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Solubility of Light Fullerenes in Oleic, Linoleic, and Linolenic Acids at 20–80°C

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Abstract—Solubility of light fullerenes (C_{60}, C_{70}, and the standard fullerene mixture containing (wt %): C_{60} 65, C_{70} 34, $C_{n>70}$ 1) in the oleic, linoleic and linolenic acids, respectively, at 20–80°C was studied and the corresponding solubility polytherms were reported.

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It was often noted that the study of solubility of fullerenes plays the primary role in the development of the methods of their extraction, isolation from the fullerene soot, the development of the methods of chromatographic, as well as pre-chromatographic separation of the fullerene mixture [1–7]. The evidence of the importance of these studies is the huge array of available published experimental data on the solubility of light fullerenes (the solubility was studied: of C_{60} in more than 160 solvents, of C_{70} in 30 solvents [1]), therewith various classes of organic and inorganic solvents (aromatic solvents, alkanes, cycloalkanes, haloalkanes, alcohols) were studied.

Currently there are relatively few publications on the study of solubility of light fullerenes C_{60} and C_{70} under polythermal conditions in a class of solvents, which are organic acids of different types: saturated monobasic carboxylic acids of normal structure [8–12] and higher isomeric carboxylic acids [13]. The solubility in unsaturated carboxylic acids, as far as we know, has not been studied. Meanwhile, such a study could be very interesting because it follows from general considerations that the solubility in these acids should be higher than in the corresponding saturated analogs (solubility in the acids C_4–C_{11} is from tens to hundreds mg per liter) [8–12] . On the other hand, these acids are important components of fats and are completely biocompatible with human and animal organisms. Another possible application of fullerene compositions with unsaturated fatty acids is their joint use as antifriction additives for fuels and lubricant oils.

The experimental study of the polythermal solubility of individual fullerenes C_{60} and C_{70} and fullerene mixture in the temperature range 20–80°C was carried out by the method of isothermal saturation in a thermally controlled shaker. The concentration after each stage of saturation of individual fullerenes and the mixture was determined spectrophotometrically. The content of the solvent in the fullerene crystal solvates was determined experimentally by gravimetry.

Figure 1 shows the resulting solubility polytherms of individual fullerenes C_{60} (Fig. 1a) and C_{70} (Fig. 1b), in Fig. 2 the solubility polytherms are depicted of fullerene C_{60} (Fig. 2a), fullerene C_{70} (Fig. 2b), and the total solubility of C_{60} + C_{70} (Fig. 2c) at theie dissolution from the standard fullerene mixture in oleic, linoleic, and linolenic acids.

These figures clearly demonstrate that:

– The solubility in all investigated unsaturated carboxylic acids ranges from hundreds mg l^{-1} to 10 g l^{-1}, which is from one to two orders of magnitude higher than the previously studied solubility in the saturated carboxylic acids [8–12],

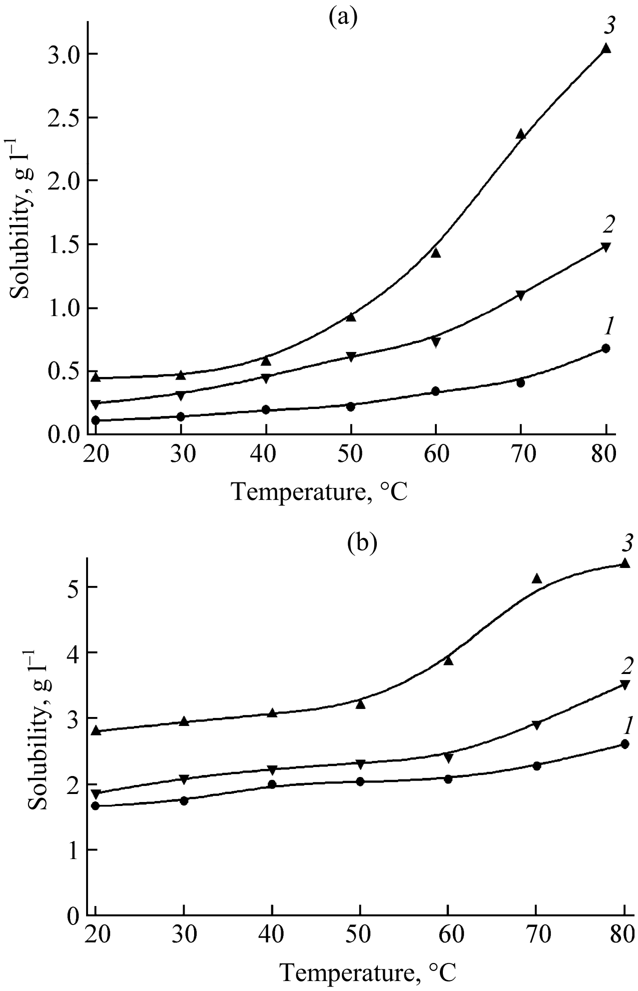

Fig. 1. Solubility of individual fullerenes (a) C_{60} and (b) C_{70} in (*1*) oleic, (*2*) linoleic, and (*3*) linolenic acids.

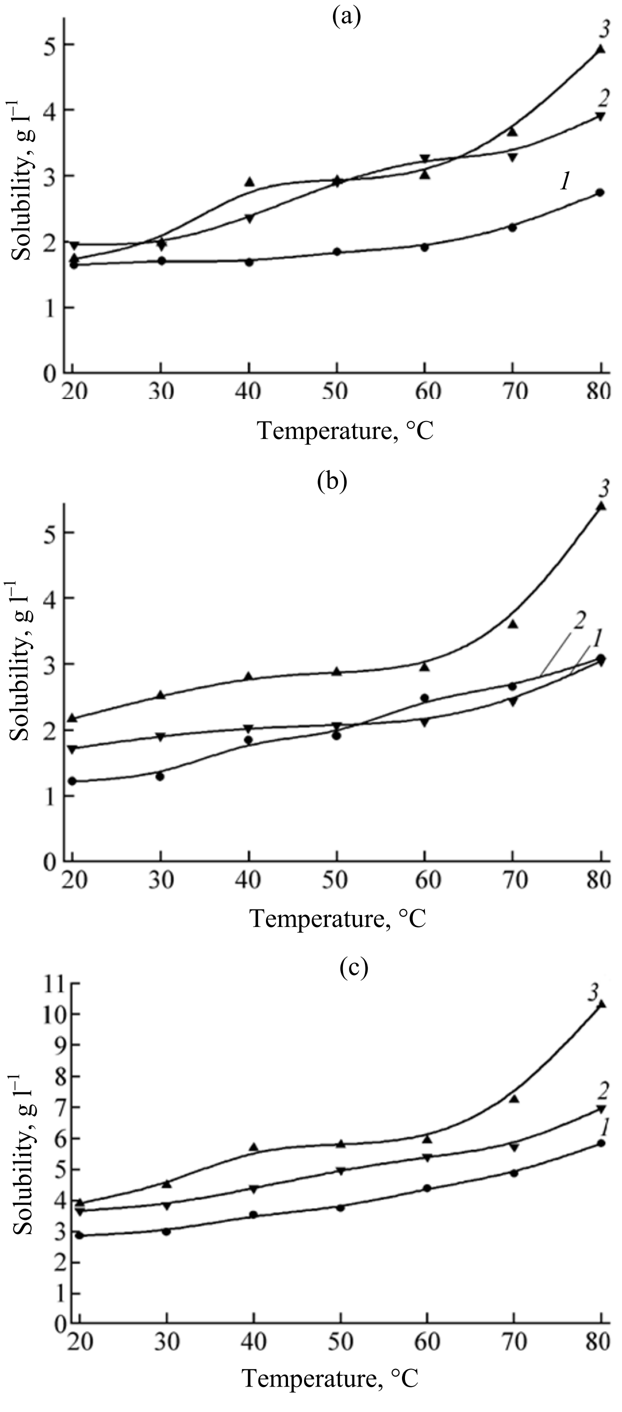

Fig. 2. Solubility of fullerene (a) C_{60}, (b) fullerene C_{70}, and (c) the total solubility of $C_{60} + C_{70}$ in (*1*) oleic, (*2*) linoleic, and (*3*) linolenic acids at the dissolution of the standard fullerene mixture.

– The solubility of both light fullerenes in all the unsaturated acids increases with increasing temperature both at dissolution of individual fullerenes, or from the standard fullerene mixture,

– In all cases, the individual solubility of the more polarizable fullerene C_{70} is higher than the solubility of the “pseudospheroid” C_{60}, that is, in principle, quite typical for the solvents dissolving the fullerenes good enough [1]: $S_{\text{acid}}(C_{60}) < S_{\text{acid}}(C_{70})$,

– At the dissolution of light fullerenes from the standard fullerene mixture the solubilities of these components are similar: $S_{\text{acid}}(C_{60}) \sim S_{\text{acid}}(C_{70})$,

– The solubility of the C_{60} fullerene at its dissolution from the standard fullerene mixture is higher than the solubility of individual C_{60}, namely, obviously occurs the salting-in effect of C_{60} on the branch of the crystallization of solid solutions rich in C_{60}. With increasing fullerene C_{70} concentration the solubility of C_{60} fullerene increases,

– The solubility of C_{70} fullerene at its dissolution from the standard fullerene mixture is practically the same as the solubility of individual C_{70}. Previously, such effects were observed in the ternary systems with aromatic solvent *o*-xylene [14],

– With the increasing number of double bonds in the acid the solubility of both light fullerenes increases: triene acid is characterized by a higher dissolving power than the diene one, and the latter in turn is a better solvent than the monoenic acid: $S_{\alpha\text{-linolenic}}(C_{60}) > S_{\text{linoleic}}(C_{60}) > S_{\text{oleic}}(C_{60}) > S_{\alpha\text{-linolenic}}(C_{70}) > S_{\text{linoleic}}(C_{70}) > S_{\text{oleic}}(C_{70})$.

By gravimetric experiment we found that the weight loss at the removing oleic acid from the C_{60} crystal solvate was 2.0 rel. wt %, and from the C_{70} crystal solvate, 1.8 rel. wt %. Taking into account the molecular weight of the acid (282 au), both these values correspond to the extremely low content of oleic acid in the corresponding crystal solvates: $C_{60}\cdot q[CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH]$ and $C_{70}\cdot q[CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH]$, where $q = 0.05 \pm 0.02$, that is, with a great confidence, we can assume that both the fullerenes are not solvated with oleic acid in the solid phase. The same is true with respect to the crystal solvates of both fullerenes with linoleic and linolenic acids.

EXPERIMENTAL

In the study we used fullerene C_{60} of 99.9 wt % purity, the main contaminant was fullerene C_{70}, whose determined content was about 0.07 wt %, fullerene C_{70} of 99.5 wt % purity contaminated mainly with the fullerene C_{60}, in content of about 0.4 wt %, and fullerene mixture consisting of 65 wt % of C_{60} + 34 wt % of C_{70} + 1 wt % of higher fullerenes C_n (n = 76, 78, 84, 90 ...), the product of ILIP company (St. Petersburg). The following fatty acids were used as solvents: $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$ (oleic acid, or *cis*-9-octadecenoic acid), $CH_3(CH_2)_3(CH_2CH{=}CH)_2(CH_2)_7\cdot COOH$ (linoleic, or *cis*-9,*cis*-12-octadecadienic acid), and $CH_3(CH_2CH{=}CH)_3(CH_2)_7COOH$ (α-linolenic, or 9,12,15-octadecatrienic acid), all of purity higher than 99 wt % (Aldrich, Tech. Care Syst., Inc.).

The experimental dependence of solubility of individual fullerenes (C_{60}, C_{70}), as well as the fullerene mixture (34% C_{70}, 65% C_{60}, 1% $C_{76–90}$) on temperature was determined by isothermal saturation. Initially, we prepared the solutions of a fullerene C_{60}, C_{70} or fullerene mixture in oleic, linoleic or linolenic acid (in each case the fullerene was taken in a significant excess: 100 mg of fullerene per 10 ml of acid). Then the obtained heterogeneous systems was subjected to saturation in the temperature range 20–80°C in a temperature-controlled shaker (accuracy of temperature control ±0.05°C) for 8 h at each temperature. Such a long duration of the experiment was due to the long enough period of reaching equilibrium in the systems. For the analysis the solution was separated from the solid phase by filtration through a glass frit (porosity 16).

The determination of concentration after each stage of saturation by fullerene C_{60}, C_{70}, and the mixture was carried out spectrophotometrically on a double-beam spectrophotometer SPECORD M-40 at the wavelengths λ = 335.7 and 472.0 nm. The accuracy of fixing the wavelength was $\Delta\lambda = \pm\ 0.5$ nm, photometric accuracy $\Delta D = \pm\ 0.005$ relative units (the spectrophotometric cell thickness l = 1 cm). The calculation of concentrations was based on the empirical formulas obtained for solutions of mixtures of fullerenes in [15]:

$$C(C_{60}) = 13.1[D_{335.7} - 1.81D_{472.0}], \quad (1)$$

$$C(C_{70}) = 42.5[D_{472.0} - 0.0081D_{335.7}], \quad (2)$$

where $C(C_i)$ is the fullerene C_i concentration in solution in mg l^{-1}, D_i is the optical density of the solution at a wavelength $\lambda = i$ nm at l = 1 cm, the concentration of higher fullerenes C_i ($i \geq 76$) in solution in these measurements was neglected. The total error in determining concentrations of light fullerenes C_i (i = 60, 70) did not exceed 5 rel. %.

Additional analysis was performed by liquid chromatography on a LYUMAKHROM chromatograph of LYUMEKS firm, St. Petersburg, as described in [16]. The detection was performed by measuring the light absorption at the wavelength 254 nm of the mixed methylene chloride–acetonitrile solutions at a total concentration of the preliminary diluted fullerene solutions with the concentration of a few milligrams per one liter. The relative error in determining concentrations of light fullerenes C_i was no more than 3 rel. %.

The data on the solvent content in the crystal solvates were obtained as follows: The solid phase freshly precipitated from the respective solution in unsaturated carboxylic acid was washed twice with ethanol, then dried at 20°C for 30 min, and weighted. Then this solid phase was repeatedly washed in a

Soxhlet apparatus with ethanol (at 78°C, 1 atm) and dried in a vacuum (0.1 mm Hg) at 200°C for 1 h and then re-weighed. From the change in the weights of the solid phase the content of solvent in the crystal solvate (or in the solid solution of fullerenes based on it) was determined.

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