

Cryometry data in the binary systems bis-adduct of C₆₀ and indispensable aminoacids – lysine, threonine, oxyproline

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The article continues the development of the investigations, presented in particular in the cycle of articles, devoted to the synthesis, identification and investigation of physical-chemical properties of water soluble derivatives of light fullerene C₆₀, such as: complex esters of dicarboxylic acids (malonates, oxalates); poly-hydroxylated forms (fullerenols); amino-acid derivatives (arginine, alanine). The investigation of the excess thermodynamic functions, to the best of our knowledge, has, until now, not been provided, except for two original works [Matuzenko M.Yu., Tyurin D.P., et al. (2015); Matuzenko M.Yu., Shestopalova A.A., et al. (2015)].

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1. Introduction

Previous articles [1–9] were devoted to the investigation of the physical-chemical properties of light fullerenes adducts with amino-acids and their solutions. Cryometry investigation in the binary systems C₆₀(C₆H₁₃N₂O₂)₂-H₂O, C₆₀(C₄H₈NO₃)₂-H₂O, C₆₀(C₅H₉NO₃)₂-H₂O at 273.15 – 272.50 K was used for determination of the concentration dependencies of the temperatures corresponding to beginning of ice crystallization from the solution (liquidus temperatures). Solution concentrations (in molar fraction) vary in the wide range $X_{bis-adduct} = 6 \times 10^{-6} - 2 \times 10^{-4}$ rel.un. Liquidus temperatures were determined with the help of Beckman thermometer with the linear resolution of the device scale $\Delta T/\Delta h \approx 0.01$ K/mm (h – height of Hg capillary raising). Cryometry data $\Delta T(X_{bis-adduct})$ in Fig. 1 (typical example for the system with oxyproline bis-adduct C₆₀(C₅H₉NO₃)₂-H₂O). The dependencies $\Delta T(X_{bis-adduct})$ are sharply nonlinear, which prove high solution non-ideality for all solutions, even very dilute ones. In Fig. 1, for comparison by the arrow, the values ΔT^{id} for the ideal non-electrolyte solution are presented. As we can see, the experimental ΔT exceeds ΔT^{id} one-two orders of magnitude (for comparable concentrated and dilute solutions). Thus, one should expect probably gigantic positive deviations of the solution from ideality in the thermodynamic sense.

For the calculation of water activity, we have used well-known equation, obtained from the equality of the chemical H₂O potentials in pure solid ice and non-ideal liquid solution [10, 11]:

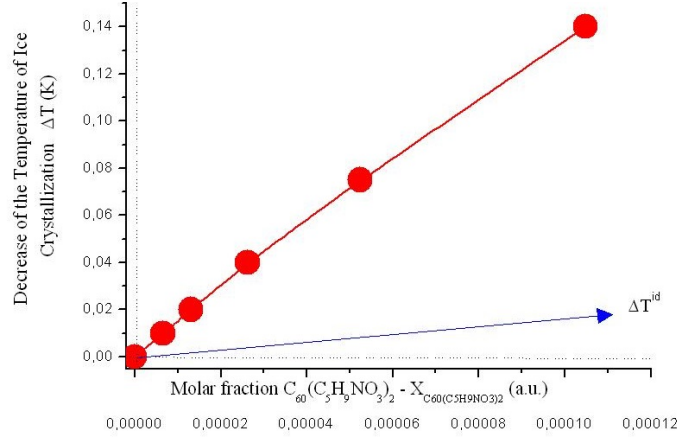
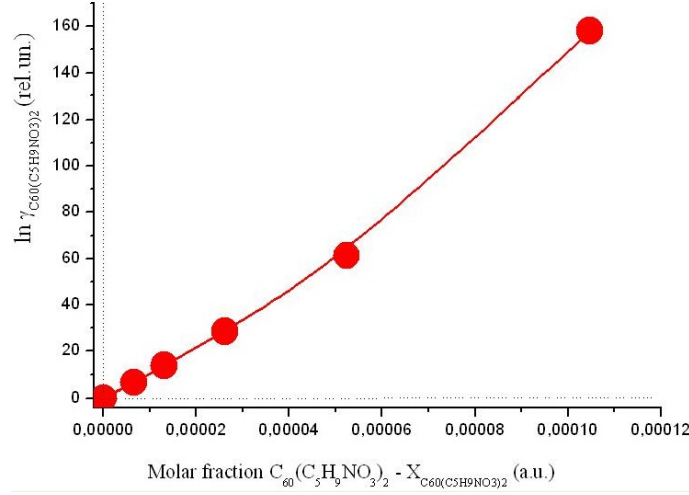
$$\frac{-\Delta H_W^f \Delta T - \Delta C_P \Delta T^2}{R(T_0^f - \Delta T)T_0^f} = \ln a_{H_2O}, \quad (1)$$

where: $\Delta H_W^f = 5990$ J/mole, $\Delta C_P = -38.893$ J/mole·K, $T_0^f = 273.15$ K are heat, temperature of ice fusion and change of heat capacity in the process of ice fusion, correspondingly. Eq. (1) was obtained in the symmetrical normalization scale for thermodynamic functions for both components:

$$a_{H_2O}(X_{H_2O} = 1) = \gamma_{H_2O}(X_{H_2O} = 1) = 1, \quad (2.1)$$

$$a_{nabis-adduct}(X_{bis-adduct} = 1) = \gamma_{bis-adduct}(X_{bis-adduct} = 1) = 1, \quad (2.2)$$

where: X_i and a_i , γ_i – molar fraction, activity and activity coefficient of i -th component. Authors [10, 11] calculated concentration dependencies in γ_{H_2O} , derivatives $d \ln \gamma_{H_2O} / dX_{bis-adduct}$ (numerically). Then authors [10, 11] calculated the dependencies $d \ln \gamma_{bis-adduct} / dX_{bis-adduct}$, (according to classical differential Gibbs–Duhem differential equation) and at the end by numerical integration the dependencies $\ln \gamma_{nabis-adduct}(X_{bis-adduct})$ were calculated. As a result, as was expected earlier, gigantic positive deviations of the solution from ideality for the functions $\ln \gamma_{bis-adduct}$ were obtained $\ln \gamma_{bis-adduct} \approx n(10^2)$ (in Fig. 2 typical example for the system with

FIG. 1. Liquidus temperature decrease in the system $C_{60}(C_5H_9NO_3)_2-H_2O$ (example)FIG. 2. Logarithm activity coefficient of bis-adduct in the system $C_{60}(C_5H_9NO_3)_2-H_2O$: dots – experiment, line – calculation according VSAD model

oxyproline bis-adduct – $C_{60}(C_5H_9NO_3)_2-H_2O$ is represented). Naturally, no existing thermodynamic model can describe such nontrivial behavior of nanocluster thermodynamic functions.

For the thermodynamic description of our systems, we have elaborated original semi-empirical model VD–AS (Virial Decomposition Asymmetric Model), based on the virial decomposition of molar Gibbs energy on the component molar fractions in the solution. This reception was often used previously for the description of binary and multicomponent solutions with different natures: electrolyte solutions [12–15], non-electrolyte melts [16–18], equivalent replacement solid solutions. The main equations of VD–AS model for the binary system are the following:

$$\ln \gamma_{H_2O}^{ass} \approx \sum_{i=2} i \Lambda_i X_{bis-adduct}^{i-1}, \quad (3.1)$$

$$\ln \gamma_{bis-adduct}^{ass} \approx \sum_{i=2} (1-i) \Lambda_i X_{bis-adduct}^i, \quad (3.2)$$

where: $\ln \gamma_i^{ass}$ – logarithm of activity coefficient of i -th solution component in asymmetrical normalization scale ($\ln \gamma_{H_2O}^0 = 0$, $\gamma_{H_2O}(X_{bis-adduct} \rightarrow 0) = \gamma_{H_2O}^0 = 1$, $\ln \gamma_{bis-adduct}^0 = 0$, $\gamma_{bis-adduct}(X_{bis-adduct} \rightarrow 0) = 1$), Λ_i – consolidated i -th virial coefficient of the decomposition.

Preliminary calculations show that three-coefficients VD–AS model (i.e. $i = 2, 3, 4$) is enough to describe our systems with high accuracy (see, for example, Fig. 2 for $\ln \gamma_{bis-adduct}^{ass}$):

$$\ln \gamma_{H_2O}^{ass} \approx 2\Lambda_2 X_{bis-adduct} + 3\Lambda_3 X_{bis-adduct}^2 + 4\Lambda_4 X_{bis-adduct}^3, \quad (4.1)$$

$$\ln \gamma_{bis-adduct}^{ass} \approx -2\Lambda_2 X_{bis-adduct}^2 - 2\Lambda_3 X_{bis-adduct}^3 - 3\Lambda_4 X_{bis-adduct}^4. \quad (4.2)$$

The VD–AS model also excellently describes pre-delamination or micro-heterogeneous-structure formation in solution (see Fig. 3). This calculation is confirmed by Dynamic Light Scattering data (ZetaSizer).

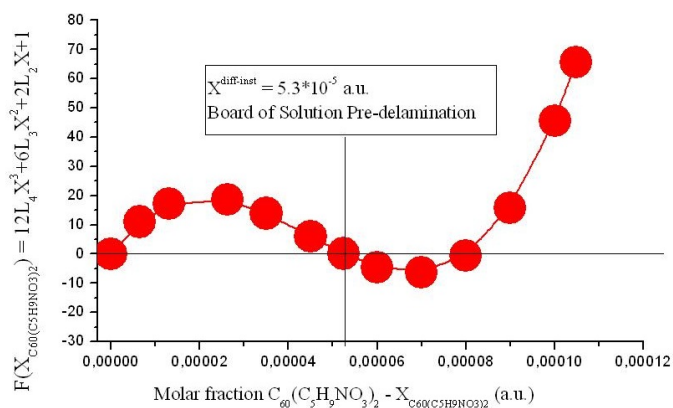


FIG. 3. Delamination board in the system $C_{60}(C_5H_9NO_3)_2-H_2O$ (example)

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