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An experimental investigation on the solubility of methane in 1-octanol and n-dodecane at ambient temperatures

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ABSTRACT

The synthetic method is used for the determination of the liquid phase solubility of methane in 1-octanol at three temperatures (273.25, 283.15, and 293.2) K and of methane in n-dodecane at 273.1 K at pressures up to about 10 MPa. The new gas solubility data is applied to evaluate the molality scale based Henry's constant of methane in those solvents: (4.31, 4.67, and 4.81 ± 0.05) MPa in 1-octanol and (2.75 ± 0.04) MPa in n-dodecane at the given temperatures, respectively. The experimental technique provides as well the density of the gas-saturated liquid phase and thus allows for evaluation of the partial molar volume of methane at infinite dilution in the solvent: (47, 49, and 49 ± 5) cm^3/mol in 1-octanol and (45 ± 5) cm^3/mol in n-dodecane, respectively. The experimental results are compared with the limited data from the open literature. At the investigated temperatures, the vapour phase can be treated as pure methane, and the extended Henry's law suffices to accurately correlate the new gas solubility data. However, that vapour-liquid equilibrium model is here expanded allowing to accurately predict the small vapour phase solubility of the solvent in compressed methane which is demonstrated by comparison with experimental data from the literature.

1. Introduction

Extending recently published experimental investigations for the solubility of methane in the pure solvents water [1], n-hexane and a hydrocarbon mixture [2], new experimental results are presented for the solubility of methane in 1-octanol at three temperatures (273.25 K, 283.15 K, and 293.2 K) and for the solubility of methane in n-dodecane at 273.1 K at pressures up to about 10 MPa. The *prime aim* of the present work is to verify and widen the very limited solubility data pool of these systems which is available in the open literature.

Like in that previous work, we applied the synthetic method (with a high pressure, constant volume view cell) for determination of the gas solubility. The experimental results are evaluated to determine Henry's constant of methane in the pure solvents 1-octanol and n-dodecane and the density of the gas saturated liquid phase. This allows as well to determine the partial molar volume of methane at infinite dilution in the pure solvents. The experimental results are compared with the few literature data.

Combining the new results for Henry's constant and the partial molar volume (of methane in the single solvents) in an extension of Henry's law allows to reliably *correlate* the influence of pressure and temperature on the solubility of methane in the solvent. That correlation assumes that the partial pressure of the solvent in the vapour phase is so small that it can be neglected. Furthermore, the activity of methane in the liquid phase is described with an equation based on Pitzer's approach for the Gibbs excess energy (on a molality scale basis) that relies on one single—solvent and temperature dependent—parameter. Finally, the fugacity of the pure gas in the vapour phase is calculated from an accurate equation of state.

Expanding this model by additionally applying an extension of Raoult's law to the solvent component, as well as by describing the fugacities of gas and solvent components in the vapour phase with a reliable equation of state for the gas mixture, allows to *predict* the small vapour phase solubility of the solvent in compressed methane. The *second aim* of the present work is to demonstrate that by linking confident experimental gas solubility data with a good model for the vapour liquid equilibrium, it is possible to reliably predict the small fraction of the solvent in the vapour phase (cf. Refs. [1,2]). This is confirmed by comparison of prediction results with experimental data from the literature.

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2. Experimental arrangement and materials

2.1. Apparatus and method

The experimental technique for determination of *gas solubility* follows the principles of the *synthetic method*. In an experiment the pressure p was measured that is required to dissolve at temperature T a known amount of methane (component 1) in a known amount of solvent (component 2, either 1-octanol or n-dodecane) in a high-pressure cell of constant volume V. In vapour-liquid equilibrium the ratio of vapour-phase volume to liquid-phase volume is very small (typically 0.0001), i.e., the volume occupied by the liquid phase can be approximated by the volume of the high-pressure cell. That (slightly temperature dependent) volume was determined in an independent experiment. The apparatus is suited for experiments at pressures between about (0.3 and 20) MPa. It was used in many prior experimental investigations. Most recent publications report experimental results for the solubility of methane in water [1] and in n-hexane as well as in a hydrocarbon mixture [2]. Details of the equipment, the experimental procedure, and the evaluation of the direct experimental results have been reported before (see for example, Rumpf [3], Rumpf and Maurer [4], Xia et al. [5], and Pérez-Salado Kamps et al. [6]). In previous publications (see, for example, Jödecke et al. [7,12]) the experimental uncertainties were given. These estimates are also valid for the present investigation—they are not repeated here, but the experimental results are reported together with their estimated standard uncertainty.

2.2. Materials and sample pretreatment

Table 1 reports details of all materials used (CAS-No., supplier, purity (as listed by the supplier), and relative molar mass). Methane was used without further purification. The solvents were degassed by vacuum distillation.

3. Experimental results and data evaluation

3.1. Gas solubility and volumetric data

The solubility of methane in 1-octanol was measured at three temperatures $T = (273.25$ K, 283.15 K and 293.2 K) that are all close to ambient temperature, and total pressures p from about (1–10) MPa. The solubility of methane in n-dodecane was measured at one single temperature $T = 273.1$ K and pressures between about (1 and 9) MPa. The experimental results are listed into Tables 2 and 3. The solubility of methane is reported in terms of molality m_1 that is the amount of methane (the number of moles) per kilogram of pure solvent. Furthermore, the ratio of cell volume V to the mass $\tilde{m}_2$ of gas-free solvent and the density ρ of the methane-saturated liquid phase, which are side-products of the gas solubility experiments, are also given. That density was calculated from:

$$\rho = \frac{\tilde{m}_2}{V} \cdot \left(1 + \frac{m_1}{m^o} \cdot \frac{M_1}{1000}\right) \tag{1}$$

with $m^o = 1$ mol/(kg gas-free solvent) and M_1 as the relative molar mass of methane.

Table 2
Experimental results (and standard uncertainties) for the solubility of CH_4 (1) in 1-octanol (2).[a]

$\frac{m_1}{\text{mol/(kg (2))}}$	$\frac{p}{\text{MPa}}$	$\frac{V/\tilde{m}_2}{\text{cm}^3\text{/(g (2))}}$	$\frac{\rho}{\text{g/cm}^3}$
T/K = 273.25 ± 0.1			
0.456 ± 0.004	2.076 ± 0.035	1.202	0.838
0.662 ± 0.004	2.936 ± 0.036	1.212	0.834
0.915 ± 0.004	4.011 ± 0.038	1.225	0.828
1.096 ± 0.005	4.802 ± 0.040	1.236	0.823
1.293 ± 0.005	5.688 ± 0.041	1.245	0.820
1.560 ± 0.005	6.820 ± 0.044	1.256	0.816
1.822 ± 0.006	8.058 ± 0.046	1.269	0.811
2.083 ± 0.007	9.338 ± 0.049	1.280	0.807
2.231 ± 0.007	10.06 ± 0.05	1.284	0.807
T/K = 283.15 ± 0.1			
0.318 ± 0.003	1.502 ± 0.033	1.206	0.833
0.591 ± 0.004	2.801 ± 0.037	1.221	0.827
0.811 ± 0.004	3.793 ± 0.039	1.233	0.822
1.030 ± 0.004	4.765 ± 0.041	1.245	0.817
1.178 ± 0.005	5.489 ± 0.042	1.246	0.818
1.524 ± 0.005	7.110 ± 0.045	1.264	0.811
1.819 ± 0.006	8.530 ± 0.048	1.281	0.803
2.150 ± 0.007	9.966 ± 0.052	1.297	0.798
T/K = 293.2 ± 0.1			
0.204 ± 0.003	1.058 ± 0.033	1.224	0.820
0.409 ± 0.004	1.985 ± 0.037	1.224	0.822
0.581 ± 0.004	2.842 ± 0.037	1.227	0.823
0.756 ± 0.004	3.654 ± 0.039	1.241	0.816
1.135 ± 0.005	5.598 ± 0.042	1.261	0.808
1.424 ± 0.005	7.079 ± 0.044	1.272	0.804
1.750 ± 0.006	8.696 ± 0.048	1.288	0.798
2.011 ± 0.006	10.14 ± 0.05	1.289	0.801

[a] The standard uncertainties for the ratio of cell volume to the mass of gas-free 1-octanol ($V/\tilde{m}_2$) and for the density of the methane-saturated liquid phase ρ are estimated to ±0.7%.

Table 3
Experimental results (and standard uncertainties) for the solubility of CH_4 (1) in n-dodecane (2).[a]

$\frac{m_1}{\text{mol/(kg (2))}}$	$\frac{p}{\text{MPa}}$	$\frac{V/\tilde{m}_2}{\text{cm}^3\text{/(g (2))}}$	$\frac{\rho}{\text{g/cm}^3}$
T/K = 273.1 ± 0.1			
0.315 ± 0.004	0.909 ± 0.030	1.317	0.763
0.643 ± 0.004	1.775 ± 0.032	1.334	0.757
1.037 ± 0.005	2.811 ± 0.033	1.351	0.753
1.335 ± 0.005	3.578 ± 0.035	1.364	0.749
1.718 ± 0.006	4.518 ± 0.038	1.382	0.744
2.047 ± 0.007	5.361 ± 0.040	1.394	0.741
2.571 ± 0.008	6.686 ± 0.043	1.418	0.734
3.019 ± 0.009	7.729 ± 0.047	1.438	0.729
3.466 ± 0.012	8.805 ± 0.050	1.462	0.722

[a] The standard uncertainties for the ratio of cell volume to the mass of gas-free n-dodecane ($V/\tilde{m}_2$) and for the density of the methane-saturated liquid phase ρ are estimated to ±0.7%.

The experimental results for the solubility pressure are plotted against the ratio of methane molality m_1 to m^o in Fig. 1.

As expected, the solubility pressure depends almost linearly on the gas molality. For 1-octanol the slope of the isotherms (expressed as MPa per mole of methane in 1 kg of solvent) increases from approximately 4.5 at 273 K to about 5.0 at 293 K, i.e., the

Table 1
Sample description.

Chemical	CAS No.	Purity (volume fraction)	Relative molar mass	Supplier
methane	74-82-8	≥0.995	16.04	Air Liquide, Germany
1-octanol	111-87-5	≥0.99	130.23	Sigma-Aldrich, Traufkirchen, Germany
n-dodecane	112-40-3	≥0.99	170.33	Sigma-Aldrich, Traufkirchen, Germany