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## Phase Equilibrium in the System $C_{60}(\text{OH})_{24}-\text{NdCl}_3-\text{H}_2\text{O}$ at $25^\circ\text{C}$

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Diagrams of phase equilibrium liquid–vapor, solid–liquid (solubility diagram) and liquid–liquid (delamination diagram) at  $25^\circ\text{C}$  in the ternary system, consists of water soluble fullerene derivative and rare earth metal salt  $C_{60}(\text{OH})_{24}-\text{NdCl}_3-\text{H}_2\text{O}$  were investigated. The existence of miscibility gap in liquid solutions, saturated by fullerol-24 ( $C_{60}(\text{OH})_{24}$ ) is proved.

**Keywords:** liquid phase delamination, dynamic light scattering, diffusion stability, diagrams of solubility, diagrams liquid–vapor.

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Water-soluble derivatives of light fullerenes (HWSFs) are polyhydroxylated fullerenes (fullerenols  $C_{60}(\text{OH})_n$ ,  $C_{70}(\text{OH})_n$ ,  $n = 4, 8, 12, 24, 40 \dots$ ) [1–5]) or their mixtures, such as fullerol-*d* (produced by direct oxidation), fullerol-*m* (mixed), etc. [6]. Compounds formed by fullerenes and carboxylic acids, amino acids, polypeptides, and low molecular weight proteins with a general formula of  $C_xR_n$  or  $C_xR_nH_n$  ( $x = 60, 70$ ;  $n = 2, 3, 4, 8$ ;  $R$  is the corresponding substituent) are also regarded as HWSFs. Phase equilibria of various kinds in HWSF-containing systems have already been examined numerous times, although these studies were fragmentary in nature. Specifically, isothermal solubility diagrams in HWSF– $\text{H}_2\text{O}$  binary systems and HWSF–Salt– $\text{H}_2\text{O}$  ternary systems (Salt stands for an inorganic salt or several inorganic salts) have been investigated in [7,8]. The obtained data may be used to isolate and purify HWSF adducts by multistage recrystallization from aqueous solutions or, conversely, purify and separate salt components by recrystallization (e.g., Tb–Gd or Nd–Pr). Studies into polythermal solid–liquid phase equilibria (fusion diagrams in the regions of ice crystallization; i.e., cryometric studies) have been performed for systems of the indicated kind in [9]. These data were used later to calculate partial thermodynamic functions of HWSFs in solutions (in accordance with the semi-empirical model of extremely strongly associated solutions (VD-AS) [8]) and the process of spinodal decomposition or diagrams of liquid delamination (liquid–liquid equilibria). Liquid-phase delamination has been examined under isothermal conditions only in binary HWSF– $\text{H}_2\text{O}$  systems both by cryometry and by dynamic light scattering (DLS) [10]. As far as we know, liquid–vapor phase equilibria have never been studied yet. At the same time, data of this type (obtained, e.g., using the isopiestic method [11], which is probably the most accurate of currently available experimental techniques) are relevant exactly to the characterization of behavior of

excess thermodynamic functions and subsequent calculation of phase equilibria.

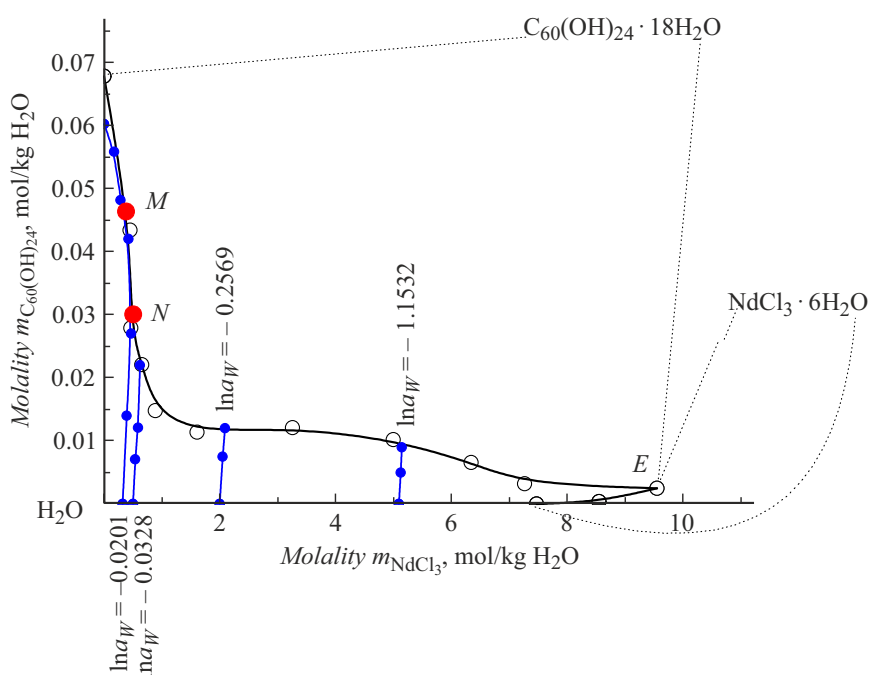
Let us assume that the boundaries of diffusion stability correspond both to the fulfillment of condition

$$(\partial^2 G / \partial X_N^2)_{T,P} = 0, \quad (\partial \mu_N / \partial X_N)_{T,P} = 0 \quad (1)$$

within an adequate thermodynamic model and to the formation of macroassociates of order III, which is verified by DLS data for these particles with linear dimensions of several micrometers. In formula (1),  $G$  is the molar Gibbs potential of a solution,  $X_N$  is the molar fraction of a water-soluble fullerene derivative, and  $\mu_N$  is its chemical potential. However, having acknowledged this, we should also accept that the solution becomes a two-phase and (with  $T$  and  $P$  fixed) nonvariant one in the region of existence of such macroassociates. Therefore, when gross concentration  $X_N$  of fullerene derivatives increases further, the compositions of both coexisting liquid phases should remain unchanged, and only their relative masses may vary. This effect persists until one of the liquid phases vanishes completely. The solution should again become structureless, monovariant, and diffusionally stable. This process will be observed up to the point of formation of a saturated solution in equilibrium with the crystalline hydrate of a fullerene derivative. Having reached saturation, the system again becomes heterogeneous (two-phase) and, consequently, nonvariant [12].

The very fact of repeat attainment of diffusion stability by binary solutions has not been noted earlier, although the Gibbs phase rule makes it evident that saturated binary solutions cannot (at  $T, P = \text{const}$ ) remain in equilibrium with a third (solid) phase. We attribute the failure to establish a repeat spinodal crossing in the indicated systems to the specifics of study of solutions by DLS associated with the opacity of concentrated solutions.

It is evident that if liquid-phase delamination (loss of diffusion stability of solutions) was observed in  $C_xR_n-\text{H}_2\text{O}$



Solubility diagram for the  $C_{60}(OH)_{24}-NdCl_3-H_2O$  ternary system at  $25^\circ C$ . Open circles represent our experimental data,  $E$  is the eutonic nonvariant point [13,14], and blue circles and lines are water isoactivates. Data on water activity logarithms are also shown. Points  $M$ ,  $N$  are the boundaries of diffusion stability of solutions and belong to the spinodal. A color version of the figure is provided in the online version of the paper.

or  $C_xR_nH_n-H_2O$  binary systems, it may also be found in systems with more components (e.g., ternary ones) of the  $C_xR_n-Salt-H_2O$  or  $C_xR_nH_n-Salt-H_2O$  type (Salt stands for an inorganic salt that is highly soluble in water) examined earlier. It is also evident that such delamination is not observed in  $C_xR_n-H_2O$  or  $C_xR_nH_n-H_2O$  binary saturated solutions at the maximum concentration of fullerene derivatives, since these solutions have restored their diffusion stability. Delamination is also infeasible in dilute solutions of fullerene derivatives at high concentrations of salt crystalline hydrates. At certain „intermediate“ concentrations of fullerene derivatives, this delamination is entirely possible and even expected, since it is observed in binary subsystems of these ternary systems. If this phenomenon is observed, it should be localized at long branches of crystallization of  $C_xR_n \cdot xH_2O$  or  $C_xR_nH_n \cdot xH_2O$  crystalline hydrates. A marked convex-concave ( $\sigma$ -like) nature, which is uncharacteristic of common aqueous salt solubility diagrams of ternary systems, provides indirect confirmation of the validity of this assumption. If the assumption is valid, three phases form in a ternary system: two delaminating liquids and one solid crystalline hydrate phase; i.e., the system should again become nonvariant. If this occurs, the resultant state of saturated solutions should correspond to a constant level of either chemical potentials, or activity, or partial pressures of water vapor. In other words, sections of the solubility branch of crystalline hydrate  $C_xR_n \cdot xH_2O$  or  $C_xR_nH_n \cdot xH_2O$  should also be a water isoactivate. To test this assumption, we chose the most widely used fullerene derivative  $C_{60}(OH)_{24}$ , which also has the highest solubility

of all known derivatives ( $m^{(s)} = 0.0678$  mol/kg  $H_2O$ ) [8], providing an opportunity to perform a reasonably accurate isopiestic experiment in the region of high  $C_{60}(OH)_{24}$  concentrations and low salt concentrations.

The solubility diagram for the  $C_{60}(OH)_{24}-NdCl_3-H_2O$  ternary system at  $25^\circ C$  is presented as an example in the figure. Open circles represent experimental solubility data, and  $E$  is the eutonic nonvariant point [13,14] that corresponds to joint saturation with two solid crystalline hydrates ( $C_{60}(OH)_{24} \cdot 18H_2O$  and  $NdCl_3 \cdot 6H_2O$ ). Blue circles and lines are water isoactivates obtained using the isopiestic method. Data on water activity logarithms are also shown in the figure. Solutions of the  $LiCl-H_2O$  binary system are used as a reference.

It should also be noted that experimental derivation of the most „dilute“ isoactivate at  $\ln a_w = -0.0201$  a.u. is a fairly slow process that took 40 days in the present case. The next isoactivate at  $\ln a_w = -0.0328$  a.u. was measured somewhat faster (in 14 days). This is attributable to the necessity of partial — isopiestic — equilibration (when chemical potentials of partial pressures of the volatile component ( $H_2O$ ) equalize, but those of dissolved nonvolatile components do not) in very dilute (in molar concentrations) solutions. This equilibration requires the transfer of fairly large relative solvent masses via the vapor phase from comparison vessels to vessels with the studied solutions (or vice versa). In addition, while a relatively fine vacuum may be produced in concentrated solutions (e.g., the isopiestic reactor for the most concentrated isoactivate in the figure at  $\ln a_w = -1.1532$  a.u. may be evacuated

to residual air pressure  $P \leq 8$  mm Hg, and the solution does not begin to boil), the feasible residual pressure for dilute solutions is much higher ( $P \sim 23$ – $24$  mm Hg for the most dilute isoactivate), and it is known that the rate of isopiestic equilibration and the residual air vapor pressure are quantities varying in a strictly inverse relation [11]. This is the actual reason why solutions of the  $C_{60}(OH)_{24}$ – $H_2O$  system close to saturation at  $m_{C_{60}(OH)_{24}} = 0.05$ – $0.07$  mol/kg  $H_2O$  may be studied by the isopiestic method, but an isopiestic experiment for sufficiently more dilute solutions at  $m_{C_{60}(OH)_{24}} = 0.001$ – $0.01$  mol/kg  $H_2O$  would take years.

It can be seen from the figure that a section of the crystallization branch of the  $C_{60}(OH)_{24} \cdot 18H_2O$  crystalline hydrate in the  $C_{60}(OH)_{24}$ – $NdCl_3$ – $H_2O$  ternary system at  $25^\circ C$  is almost perfectly aligned with the water isoactivate at  $\ln a_w = -0.0201$  a.u.; i.e., the system is delaminated (between points  $M$  and  $N$  in the figure). There is a slightly different line of reasoning that also leads to the same conclusion regarding the loss of diffusion stability of a saturated solution. As was demonstrated in [13,14], the activity of water in the state of stable equilibrium of the liquid phase should decrease monotonically as one moves along the branch of crystallization of a phase with a constant composition toward the eutonic point. In the present case, however, the water activity remains unchanged within the  $M$ – $N$  section, contradicting the criteria of diffusion stability.

Thus, the phenomenon of sequential hierarchical association observed in binary and ternary aqueous solutions of derivatives of light fullerenes  $C_{60}$  and  $C_{70}$  (fullerenols, and adducts of fullerenes with carboxylic acids, amino acids, polypeptides, and low molecular weight proteins) was characterized. This phenomenon induces the formation of liquid-phase microheterogeneous systems in the region of intermediate concentrations (between a pure solvent and saturated solutions). Consistent experimental data were obtained as a result of examination of dynamic light scattering, cryometric measurements in binary aqueous solutions of fullerene derivatives, and the study of solubility in ternary aqueous salt systems with inorganic metal salts.

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## Conflict of interest

The authors declare that they have no conflict of interest.

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