Journal of Molecular Liquids 256 (2018) 305–311

Contents lists available at ScienceDirect

Journal of Molecular Liquids

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

Excess thermodynamic functions in aqueous systems containing soluble fullerene derivatives

Nikolay A. Charykov [a], Konstantin N. Semenov [b,*], Enriqueta R. López [c], Josefa Fernández [c], Evgeny B. Serebryakov [b], Viktor A. Keskinov [a], Igor V. Murin [b]

[a] Saint-Petersburg State Technological Institute, Technical University, St. Petersburg 190013, Moskovskii pr., 26, Russia
[b] Saint-Petersburg State University, St. Petersburg 198504, Universitetskii pr. 26, Russia
[c] Thermophysical Properties Laboratory, NaFoMat Group, Applied Physics Department, University of Santiago de Compostela, Santiago de Compostela E-15782, Spain

ARTICLE INFO

Article history:
Received 16 September 2017
Received in revised form 17 January 2018
Accepted 30 January 2018
Available online 02 February 2018

Keywords:
Fullerene derivatives
Cryoscopy
Depression of freezing point
Activity coefficients
Gibbs energy

ABSTRACT

Using a Beckman thermometer, the concentration dependence of water crystallization temperatures was investigated for $C_{60}(OH)_{22-24}$ – H_2O, $C_{70}(OH)_{12}$ – H_2O, $C_{70}[C(COOH)_2]_3$ – H_2O, $C_{60}(C_5H_9NO_3)_2$ - H_2O, $C_{60}(C_6H_{14}N_2O_2)_2$ – H_2O binary systems. The semi-empirical Virial Decomposition Asymmetric Model of virial expansion of the excess Gibbs energy of the light fullerene derivatives solutions was applied. On the basis of the proposed model, partial and average molar thermodynamic functions of binary solutions as well as the conditions of stability against phase separation were determined.

1. Introduction

Investigation of water soluble derivatives of light fullerenes (in particular fullerenols, carboxylated derivatives of fullerenes and light fullerene derivatives with amino acids and peptides) is at a leading edge of nanoscience and nanobiotechnology [1–3]. This fact is connected with a variety of application methods of the light fullerene derivatives in different fields of science and technology especially in nanobiotechnology and nanomedicine due to the unique properties of these compounds such as: cytotoxicity against human tumor cell lines; effects on cell cycle and apoptosis, in vivo radioprotective and cardioprotective effects, antioxidative and free radical scavenger activities, protective effects against various cytotoxic drugs and irradiation [1–6].

The present article is devoted to the investigation of excess thermodynamic functions of systems containing water soluble fullerene derivatives (fullerenols, carboxylated fullerenes, light fullerene derivatives with amino acids, in particular with L-lysin, and L-hydroxyproline). For the thermodynamic description of the light fullerene derivatives aqueous solution, we have applied the semi-empirical VD-AS model (Virial Decomposition Asymmetric Model) model [7]. This model is based on the virial expansion of the excess Gibbs energy according to mole numbers of the system components. This method was previously applied for description of electrolyte solutions [8–10], non-electrolyte melts (in particular semi-conductors) [11], as well as for solid solutions [12,13]. In comparison with approach developed by Hill et al. [14–21] devoted to extension of classical thermodynamics to nanothermodynamics, the VD-AS model based on the classical thermodynamic paradigm.

We have also calculated the concentration dependence of the activity coefficients of the solution components and the Gibbs energy of mixing at 273.15 K as well as the phase boundaries of the diffusion stability of the nanocluster solutions.

Analysis of literature shows the lack of the data devoted to physico-chemical properties of water-soluble derivatives of fullerenes; we can refer only two types of studies:

(i) authors of [22–46] investigated the physico-chemical properties of such fullerene derivatives as fullerenols, carboxylated fullerenes, derivatives of light fullerenes with L-amino acids and obtained the experimental data on concentration dependences of densities, refractive indices, hydrogen ion concentrations, specific and equivalent conductivities, dissociation constants, apparent degree of dissociation, size distribution, diffusion coefficients, viscosities, etc. as well as determined the solubility diagrams in binary and ternary systems containing water-soluble derivatives of fullerenes;

(ii) several authors of carried out theoretical investigations of light fullerene derivatives with amino acids, in particular the ability of C_{60} to interact with amino acids, the molecular structure of hybrid derivatives based on C_{60} and amino acids, the dissociation constants (pK_a) of

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

https://doi.org/10.1016/j.molliq.2018.01.177
0167-7322/

fullerene derivatives with amino acids [47–49]. Other researchers [42–48] performed theoretical investigations of the molecular structure, vibration spectra and solvation mechanism as well as optical properties and conductivity, of fullerenol.

2. Experimental

Water soluble derivatives of fullerenes (carboxylated fullerene - $C_{70}[C(COOH)_2]_3$, fullerenols - $C_{60}(OH)_{22-24}$, $C_{70}(OH)_{12}$ and derivatives of C_{60} with L-lysine - $C_{60}(C_6H_{14}N_2O_2)_2$, L-hydroxyproline - $C_{60}(C_5H_9NO_3)_2$ of mass fraction purity 99.7–99.9% were used for the physicochemical investigation of their aqueous solutions. The reagents were produced in Ltd. ZAO "ILIP" (St. Petersburg). The samples were used without further purification. The HPLC analysis of the water-soluble fullerene derivatives was performed using Shimadzu LC-20 Prominence apparatus with UV-detection at 300 nm equipped with «Phenomenex® NH2» (150 mm x 2.0 mm, 5 μm, 100 A) column, injection volume was equal to 20 μl, injection speed – 0.2 ml·min^{-1}, eluent – acetonitrile/0.1% aqueous solution of acetic acid (5/95). The characteristics of the samples are indicated in Table 1.

For carrying out the cryoscopic investigations of binary systems, containing water-soluble derivatives of light fullerenes ($C_{70}[C(COOH)_2]_3$, $C_{60}(OH)_{22-24}$, $C_{70}(OH)_{12}$, $C_{60}(C_6H_{14}N_2O_2)_2$, $C_{60}(C_5H_9NO_3)_2$) we have measured the concentration dependences of ice crystallization temperatures for aqueous solutions of fullerenes derivatives. The mole fractions of fullerene derivatives range from $1.6\cdot10^{-6}$ to $3.5\cdot10^{-4}$. The ice crystallization temperatures were determined using a Beckman thermometer with linear resolution ability of scale, $\frac{\Delta T}{\Delta h}$, ($\Delta h$ is the height of mercury raising in the capillary) equal to 0.01 K·mm^{-1}.

3. Results and discussion

3.1. Cryoscopic investigation of the soluble fullerene derivatives – H_2O binary systems

The experimental values of the lowering of the ice crystallization temperature for aqueous solutions of the light fullerene derivatives ($C_{70}[C(COOH)_2]_3$, $C_{60}(OH)_{22-24}$, $C_{70}(OH)_{12}$, $C_{60}(C_6H_{14}N_2O_2)_2$, $C_{60}(C_5H_9NO_3)_2$) are presented in Fig. 1 and Table 2. Fig. 1 shows that the obtained dependences are extremely non-linear (the curves are concave) in the whole studied concentration range even in very diluted solutions. The latest fact indicates the significant non-ideality of the light fullerene derivatives aqueous solutions. For comparison we have added in Fig. 1 the concentration dependence of changing of the ice crystallization temperatures for ideal solutions. It can be seen that the obtained values of the decrease of the ice crystallization temperatures for the fullerene derivatives solutions are one or two orders of magnitude greater than the corresponding decrease for the ideal solutions. Thus, we can expect significant positive deviations from ideality of binary solutions, containing water –soluble derivatives of fullerenes (Fig. 2).

For the water activity calculation, we have used the well-known equation that can be obtained from the equality of the chemical

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

Name	Supplier	Mass fraction purity[a]	Analysis method
$C_{70}[C(COOH)_2]_3$	ZAO "ILIP"	99.7	Liquid chromatography
$C_{60}(OH)_{22-24}$	ZAO "ILIP"	99.9	Liquid chromatography
$C_{70}(OH)_{12}$	ZAO "ILIP"	99.8	Liquid chromatography
$C_{60}(C_6H_{14}N_2O_2)_2$	ZAO "ILIP"	99.8	Liquid chromatography
$C_{60}(C_5H_9NO_3)_2$	ZAO "ILIP"	99.8	Liquid chromatography

[a] The purity analysis was additionally performed in our laboratory; the results obtained by the supplier and in our laboratory are in agreement.

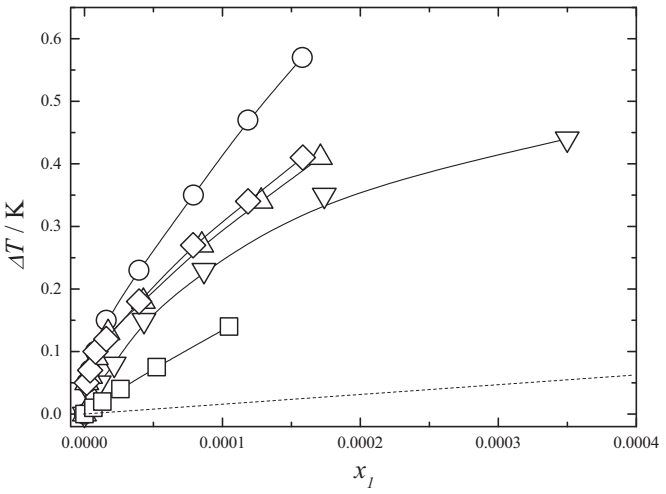

Fig. 1. Decreasing of the ice crystallization temperature (ΔT) of the $C_{60}(C_6H_{14}N_2O_2)_2$ – H_2O (▽), $C_{60}(OH)_{22-24}$ – H_2O (○), $C_{70}[C(COOH)_2]_3$ – H_2O (△), $C_{60}(C_5H_9NO_3)_2$ - H_2O (□), $C_{70}(OH)_{12}$ - H_2O (◇) binary systems. x_1 - mole fraction of solute in aqueous solution. Dashed line corresponds to decreasing of the ice crystallization temperature of the ideal solutions of non-electrolytes. Continuous lines represent the VD-AS model.

potentials of water in the pure ice and in the non-ideal aqueous solution:

$$\ln a_{H_2O} = \frac{-\Delta H^f_{H_2O}\Delta T - \Delta C_p \Delta T^2}{R\left(T^f_0 - \Delta T\right)T^f_0} \quad (1)$$

where $\Delta H_{H_2O}{}^f$ is the melting enthalpy of ice (5990 J·mol^{-1}), ΔC_p is the change of isobaric heat capacity for the ice melting process (−38.893 J·mol^{-1}·K^{-1}), T^f_0 is the temperature of pure ice melting (273.15 K), $\Delta T = T^f_0 - T$, T is the temperature of the beginning of crystallization process in the solution and R the universal gas constant. Table 2 shows the $\ln a_{H2O}$ values for the four studied systems obtained from the experimental ΔT values.

For all investigated binary systems we have calculated $\ln\gamma_{H_2O}$ (see Table 2) using the following equation:

$$\ln\gamma_{H_2O} = \ln a_{H_2O} - \ln x_{H_2O} = \ln a_{H_2O} - \ln(1-x_1). \quad (2)$$

Eq. (1) was obtained in the symmetric reference state of thermodynamic functions. In this case, for both solution components we can apply the following:

$$a_{H_2O}(x_{H_2O} = 1) = \gamma_{H_2O}(x_{H_2O} = 1), \quad (3)$$

$$a_{nanocluster}(x_{nanocluster} = 1) = \gamma_{nanocluster}(x_{nanocluster} = 1), \quad (4)$$

where x_i, a_i and γ_i are the mole fraction, activity, and activity coefficient of the i-th solution component, respectively.

On the basis of experimental data on water activity, Matuzenko et al. [49] have calculated the concentration dependences of $\ln\gamma_{H_2O}$ and $\frac{d\ln\gamma_{H_2O}}{dx_{nanocluster}}$ derivative using a numerical approach for the $C_{60}(C_6H_{12}NaN_4O_2)_8H_8$ – H_2O binary system According to Gibbs-Duhem equation the calculation of concentration dependence of $\frac{d\ln\gamma_{nanocluster}}{dx_{nanocluster}}$ was performed by tabular integration. As a result the authors of [49] obtained great positive values of $\ln\gamma_{nanocluster}$. The latest fact is connected with the type of normalization of the activity coefficients. There are two principal conventions for the normalization of the activity coefficients:

(i) The "symmetric reference state". In this case it is necessary to imagine the state of supercooled metastable pseudo-melt, which consists of fullerene derivatives in monomeric state. The partial