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Pressure dependence of the solubility of light fullerenes in 1-hexanol from 298.15 K to 363.15 K

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ABSTRACT

The solubility of light fullerenes (C_{60} and C_{70}) in 1-hexanol was investigated in the range of pressures of 0.1–100 MPa and in the range of temperatures of 298.15–363.15 K. In all of the studied temperatures, solubility increases monotonously with increasing pressure. At ambient pressure, we have found that the temperature dependence of solubility in the binary system C_{60}–1-hexanol is non-monotonic: the solubility diagram consists of two branches corresponding to the crystallization of different solid phases and one invariant point corresponding to the simultaneous saturation of both phases (monosolvated fullerene C_{60} and non-solvated C_{60}). The composition of the solid crystallosolvate was determined by thermogravimetric analysis. The solubility diagram of the binary system C_{70}–1-hexanol in the temperature range of 298.15–328.15 K at 0.1 MPa consists of only one branch corresponding to the crystallization of non-solvated C_{70}.

1. Introduction

The knowledge of the solubility of light fullerenes in various solvents is important in many of its practical applications, but it is also an essential tool for verifying the established regularities of the thermodynamics of nonelectrolytes. Today there is a large number of articles on experimental solubility data of the individual light fullerenes (C_{60} and C_{70}) and industrial fullerene mixtures of different compositions, which were recently reviewed by Semenov et al. [1] and McHedlov-Petrossyan [2]. This last author concludes that molecular solutions of C_{60} may possess a dual nature: a non-electrolyte solution and a lyophobic colloidal system, and that for this kind of mixture, the theory of molecular solutions and the concepts of colloid chemistry are colliding.

Much experimental data have been reported concerning the solubility of light fullerenes for binary systems composed by an individual fullerene–pure solvent or pseudo-binary systems (fullerene mixtures of constant composition–pure solvent) at atmospheric pressure [3–14]. Data on solubility on the ternary systems fullerene C_{60}–fullerene C_{70}–pure solvent or fullerene C_{60} (or fullerene C_{70})–solvent (1)–solvent (2) are much more scarce and incomplete [15–18]. Additionally, the solubility of light fullerenes was measured for multicomponent systems composed by individual light fullerenes or industrial fullerene mixtures and biocompatible solvents (vegetable oils, essences, animal fats, fatty acid esters, etc.) [19–23]. These data may be easily used in food industry, pharmacology or perfumery, medicinal chemistry and cosmetics [24–27].

Analysis of literature shows that experimental values on pressure dependence of the light fullerene solubility are few [28,29]. This fact is due to the considerable difficulty of such experimental investigations. Up to now, solubility of fullerenes at high pressures was investigated only for two binary systems: fullerene C_{60}–toluene and fullerene C_{60}–n-hexane [28,29]. Let us describe briefly the main results obtained in these articles. Sawamura and Fujita [28] investigated the pressure dependence of solubility for the binary (C_{60}–n-hexane) system at 298.15 K up to 400 MPa. The solubility of C_{60} strongly increases when the pressure increases, although for molecular solids the solubility usually decreases. This unusual pressure dependence of C_{60} solubility was explained by the authors to be due to the higher molar volume of the solid fullerene as compared with its partial molar volume in hexane, i.e., the molar volume of C_{60} in the crystal decreases with solvation. The decreasing of the C_{60} molar volumes causes a typical effect on the increase of solubility with the increasing of pressure according to Planck–van Laar equation:

$$\left(\frac{d\ln x^{(l)}_{C_{60}}}{dp}\right)_T = -\frac{\Delta V}{RT} \tag{1}$$

where ΔV is the change of molar volumes of C_{60} in the process of transition from solid crystalline C_{60} to saturated solution (this equation is absolutely correct in the cases of ideal or infinitely diluted solution).

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On the other hand, the article of Sawamura and Fujita [29] should be noted especially because it is the first time that a three-dimensional *pTx* diagram for a binary system containing fullerene appears. Thus, these authors investigated the binary C_{60}–toluene system in a wide range of temperatures (T) and pressures (p), and found a maximum on the solubility within the range of 43–111 MPa, depending on temperature. These results were explained assuming the existence of "crystalline solvates" (i.e., solids with intercalated solvent molecules). Adamenko et al. [30,31] carried out *pVT* measurements in the binary (C_{60}–toluene) and (C_{60}–water) systems in the temperature range of 313–371 K and in the pressure range of 0.1–103.1 MPa [30,31].

In this work, the solubility of light fullerenes (C_{60} and C_{70}) in 1-hexanol was measured from ambient pressure to 100 MPa and from 298.15 K to 363.15 K in order to analyze how the pressure affects the solubility at several temperatures. It should be marked that temperature dependences of the individual light fullerenes and industrial fullerene mixture solubility in 1-alkanols $C_nH_{2n+1}OH$ (n = 1–11) were extensively studied previously only at atmospheric pressure [1,12–14, 32–35]. Semenov et al. [32,33] have studied the temperature dependences of solubility of the individual light fullerenes in alkanols (C_1–C_{11}) in the temperature range (293 to 353) K as well as the solubility of industrial fullerene mixture (39% C_{70}; 60% C_{60}; 1% C_n (n > 70)). Heyman [34,35] has studied the solubility of individual light fullerenes at 293.15 K in alkanols.

2. Experimental section

2.1. Materials

We have used samples of C_{60} fullerene (99.9 wt.%) and C_{70} fullerene (99.5 wt.%) purchased from ILIP, St. Petersburg, with controllable principal admixtures of C_{70} in C_{60} and C_{60} in C_{70} of (0.1 and 0.5) wt.%, correspondingly. 1-Hexanol sample was anhydrous (>99 wt.%), purchased from Sigma Aldrich.

2.2. Solubility measurement techniques at atmospheric pressure

The concentrations of C_{60} and C_{70} fullerenes in liquid 1-hexanol at atmospheric pressure at saturated conditions in the temperature range of 298.3–363.3 K were measured with a spectrophotometric technique (using the double-beam spectrophotometer Specord M40 made in Germany, Karl Zeiss) at characteristic wavelengths of (335 and 472) nm corresponding to the maximum absorbance. The accuracy of wavelength maintenance was 0.5 nm, the photometric accuracy (ΔD) was equal to 0.005, and the thickness of the absorption layer was 1 cm. The overall uncertainty of the concentrations of light fullerenes (C_{60} and C_{70}) in a saturated solution was nearly 5%. The temperature dependence of the solubility of light fullerenes (C_{60} and C_{70}) in 1-hexanol from 293.15 K to 363.15 K at atmospheric pressure was determined using a temperature-controlled magnetic stirrer. The saturation time was 8 h; the temperature was maintained with accuracy equal to ±0.1 K. The following experimental method was used for the determination of the solvent content in solid crystal solutes. The solid phase deposited from 1-hexanol solution was filtered on a Schott filter (porosity factor 10), rinsed quickly with ethanol, and then dried for (10 to 15) min at 293 K. The solid phase was then weighted, repeatedly washed with ethanol in a Soxhlet apparatus at 351 K and 1 atm, dried for 1 h under vacuum (13.3 Pa) at 473 K, and weighed again. The weight change corresponded to the solvent content in the initial crystal solutes. The described experimental method for the determination of solid phase compositions was verified by thermogravimetric analysis under nitrogen atmosphere on Hungarian thermo-gravimeter Q-1500, from 298.15 to 523.15 K, and the heating rate of 5 K/min.

2.3. Solubility measurement technique at high pressures

Phase equilibria measurements have been performed in a pressure cell recently used for the investigation of the phase equilibria of two carbon dioxide–biodegradable oil systems [36]. The apparatus was slightly modified to perform the measurements of this work. The new scheme is shown in Fig. 1. The cell is constructed in stainless steel, and supports working pressures and temperatures of up to 100 MPa and 423 K, respectively. A video acquisition system is located in front of a sapphire window for viewing inside the measuring cell. A pressure transducer (Kulite, model HEM375), directly connected to minimize the dead volumes, allows to measure the pressure with a typical uncertainty less than ±0.03 MPa. The temperature is kept constant by circulating a fluid from a thermostatic bath through three internal lines in the cell wall, and it is measured with an uncertainty of ±0.02 K by means of a Pt100 probe. The operating procedure was as follows: initially the cell was charged with a known amount of the light fullerene (C_{60} and C_{70}) solution in 1-hexanol precisely measured with a Sartorius MC210P balance (the light fullerene concentration in the initial solution was

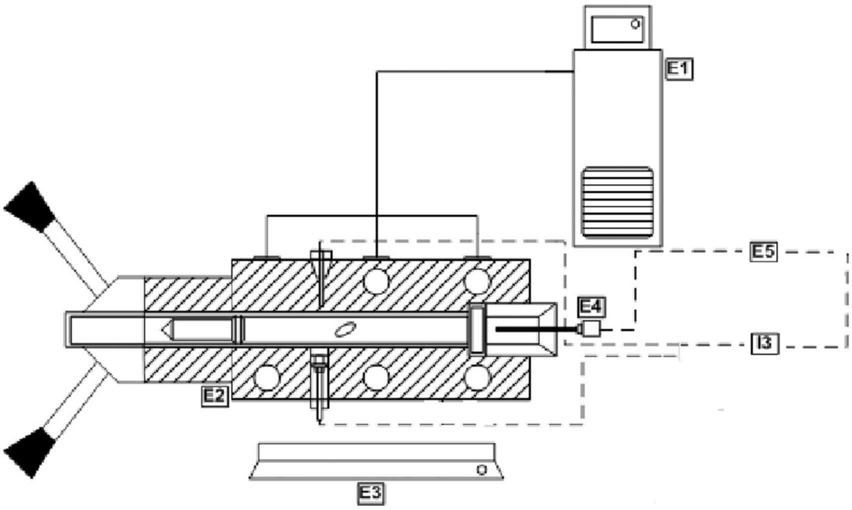

Fig. 1. Schematic experimental set-up of the phase equilibrium equipment. (E1) Thermostatic bath, (E2) high pressure cell, (E3) magnetic stirrer, (E4) endoscope and video camera, (E5) computer and (I3) data acquisition unit.