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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Effect of C_{60} Fullerene on the Boiling Point of Its Solutions in Some Aromatic Solvents

B. M. Ginzburg, Sh. Tuichiev, and S. Kh. Tabarov

Institute of Machine Building Problems, Russian Academy of Sciences, St. Petersburg, Russia
Tajik State National University, Dushanbe, Tajikistan

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Abstract—Concentration dependences of the boiling points T_b^{exp} of C_{60} fullerene solutions in four aromatic solvents were determined. For benzene and *p*-xylene, processing of the increasing dependence in terms of the Raoult law enabled estimation of the cooperativity parameters of the interaction between fullerene and solvent molecules.

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The aim of our study was to determine the concentration dependences of the boiling point of C_{60} solutions in a series of four aromatic solvents: benzene, toluene, *p*-xylene, and 1,2-*o*-dichlorobenzene (DCB). It was found that the run of these dependences is governed by the symmetry of the solvent molecules. Among the mentioned molecules, that of benzene is the most symmetric. It has a sixth-order rotation axis passing through the center of the molecule perpendicularly to its plane and six symmetry planes passing in pairs through atoms in *para*-positions (three planes) and through mid-points of the C–C bonds, arranged opposite one another (three more planes).

In the case of toluene, the situation changes dramatically. The toluene molecule has only a single element of symmetry, which is the symmetry plane passing perpendicularly to the plane of the benzene ring through its center and the carbon atom of the methyl group. Apparently, the symmetry of the *p*-xylene molecule is higher than that of the toluene molecule: there are two symmetry planes and one second-order rotation axis. In the case of DCB, the symmetry of the molecule is as low as that of toluene. Presumably, the symmetry of the solvent molecules affects their interaction with C_{60} fullerene molecules, which, in the end, is manifested in the run of the concentration dependences of the boiling points. Some parameters of the solvents studied are listed in Table 1.

EXPERIMENTAL

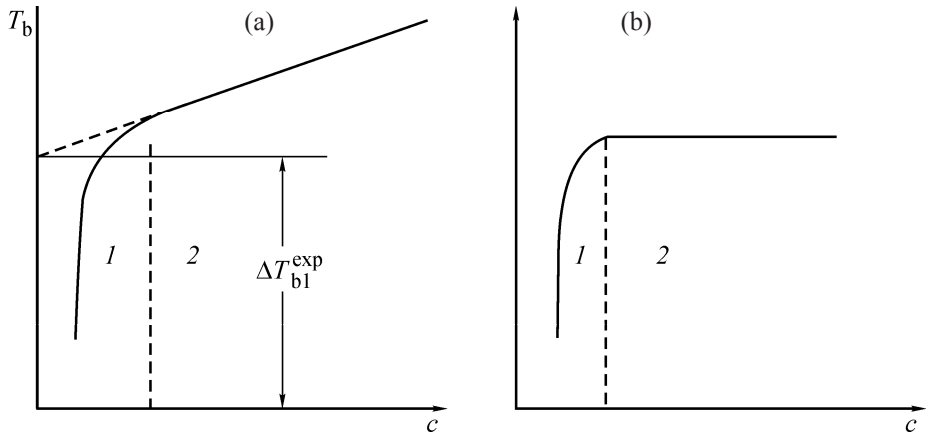
We chose for experiments the Sivolobov method [3] developed for determining the boiling point in comparatively small volumes.

We prepared the solutions to be studied from C_{60} fullerene (99.7% purity) produced by the Kratschmer–Huffman method [4] and solvents of chemically pure grade subjected to distillation. First, the mother liquor of a preliminarily known limiting concentration c_{max} (%) was prepared. Then, this mother liquor was diluted to obtain solutions with intermediate concentrations. The concentrations of the solutions were varied from 10^{-4}% (here and hereinafter the concentrations are given in weight percent) to concentrations close to that of a saturated fullerene solution. The determination errors for the lowest and highest concentrations were 1–2% and ≤0.1–0.2%, respectively.

We made 10 to 30 measurements of the boiling point T_b^{exp} for samples of each concentration. The measurement error $\pm\Delta t$ was found using the formula

$$\Delta t = T_\alpha \cdot \Delta S_{<N>}, \quad (1)$$

where $\Delta S_{<N>}$ is the standard error of a result of N measurements, and T_α is the Student coefficient whose



Schematic dependences of the boiling points of solutions on the C_{60} fullerene concentration c. Aromatic solvent: (a) with high symmetry of molecules and (b) with low symmetry of molecules.

values for different numbers of measurements and confidence levels α are listed in special tables [5].

With a probability of 90%, the relative measurement error ($\Delta t/T_b^{exp}$) 100% did not exceed 0.1% (here T_b^{exp} are given on Kelvin's scale).

All the experimentally obtained data (at an external pressure of 697 mm Hg) are listed in Tables 2–4, and the concentration dependences of the boiling points T_b^{exp} for C_{60} solutions are schematically shown in the figure. In all the cases, the concentration dependences of T_b^{exp} can be divided into two regions: region 1 of a steep rise in T_b^{exp} at the lowest fullerene concentrations and region 2 of a more gradual increase in T_b^{exp} for benzene and *p*-xylene (see figure, a) or even a plateau for toluene and DCB (see figure, b).

The existence of region 1 is in agreement with the change in the structure of the solvents, i.e., with their ordering previously observed by means of X-ray diffraction analysis [6–9]. Table 2 lists parameters characterizing the effect of a steep rise in the boiling point. It can be seen that the solvents are arranged in order of decreasing effect as follows: *p*-xylene, toluene, DCB, benzene.

After the ordering process is complete, further increase in the concentration (region 2) leads to a rise in T_b^{exp} only for the "symmetric" solvents, benzene and *p*-xylene, in a directly proportional dependence on the concentration.

The straight lines approximating the dependences of the boiling point on the fullerene concentration for benzene and *p*-xylene by the functions of the type $y = A + Bx$ were found by the least-squares method (Table 3). The large values of the correlation coefficient indicate that the experimental dependence is well approximated by the linear function. Coefficient A in Table 3 is the boiling point T_b^{exp} found by extrapolation of this linear dependence till intersection with the ordinate axis and corresponding to a structured solvent at a zero fullerene concentration.

Table 1. Parameters of the aromatic solvents studied[a]

Solvent	M [1]	T_b, °C [2]	δ(C_{60}), mg ml^{-1} [1]
Benzene	78.12	80.1	1.7
Toluene	92.15	110.6	2.8
p-Xylene	106.17	138.35	
DCB	147.006	180.48	27

[a] M is the molecular mass; T_b, boiling point; d_4^{20}, density under the standard conditions, related to the density of water at 4°C; and δ, solubility of C_{60}; the parameters T_b and δ are given for the standard conditions.

Table 2. Parameters characterizing region 1 of variation of the solvent structure[a]

Solvent	T_b^{exp}, K	ΔT_{b1}^{exp}, deg	$\Delta T_{b1}^{exp}/T_b^{exp}$
Benzene	351.25	2.2	0.00626
Toluene	380.55	3.4	0.00893
p-Xylene	407.95	4.0	0.00980
DCB	451.25	3.6	0.00798

[a] T_b^{exp} is the initial, experimentally measured boiling point; ΔT_{b1}^{exp}, absolute value of the increase in the boiling point; and $\Delta T_{b1}^{exp}/T_b^{exp}$, relative effect.

Table 3. Parameters characterizing the approximating functions in region 2 for benzene and *n*-xylene[a]

Solvent	$A = T_b^{extr}$	SD_A	B	SD_B	SD	R^2	ΔT_{b2}^{exp}, deg
			deg/%				
Benzene	80.41	0.0281	29.30	0.5371	0.025	0.9996	2.2
n-Xylene	138.70	0.0949	4.60	0.3464	0.077	0.9889	1.8

[a] T_b^{extr} are data obtained by extrapolation; $\Delta T_{b2}^{exp} = A + Bc$; c, concentration, %; SD_A, SD_B, and SD, standard deviations of coefficients A and B and experimental points from the approximating function; R^2, correlation coefficient; and ΔT_{b2}^{exp}, maximum increase in the boiling point.

Various values of the boiling points are listed in Table 4. The table gives in parentheses the boiling points calculated for 697 mm Hg from reference data (for the standard pressure of 760 mm Hg) by Kraft's rule [1]:

$$\Delta T_P = GT\text{b}(760 - P), \quad (2)$$

where ΔT_P is the depression of the boiling point upon a decrease in pressure to a value P (mm Hg); T_b, boiling point (K); G = 0.00010 for alcohols, water, and carboxylic acids; G = 0.00014 for substances with a very low boiling point (nitrogen, ammonia, etc.); G = 0.00012 can be taken for other substances (and those examined in our study).

The experimental values of the boiling points and reference data recalculated to the real pressure are in good agreement. However, the primarily important characteristic is the run of the concentration dependences of the boiling points, i.e., relative changes in the boiling point on passing from one concentration to another and the corresponding inaccuracies determined by random errors, rather than the absolute values of the experimentally measured boiling points. In this approach, the possible systematic errors (e.g., those related to the purity of solvents) are excluded from consideration.

Let us consider the increase in the boiling point of a structured solvent in terms of the Raoult law known for dilute solutions [10]:

$$\Delta T = (n/1000)\,(RT_0^2/\text{H}_V^{sp}), \quad (3a)$$

or

$$\Delta T = nE, \quad (3b)$$

where ΔT is the increase in the boiling point of the solution, compared with that of the pure solvent; n, number of solute moles in the solution; R = 8.314 J mol^{-1} deg^{-1}, universal gas constant; T_0, boiling point of the pure solvent; H_V^{sp}, specific vaporization heat of the pure solvent at the boiling point; and $E = RT_0^2/1000H_V^{sp}$, ebullioscopic constant of the solvent; the absolute zero temperature was taken to be –273.15°C.

The ebullioscopic constants for structured solvents were obtained using the following values of the parameters appearing in Eq. (3a). For *p*-xylene: T_b^{extr} = 411.95 K; molar vaporization heat at the boiling point, H_V^M = 36.09 kJ mol^{-1}; molecular mass M = 106.16 g mol^{-1}; and $H_V^{sp} = H_V^M/M$ = 340 J g^{-1} [1]. For benzene: T_b^{extr} = 353.253 K, H_V^M = 30.7855 kJ mol^{-1}, M = 78.108 g mol^{-1}, and $H_V^{sp} = H_V^M/M$ = 394 J g^{-1} [1]. Similar data were used to calculate the ebullioscopic constants for toluene and DCB. Various values of the ebullioscopic

Table 4. Boiling points of the solvents[a]

Solvent	T_b [1]	T_b^{exp}	T_b^{extr}
	K		
Benzene	353.253 (350.41)[b]	351.25	353.56
p-Xylene	411.500 (408.400)[b]	407.95	411.85

[a] T_b is the value for the standard pressure (760 mm Hg); T_b^{exp} and T_b^{extr}, experimental data and results of extrapolation for the structured solvent, respectively, at 697 mm Hg.

[b] Values calculated for 697 mm Hg from reference data.

Table 5. Ebullioscopic constants[a]

Solvent	E_{tab}	E_{calc}	E_{calc}^{str}
	deg mol^{-1}/1000 g		
Benzene	2.53	2.63	2.64
Toluene	3.28	3.37	3.37
p-Xylene	–	4.14	4.15
DCB	–	6.33	6.37

[a] E_{tab} are tabulated data from [1]; E_{calc}, values calculated from published data [1]; and E_{calc}^{str}, values calculated from extrapolated experimental data for a structured solvent.

constants are listed in Table 5. The good agreement of the calculated and experimentally obtained ebullioscopic constants confirms the high reliability of the experimental results.

Now we calculate ΔT_{calc} by Eq. (3b). For *p*-xylene, we take into account that the maximum fullerene concentration in our experiments was 0.4% (i.e., n = 4/720 mol, where 720 g mol^{-1} is the molecular mass of C_{60}). Then, ΔT_{calc} = (4/720)4.15 = 0.023°, a substantially smaller value than the experimentally observed increase, ΔT_{exp} = 140.6° – 138.8° = 1.8°.

A possible explanation of this fact is that the effect of a fullerene molecule in structuring of *p*-xylene extends over $N_{coop} \approx \Delta T_{exp}/\Delta T_{calc} \approx 80$ solvent molecules (we name the number N_{coop} the cooperativity factor). If we assume that the effective molecular mass of the solvent increases by approximately a factor of 80, then the calculated value ΔT_{calc} should increase to the same extent. It is noteworthy that determination of the number of molecules in an associate of the solute is a widely used experimental procedure [11]; however, the calculated number of molecules in an associate has not exceeded several units so far.

Similarly, we assume for benzene that the maximum concentration of fullerene in the experiment is 0.075% (i.e., n = 0.75/720 mol). Then $\Delta T_{calc} = nE$ = (0.75/720)2.64 = 0.00275° and $N_{coop} = \Delta T_{exp}/\Delta T_{calc} \approx$ 800, a value by an order of magnitude larger than that for *p*-xylene, which seems to be reasonable because of the more pronounced tendency of benzene toward self-organization [6–8].

Apparently, the intermolecular interaction in benzene is so strong that it noticeably competes with benzene–fullerene interactions. As a result, the solubility of fullerene in benzene is lower than that in toluene and substantially lower than the solubility in DCB [2]. In the case of toluene and DCB, whose molecules have a week symmetry, associates are presumably not formed at all.

CONCLUSIONS

(1) The concentration dependences of the bulk boiling points T_b^{exp} of fullerene C_{60} solutions in benzene, toluene, *p*-xylene, and *o*-dichlorobenzene can be divided into two regions: region 1 of a steep rise in T_b^{exp} at the lowest fullerene concentrations and region 2 of a slower increase or invariable T_b^{exp}.

(2) Region 1 is associated with the solvent structuring. The run of the dependences in region 2 is determined by the symmetry of the solvent molecules. The more symmetric molecules of benzene and *p*-xylene give increasing dependences, whereas for the less symmetric molecules of toluene and *o*-dichlorobenzene, T_b^{exp} is invariable.

(3) The cooperativity parameter of the interaction between fullerene and solvent molecules near the boiling point, found by processing of the increasing dependences in region 2 in terms of the Raoult law, is ~800 molecules for benzene and ~80 molecules for *p*-xylene.

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