J. Chem. Thermodynamics 112 (2017) 259–266

Contents lists available at ScienceDirect

J. Chem. Thermodynamics

journal homepage: www.elsevier.com/locate/jct

Pressure dependence of the solubility of light fullerenes in *n*-nonane

Konstantin N. Semenov [a,*], Nikolay A. Charykov [c], Enriqueta R. López [b], Josefa Fernández [b], Vladimir V. Sharoyko [a], Igor V. Murin [a]

[a] Institute of Chemistry, Saint-Petersburg State University, Saint-Petersburg 198504, Universitetskii pr. 26, Russia
[b] Nafomat Group, Applied Physics Department, Santiago de Compostela University, Santiago de Compostela E-15782, Spain
[c] Saint-Petersburg State Technological Institute (Technical University), Saint-Petersburg 190013, Moskovskii pr. 26, Russia

ARTICLE INFO

Article history:
Received 12 July 2016
Received in revised form 25 April 2017
Accepted 11 May 2017
Available online 13 May 2017

Keywords:
Light fullerenes
C_{60}
C_{70}
Solubility
High pressure
n-Nonane

ABSTRACT

Solubility of light fullerenes (C_{60} and C_{70}) in *n*-nonane was investigated in the ranges of pressure form 0.1 MPa up to 100 MPa and temperature from 298.3 K to 353.3 K. Under isothermal conditions, the solubility, expressed as weight fraction of the fullerene in the solution, increases monotonously with increasing pressure. At ambient pressure, we have found that the temperature dependence of the solubility of C_{60} in *n*-nonane is non-monotonic: the solubility diagram consists of two branches corresponding to crystallization of different solid phases and one invariant point corresponding to simultaneous saturation of both phases. At 0.1 MPa, the solubility diagram of the binary system C_{70} – *n*-nonane in the analysed temperature range consists of only one branch corresponding to crystallization of non-solvated C_{70}.

1. Introduction

In recent years one of the most developing areas of modern chemistry is physical chemistry of nanostructures, in particular of carbon nanoclusters (fullerenes and their derivatives) [1–3]. These compounds present unique properties in the context of electronic structure, physical and chemical properties [1].

Phase equilibria research of systems containing fullerenes is extremely important for the development of extraction and crystallization isolation of fullerenes from the fullerene mixture and fullerene black, for elaboration of chromatographic and pre-chromatographic methods of the fullerenes separation, for investigation of chemical reactions in systems containing fullerenes, for preparation of biologically active phases based on fullerenes and for optimization of the light fullerenes applications as nanomodifiers, among others [4–9]. The great relevance of this research topic in the fullerene-containing systems can be easily illustrated by the large amount of experimental data on solubility of individual light fullerenes (C_{60} and C_{70}) in various organic and inorganic solvents as well as in solvent mixtures under different *T*, *P* conditions [4–20]. In this regard, several reviews on phase equilibria of fullerene-containing systems as well as on physicochemical properties of fullerene solutions were published [4–7]. In addition, extraction equilibria in several systems (C_{60} – C_{70} – o-xylene – butylamine – H_2O, C_{60} – C_{70} – o-xylene – monoethanolamine, C_{60} – C_{70} – o-xylene – dymethylformamide – H_2O, C_{60} – C_{70} – toluene – dymethylformamide – H_2O, C_{60} – C_{70} – α – pinene – ethanol – H_2O, C_{60} – C_{70} – o-xylene – ethanol – H_2O, C_{60} – C_{70} – 1,2,4-trichlorobenzene – ethanol – H_2O) were studied [7,9]. These systems can be effectively used for purification of light fullerenes and for separation of industrial fullerene mixtures. Another set of scientific papers is devoted to investigation of sorption equilibria in systems containing fullerenes. In particular, authors of Refs. [21–23] investigated the adsorption properties of the Norit-Azo carbon and multi-walled carbon nanotubes (MWCNT) in relation to light fullerenes.

The present paper is devoted to the investigation of individual light fullerenes solubility in *n*-nonane in the temperature range from 298.3 K to 353.3 K and pressures up to 100 MPa, as well as to the thermodynamic description of the obtained experimental data. Analysis of the literature reveals that the experimental data concerning the *P-T-x* diagrams of binary fullerene-solvent systems are scarce due to the considerable difficulty of such experimental investigations. Up to this time, only few systems were studied: C_{60}-1-hexanol and C_{70}-1-hexanol (in the ranges of pressure 0.1 MPa–100 MPa and temperature 298.15 K–363.15 K) [24], C_{60} – toluene [25] (in the range of temperatures from 278.2 K to 308.2 K and pressures up to 340 MPa), C_{60} – n-hexane [26] (at 298.15 K in the range of pressure up to 400 MPa), C_{60} – toluene and C_{60} – water (in the temperature range 313 K–371 K and in the range of pressure 0.1 MPa–103.1 MPa) [27,28]. It is noteworthy

* Corresponding author.
E-mail address: k.semenov@spbu.ru (K.N. Semenov).

http://dx.doi.org/10.1016/j.jct.2017.05.017
0021-9614/

that no studies on the solubility at atmospheric pressure of the individual light fullerenes in *n*-nonane were performed.

2. Experimental

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 C_{70} in C_{60} and C_{60} in C_{70} of (0.1 and 0.5)% wt, respectively. The *n*-nonane sample was anhydrous (>99% wt) and purchased from Sigma Aldrich. The samples were used without further purification. The characteristics of the samples are indicated in Table 1.

2.2. Solubility measurements techniques at atmospheric pressure

The temperature dependence of the light fullerenes (C_{60} or C_{70}) solubility in *n*-nonane in the temperature range 293.3 K–353.3 K was carried out by the method of isothermal saturation in ampoules. The saturation time was equal to 8 h. Temperature was measured with an uncertainty of 0.1 K (k = 2). For the saturation of the fullerene solutions, a thermostatic shaker (LAUDA ET 20) was used at a shaking frequency $\omega \approx 80$ Hz. The fullerenes concentrations (after the dilution and cooling of saturated solutions) was determined using a double-beam spectrophotometer (Specord M40, Karl Zeiss, Germany) at characteristic wavelengths of (335 and 472) nm corresponding to the maximum absorbance. The accuracy of wavelength was 0.5 nm, the photometric accuracy (ΔD) was 0.005, and the thick of the absorption layer was 1 cm. The experimental method was previously used to study the C_{60} (or C_{70}) solubility in 1-hexanol [24]. The relative expanded uncertainty of the solubility values was 10%. Relative air humidity was (40–50)%.

For the determination of the solvent content in solid crystal solutes, the following experimental method was used. The solid phase deposited from *n*-nonane solution was filtered on a Schott filter (porosity factor 10), rinsed quickly with ethanol, and then dried for (10–15) min at 293 K. Then, the solid phase was weighted, repeatedly washed with ethanol in a Soxhlet apparatus at 351 K and 0.101 MPa, dried for 1 h under vacuum (13.3 Pa) at 473 K, and weighed again. The weight change corresponded to the *n*-nonane content in the initial crystal solutes. The estimated uncertainty the solid solvate concentration in the mixture is 5% (k = 2).

2.3. Solubility measurement technique at high pressures

High pressure phase equilibria measurements have been performed in a cylindrical stainless steel variable-volume view cell. Both the experimental device and procedure have been described in detail previously [29]. The cell supports working pressures and temperatures up to 100 MPa and 423 K, respectively. Two sapphire windows are located in the front and in the lateral wall of the cell. The second one permits lighting inside the cell whereas in the first one it is located an endoscope which allows us observe the sample under study. The pressure is measured by means of a pressure transducer (Kulite, model HEM375) with a typical uncertainty less than ± 0.03 MPa. The temperature is measured with a Pt100 probe with an uncertainty of ±0.02 K. Initially the cell was charged with a known amount of solution of the light fullerene (C_{60} or C_{70}) in *n*-nonane precisely measured with a Sartorius MC210P balance. The light fullerene concentration in this initial solution was determined using the spectrophotometric method. After that a weighted sample of fullerene powders was added to the cell. Under isothermal conditions, the mixture of known composition was compressed to achieve a single phase under continuous stirring. For a fixed temperature, several trials have been performed, being the lowest value associated to the experimental equilibrium pressure. After that, a new temperature is setup. When all the selected temperatures are investigated, a new portion of fullerene (C_{60} or C_{70}) was added. The overall uncertainty of the fullerene weight fraction is 10% (k = 2). For the equilibrium pressure the uncertainty is 0.1 MPa (k = 2).

Table 1
Provenance and mass fraction purity of the samples studied in this work.

Name	Supplier	Mole fraction purity[a]	Analysis method
n-Nonane	Aldrich	>0.99	Gas chromatography
C_{60}	ILIP	0.999	Liquid chromatography
C_{70}	ILIP	0.995	Liquid chromatography

[a] The purity analysis was performed by supplier.

3. Results and discussion

3.1. Experimental values for solubility of C_{60} or C_{70} in n-nonane

Table 2 contains values to illustrate the temperature dependence of solubility of the individual fullerenes (C_{60} or C_{70}) in

Table 2
Solubility of individual light fullerenes (C_{60}, C_{70}) in *n*-nonane at 0.1 MPa. *w* is the mass fraction of fullerene in the saturated solution in weight percentage, *T* – temperature.

T/K	*w* (C_{60})/%	Solid phase	*w* (C_{70})/%	Solid phase
298.3	0.0044	C_{60}·*n*-C_9H_{20}	0.0030	C_{70}
	0.0043		0.0028	
	0.0044		0.0029	
303.3	0.0045	C_{60}·*n*-C_9H_{20}	0.0032	C_{70}
	0.0046		0.0027	
	0.0044		0.0033	
308.3	0.0045	C_{60}·*n*-C_9H_{20}	0.0036	C_{70}
	0.0043		0.0034	
	0.0045		0.0037	
313.3	0.0046	C_{60}·*n*-C_9H_{20}	0.0049	C_{70}
	0.0046		0.0052	
	0.0043		0.0049	
318.3	0.0047	C_{60}·*n*-C_9H_{20}	0.0071	C_{70}
	0.0046		0.0070	
	0.0048		0.0068	
322.3	0.0082	C_{60}·*n*-C_9H_{20}		
	0.0081			
	0.0080			
323.3	0.0139	C_{60}·*n*-C_9H_{20} + C_{60}	0.0090	C_{70}
	0.0140		0.0089	
	0.0142		0.0091	
328.3	0.0149	C_{60}	0.0105	C_{70}
	0.0146		0.0108	
	0.0145		0.0104	
333.3	0.0155	C_{60}	0.0108	C_{70}
	0.0151		0.0110	
	0.0152		0.0108	
338.3	0.0158	C_{60}	0.0120	C_{70}
	0.0161		0.0121	
	0.0162		0.0119	
343.3	0.0165	C_{60}	0.0137	C_{70}
	0.0174		0.0136	
	0.0176		0.0138	
348.3	0.0207	C_{60}	0.0151	C_{70}
	0.0198		0.0151	
	0.0196		0.0149	
353.3	0.0225	C_{60}	0.0162	C_{70}
	0.0222		0.0160	
	0.0223		0.0158	

Expanded uncertainties (k = 2) are U(*T*) = ±0.1 K, $U_r(p)$ = 0.5% and $U_r(w)$ = 10%.