρ_{Ar} , $\text{kg} \cdot \text{m}^{-3}$	29.603	9.784	2.523	29.603	9.784	2.523	29.603	10.436	2.523
$m_{Ar} \cdot 10^5$, kg	43.960	14.529	3.747	43.960	14.529	3.747	43.960	15.497	3.747
T_{2-PrOH}^1 , K	294.050	294.260	293.810	294.050	294.260	293.810	294.050	295.830	293.810
p_{2-PrOH}^1 , MPa	1.860	2.339	3.531	1.860	2.339	3.531	1.860	1.867	3.531
ρ_{2-PrOH}^1 , $\text{kg} \cdot \text{m}^{-3}$	788.113	788.233	789.463	788.113	788.233	789.463	788.113	786.399	789.463
z_1	65.8	48.2	94.9	65.8	48.2	94.9	65.8	76.1	94.9
$V_{2-PrOH}^1 \cdot 10^6$, m^3	28.3521	33.6075	19.6628	28.3521	33.6075	19.6628	28.3521	25.2765	19.6628
$m_{2-PrOH}^1 \cdot 10^3$, kg	22.3447	26.4905	15.5231	22.3447	26.4905	15.5231	22.3447	19.8774	15.5231
T_{2-PrOH}^2 , K	295.350	295.680	295.000	295.580	295.980	295.600	293.650	295.880	294.510
p_{2-PrOH}^2 , MPa	2.037	1.269	2.430	1.364	2.012	2.315	2.259	2.458	2.125
ρ_{2-PrOH}^2 , $\text{kg} \cdot \text{m}^{-3}$	786.979	786.137	787.582	786.298	786.353	786.926	788.766	786.753	787.848
z_2	102.1	85.4	132.5	112.8	94.3	141.3	117.8	126.7	146.8
$V_{2-PrOH}^2 \cdot 10^6$, m^3	17.5129	22.4995	8.4355	14.3179	19.8420	5.8078	12.8249	10.1673	4.1655
$m_{2-PrOH}^2 \cdot 10^3$, kg	13.7823	17.6877	6.6436	11.2581	15.6028	4.5703	10.1158	7.9992	3.2818
$m_{2-PrOH} \cdot 10^3$, kg	8.5624	8.8028	8.8795	11.0866	10.8877	10.9528	12.2289	11.8782	12.2413
$x_{Ar} \cdot 10^3$, mol / mol	71.6915	24.2249	6.3069	56.2877	19.6773	5.1191	51.2996	19.2475	4.5828
p_m , MPa	6.769	4.104	3.070	6.213	2.712	1.105	5.951	2.391	0.613

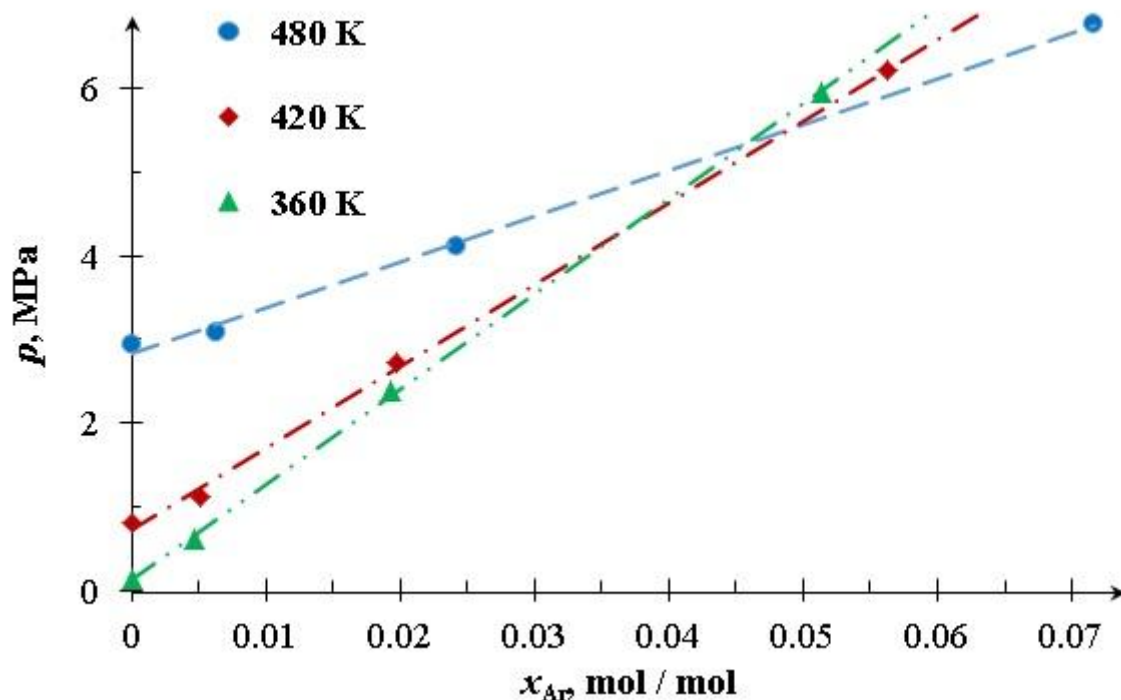


Fig. S6. Dependence of the phase equilibrium pressure over the solutions of argon in propan-2-ol as a function of argon mole fraction at temperatures of 360, 420 and 480 K.

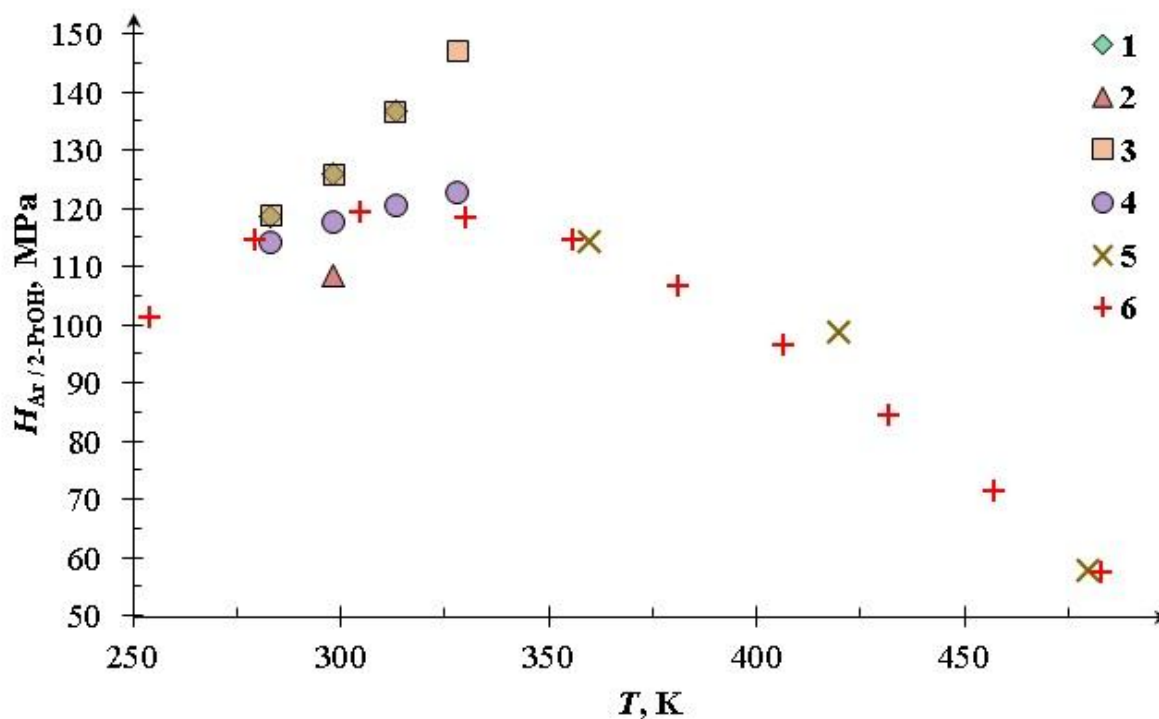


Fig. S7. Henry's law constant for the solution of argon in propan-2-ol: **1** – data from Ref.¹⁸; **2** – data from Ref.¹⁹; **3** – data from Ref.²⁰; **4** – data from Ref.²¹; **5** – this work, experimental values; **6** – this work, simulated values.

Table S4. Henry's law constant for the solution of argon in propan-2-ol at various temperatures.

T , K	$H_{Ar/2-PrOH}$, MPa	Reference
283.15	118.8	18
298.15	125.8	
313.15	136.7	
298.15	108.4	19
283	118.8	20
298	125.9	
313	136.7	
328	147.1	
283.15	114.1	21
298.15	117.8	
313.15	120.6	
328.15	122.7	
360.00 ± 0.04	$114 \pm 2^\dagger$	Experiment, this work
420.00 ± 0.04	99 ± 3	
480.00 ± 0.04	58 ± 3	
254.1	$101.1 \pm 0.9^\ddagger$	Molecular simulation, this work
279.6	114.6 ± 0.8	
305.0	119.3 ± 0.5	
330.4	118.1 ± 0.3	
355.8	114.4 ± 0.3	
381.2	106.4 ± 0.2	
406.6	96.4 ± 0.2	
432.0	84.4 ± 0.1	
457.5	71.4 ± 0.1	
482.9	57.4 ± 0.1	

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[†] The calculation of experimental errors is discussed in Appendix 2.

[‡] Simulation uncertainties relate to the particular molecular model, not to the real fluid.

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Appendices

1. Figures S8, S9 and S10 present a comparison between the thermophysical data for propan-2-ol calculated by the PC-SAFT equation of state⁴ and critically evaluated data provided by the DIPPR database (www.aiche.org/dippr), project 801. This includes the saturated vapour pressure (Figures S8 and S9) and the saturated liquid and vapour density (Figure S10). The comparison reveals a good agreement between the data; the relative difference does not exceed 1%.

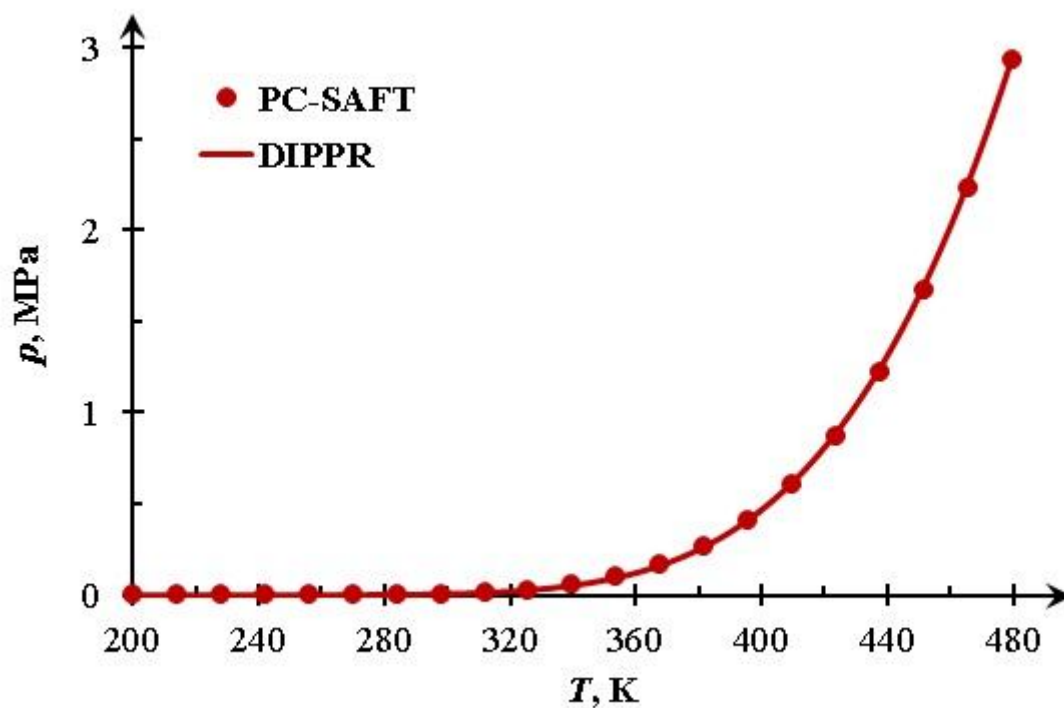


Fig. S8. Comparison between the data for saturated vapour pressure of propan-2-ol calculated by the PC-SAFT equation of state and from the DIPPR database.

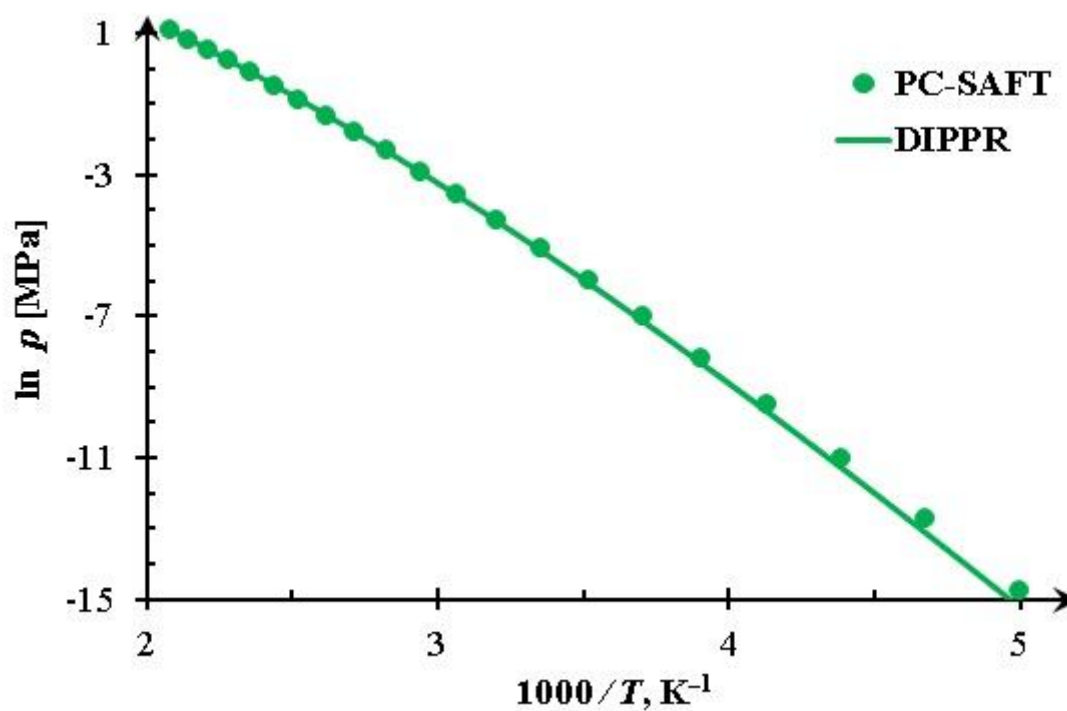


Fig. S9. Comparison between the data for saturated vapour pressure of propan-2-ol calculated by the PC-SAFT equation of state and from the DIPPR database.

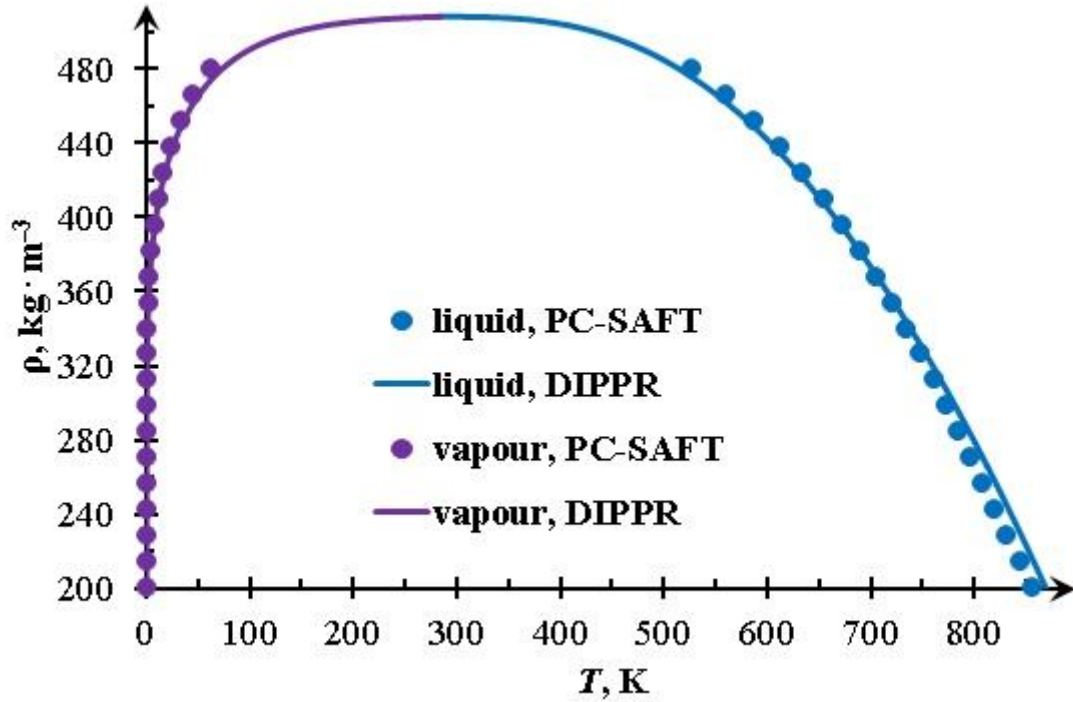


Fig. S10. Comparison between the data for saturated liquid and vapour density of propan-2-ol calculated by the PC-SAFT equation of state and from the DIPPR database.

2. The experimental errors were calculated in the following way.

The maximal uncertainty of argon density calculated by the equation of state² does not exceed 0.2%. It is also influenced by the uncertainties in measured temperature ($\Delta T_{\text{Ar}} = 0.04$ K) and pressure ($\Delta p_{\text{Ar}} = 0.02$ MPa), but the total uncertainty does not exceed 0.5%

$$\Delta \rho_{\text{Ar}} = 0.005 \cdot \rho_{\text{Ar}}.$$

The uncertainties of mass and amount of substance of argon in the experimental mixture are calculated straightforwardly

$$\Delta m_{\text{Ar}} = V \cdot \Delta \rho_{\text{Ar}},$$

$$\Delta n_{\text{Ar}} = \frac{1}{M_{\text{Ar}}} \cdot \Delta m_{\text{Ar}}.$$

Analogously, the maximum uncertainty of the density of propan-2-ol calculated by the equation of state⁴ does not exceed 1%, and together with errors originating from uncertainties terms of the measured temperature and pressure the total uncertainty does not exceed 1.5%

$$\Delta \rho_{2\text{-PrOH}}^1 = 0.015 \cdot \rho_{2\text{-PrOH}}^1,$$

$$\Delta \rho_{2\text{-PrOH}}^2 = 0.015 \cdot \rho_{2\text{-PrOH}}^2.$$

The maximum uncertainty of the volumes occupied by propan-2-ol in the reservoir **H** at the beginning and the end of the experiment is determined by the uncertainty of the number of spindle turns ($\Delta z = 0.02$ turns)

$$\Delta V_{2-\text{PrOH}}^1 = \Delta V_{2-\text{PrOH}}^2 = V'' \cdot \frac{\Delta z}{160.75}.$$

The uncertainty of the mass of propan-2-ol in the reservoir **H** at the beginning and the end of the experiment was calculated by an equation for the uncertainties of indirectly measured quantities²²

$$\begin{aligned}\Delta m_{2-\text{PrOH}}^1 &= V_{2-\text{PrOH}}^1 \cdot \Delta \rho_{2-\text{PrOH}}^1 + \Delta V_{2-\text{PrOH}}^1 \cdot \rho_{2-\text{PrOH}}^1, \\ \Delta m_{2-\text{PrOH}}^2 &= V_{2-\text{PrOH}}^2 \cdot \Delta \rho_{2-\text{PrOH}}^2 + \Delta V_{2-\text{PrOH}}^2 \cdot \rho_{2-\text{PrOH}}^2.\end{aligned}$$

The uncertainties of mass and amount of substance of propan-2-ol in the mixture were calculated straightforwardly

$$\begin{aligned}\Delta m_{2-\text{PrOH}} &= \Delta m_{2-\text{PrOH}}^1 + \Delta m_{2-\text{PrOH}}^2, \\ \Delta n_{2-\text{PrOH}} &= \frac{1}{M_{2-\text{PrOH}}} \cdot \Delta m_{2-\text{PrOH}}.\end{aligned}$$

The uncertainty of argon mole fraction in the mixture was calculated by²²

$$\Delta x_{\text{Ar}} = x_{\text{Ar}} \cdot \sqrt{\left(\frac{\partial \ln x_{\text{Ar}}}{\partial n_{\text{Ar}}} \cdot \Delta n_{\text{Ar}} \right)^2 + \left(\frac{\partial \ln x_{\text{Ar}}}{\partial n_{2-\text{PrOH}}} \cdot \Delta n_{2-\text{PrOH}} \right)^2}.$$

The slope of the graph in the coordinates $p_m - x_{\text{Ar}}$ was calculated using the least squares technique. When both variables have the errors, the uncertainty of the calculated slope consists of both systematic (Δ_{sys}) and random (Δ_{rand}) errors. The former one is calculated as described in Ref.²³, and the later one as usual.^{8,22} Then the total uncertainty is given by

$$\Delta(H_{\text{Ar}/2-\text{PrOH}} - p_{2-\text{PrOH}}^*) = \sqrt{\Delta_{\text{sys}}^2 + \Delta_{\text{rand}}^2}.$$

The maximum uncertainty of the saturated vapour pressure of propan-2-ol calculated by the equation of state⁴ does not exceed 1%

$$\Delta p_{2-\text{PrOH}}^* = 0.01 \cdot p_{2-\text{PrOH}}^*.$$

Finally, the uncertainty of Henry's law constant for the solution of argon in propan-2-ol is calculated by

$$\Delta H_{\text{Ar}/2-\text{PrOH}} = \Delta(H_{\text{Ar}/2-\text{PrOH}} - p_{2-\text{PrOH}}^*) + \Delta p_{2-\text{PrOH}}^*.$$