

## Solvatochromism of fullerene C<sub>60</sub> in solvent mixtures: application of the preferential solvation model

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**Abstract.** Absorption spectra of fullerene C<sub>60</sub> were recorded between 300 and 700 nm in seven different binary solvent mixtures (toluene–acetic acid, toluene–methanol, toluene–acetonitrile, toluene–dimethyl sulphoxide, toluene–dimethylformamide, pyridine–methanol, and pyridine–water). The appearance of the UV-vis spectra of fullerene C<sub>60</sub> was found to be influenced by the composition of the mixture. The influence of the composition of the mixture on the position of four absorption bands (C, A<sub>1</sub>, δ<sub>1</sub>, and γ<sub>2</sub>) was studied. The solvent-induced shifts of the absorption maxima were generally in the range of several nanometers, the longest being 10.3 nm in the mixture of toluene and dimethylformamide. The data were analysed in terms of the preferential solvation model. Fullerene was found to be strongly preferentially solvated by toluene and pyridine compared to the more polar components of the mixtures. The selective solvation model was found to be applicable to the description of solvatochromism of C<sub>60</sub> in binary solvent mixtures, at least formally. Particularly interesting solvent effects – marked changes in the shape of the spectrum – were found in the mixtures toluene–dimethylformamide and pyridine–water.

**Key words:** binary mixtures, UV-vis spectroscopy, solvent-induced shifts, absorption maxima.

### INTRODUCTION

During the last decade different properties of fullerene C<sub>60</sub> were very extensively studied [1–4]. However, there has been comparatively limited work on solvent effects on the UV-vis spectrum of C<sub>60</sub> [5, 6]. It has been known for quite some time that fullerenes, including C<sub>60</sub>, exhibit solvatochromism [7–13]. However, the interpretation is far from clear.

The solvatochromic shifts of two maxima ( $C_0$  transition around 330 nm and  $A_0$  transition around 405 nm) on the electronic spectrum of  $C_{60}$  in 15 different organic solvents were investigated by Gallagher et al. [8]. Renge [9] investigated solvent shifts of nine maxima on UV-vis spectrum of  $C_{60}$  in *n*-alkanes. By analysing the UV-vis spectra for  $C_{60}$  in a series of *n*-alkanes and using linear relations between the former positions and the corresponding Lorentz–Lorenz functions of the solvents, Catalan [10] estimated the positions of the absorption peaks in the gas phase.

The solvatochromism of a nonpolar solute in a nonpolar solvent is commonly known to be solely dependent on dispersion forces (and hence on the polarizability of the solvent) [14–17]. The higher the polarizability, the stronger the bathochromic shift (relative to the spectrum in the gas phase). On the other hand Gallagher et al. [8] argue that if the redistribution of charge in the excited state leads to a dipolar or quadrupolar structure, then the solvent polarity parameters become important as well [14–17].

The information about solvatochromism of  $C_{60}$  in solvent mixtures is even scarcer. It is scattered and mostly limited to mixtures of nonpolar solvents [6]. In solvent mixtures the influence of solvent polarity and polarizability as non-specific solvent–solute interactions is complicated by intervention of the effects of selective solvation, sometimes called also preferential solvation [14–17]. That is, the composition of the solvent shell immediately around the solvatochromic indicator is different from the composition of the bulk solvent. This phenomenon is especially important in the mixtures involving polar solvents.

Various approaches have been proposed to interpret solvatochromism of different solvatochromic indicators in binary solvent mixtures. They are mostly based on the assumption that the specific solvent–solute interactions between the solute and components of the binary mixture as well as their self- and hetero-association are playing the major role in solvent-induced changes of positions of spectral maxima, rate constants, etc. [18–32].

Suggestions to take (besides the effects of specific solvation) into account the changes in the polarity and polarizability of the binary solvent upon variation of the composition of the mixture were also made [14–17, 33]. In mixtures with polar solvents various rather simple models involving preferential solvation and also formation of solvent associates have proved, at least formally, reasonably successful [18–32].

Most of the solvatochromic indicators studied are polar compounds with a large dipole moment change on excitation [14–17]. In this respect fullerene  $C_{60}$  is a very different compound. It possesses no dipole moment in the ground state. The solvatochromic behaviour of such molecules (e.g.,  $C_6H_6$ , etc.) in individual solvents is known to be determined mostly by the variation of the polarizability of the solvents [9, 14–17]. No such study has been undertaken for binary solvent mixtures. Therefore it would be interesting to investigate the applicability of the preferential solvation model to  $C_{60}$ .

We set two main goals:

1. To investigate the solvatochromism of fullerene  $C_{60}$  in binary solvent mixtures encompassing a wide range of solvent properties and involving polar solvents.

2. To interpret and analyse the data in terms of the preferential solvation model first proposed by Skwierczynski & Connors [30] and to obtain information on preferential solvation of  $C_{60}$  in solvent mixtures involving polar solvents.

## EXPERIMENTAL

### Chemicals

The fullerene  $C_{60}$  was a kind donation from Professor G. K. S. Prakash (University of Southern California). Its preparation and purification have been described elsewhere [34].

The following solvents were used: pyridine (>99.8%, Fluka), methanol (>99.8%, Merck), N,N-dimethylformamide (>99.8%, Aldrich), toluene (>99.7%, J. T. Baker), acetonitrile (>99.5%, Chempure), dimethyl sulphoxide (>99.5%, Fluka), and acetic acid (chemically pure, Reakhim).

The solvents were used as received. The water used for the experiments was prepared with a Purite Analyst HP 5 analytical water system.

### Apparatus

Absorption spectra were recorded on a Perkin-Elmer Lambda 2S spectrophotometer at room temperature using quartz cells with 1 cm path length. The slit width was constant and equal to 2 nm. This slit width is sufficient for our studies because the bands of  $C_{60}$  in aromatic solvents are quite broad [8]. The reference cell contained the same solvent mixture without  $C_{60}$ .

The wavelength scale of the spectrophotometer was calibrated with a didymium filter (Hitachi) having sharp absorption bands at 403.0, 529.5, and 586.0 nm.

### Procedure

The stock solutions of  $C_{60}$  were prepared by adding about 1 mg of  $C_{60}$  to 10 mL of toluene or pyridine and by agitating the mixtures with PTFE-coated stirring bar for 15 min. Additional mixing was effected by sonicating the mixtures in an ultrasound bath for 10 min. The mixtures were prepared by adding the second solvent to the stock solution of  $C_{60}$ . The solutions were stirred again for a period not less than 15 min.

Because of the very low solubility of fullerene C<sub>60</sub> in most of the solvents used (except toluene and pyridine), addition of the second solvent to the stock solution caused a decrease in the solubility of C<sub>60</sub>, which sometimes led to the formation of very fine precipitate of fullerene C<sub>60</sub>. Therefore, all prepared solutions were filtered through a 0.2 μm PTFE or glass filter. This treatment eliminated the problem completely.

### Data treatment

As the intensity of the spectra of fullerene C<sub>60</sub> is low in most solvent mixtures used in the present work, the exact locations of absorption maxima were quite difficult to find. To resolve this problem different algorithms [35] were tested. The best results were obtained by using a polynomial regression equation in the form:

$$y = ax^3 + bx + c, \quad (1)$$

where  $y$  is absorbance (optical density) at wavelength  $x$  and  $a$ ,  $b$ , and  $c$  are regression coefficients.

The location of the absorption band maximum is the point where the first derivative of this function is equal to zero:

$$y' = 3ax^2 + b = 0. \quad (2)$$

The spectral line was analysed between inflection points lying on both sides of the absorption maximum and the wavelength of absorption band maximum was found from the equation:

$$x = \sqrt{-\frac{b}{3a}}. \quad (3)$$

The results were evaluated applying standard deviation and by visual comparison of real spectra and the line formed using the regression coefficients found before.

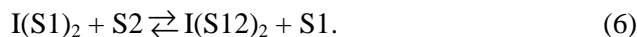
The accuracy of the band maxima is 0.2 nm for absorption bands lying at 335.4 and 406.8 nm (fullerene C<sub>60</sub> solution in toluene). For bands lying at 535.4 and 596.9 nm the accuracy may be lower (1 nm).

The band maxima expressed as molar transition energy,  $E_T$ , defined by Eq. 4, were used for further calculations:

$$E_T (\text{kcal mol}^{-1}) = hc\tilde{\nu} N_A = 2.8591 \times 10^{-3} \tilde{\nu}_{\text{max}} = \frac{28591}{\lambda_{\text{max}}}, \quad (4)$$

where  $h$  is Planck's constant,  $c$  is the velocity of light, and  $\tilde{\nu}_{\text{max}}$  and  $\lambda_{\text{max}}$  are the wavenumber (in cm<sup>-1</sup>) and the wavelength (in nm) of the absorption band maximum, respectively.

The interpretation of the data was carried out in terms of the preferential solvation model first proposed by Skwierczynski & Connors [30]. The model is based on the two-step solvent exchange equilibria:



In these equilibria S1 and S2 indicate the two pure solvents mixed and S12 represents a solvent formed by the interaction of solvents 1 and 2 [15].  $I(S1)_2$ ,  $I(S2)_2$ , and  $I(S12)_2$  represent the molecule of the solvatochromic indicator (fullerene  $C_{60}$  in our case) solvated by solvents S1, S2, and S12, respectively.

The two solvent exchange processes can be defined by two preferential solvation parameters,  $f_{2/1}$  and  $f_{12/1}$ , which measure the tendency of the solute to be solvated by solvents S2 and S12 with reference to solvent S1 solvation [18, 21–27]:

$$f_{2/1} = \frac{x_2^S / x_1^S}{(x_2^0 / x_1^0)^2}, \quad (7)$$

$$f_{12/1} = \frac{x_{12}^S / x_1^S}{x_2^0 / x_1^0}. \quad (8)$$

In Eqs. 7 and 8,  $x_1^S$ ,  $x_2^S$ , and  $x_{12}^S$  are the mole fractions of solvents S1, S2, and S12, respectively, in the sphere of the solvation of the indicator, and  $x_1^0$  and  $x_2^0$  are the mole fractions of the two solvents in the bulk mixed solvent. The  $E_T$  of the mixed solvent is calculated as an average of the  $E_T$  values of solvents S1, S2, and S12 in the sphere of the solvation of the indicator:

$$E_T = x_1^S E_{T1} + x_2^S E_{T2} + x_{12}^S E_{T12}. \quad (9)$$

From Eqs. 7–9, a general equation that relates the  $E_T$  of a binary mixture to the  $E_T$  of the two pure solvents, the preferential solvation parameters, and the solvent composition can be derived as follows:

$$E_T = \frac{E_{T1}(1-x_2^0)^2 + E_{T2}f_{2/1}(x_2^0)^2 + E_{T12}f_{12/1}(1-x_2^0)x_2^0}{(1-x_2^0)^2 + f_{2/1}(x_2^0)^2 + f_{12/1}(1-x_2^0)x_2^0}. \quad (10)$$

This general equation has been applied to many different binary solvent mixtures using different solvatochromic dyes [18, 21–27, 30] and aromatic nucleophilic substitution reaction rate constants [31].

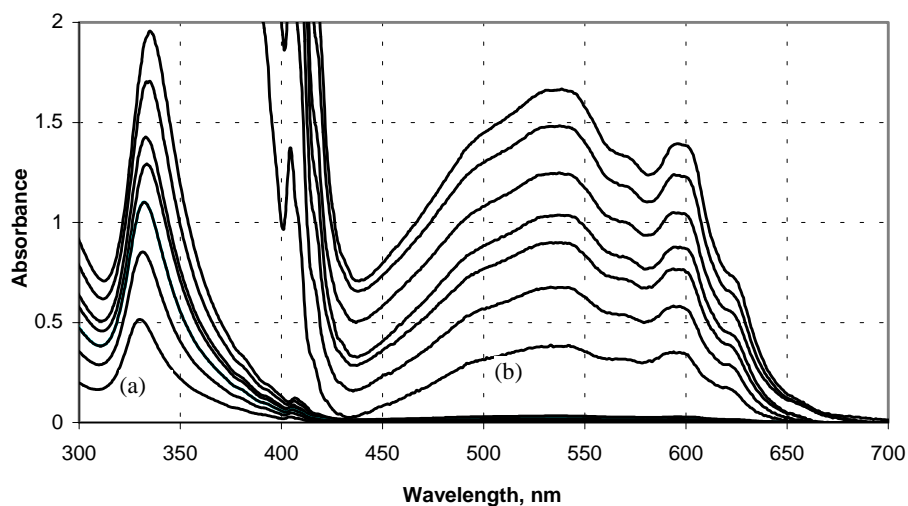
The  $E_{T1}$ ,  $E_{T2}$ ,  $E_{T12}$ ,  $f_{2/1}$ , and  $f_{12/1}$  parameters that minimize the sum of squared residuals of  $E_T$  values of each binary solvent system studied were calculated by non-linear regression as described previously [27].

## ZINDO calculations

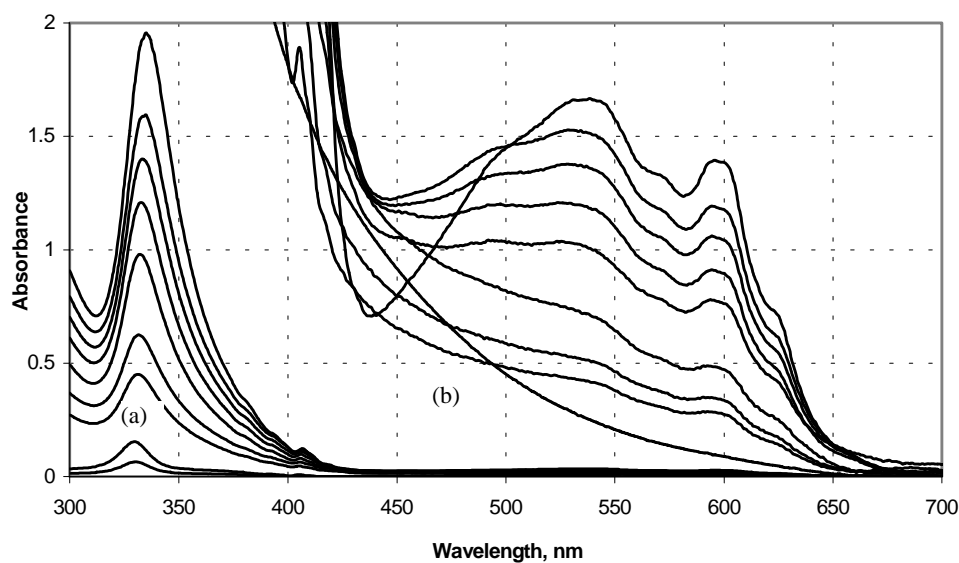
All calculations were performed with ArgusLab 2.0 [36–39] program package. Molecular geometry was optimized using the semiempirical AM1 method [40]. Energies and dipole and quadrupole moments of excited states were calculated using the ZINDO method. The ZINDO method is based on an Intermediate Neglect of Differential Overlap Hamiltonian (INDO), specifically the INDO1/s parameterization first published by Zerner's group [41, 42]. This method has enjoyed tremendous success in predicting excited state properties of a wide variety of organic and organometallic compounds [43, 44]. The name ZINDO has become synonymous with the INDO1/s since the method was first implemented in the ZINDO program developed by Zerner's group. In the current work 30 highest occupied molecular orbitals and 30 lowest unoccupied molecular orbitals were included in the active space for CIS (configurational interaction singles) calculations.

## RESULTS

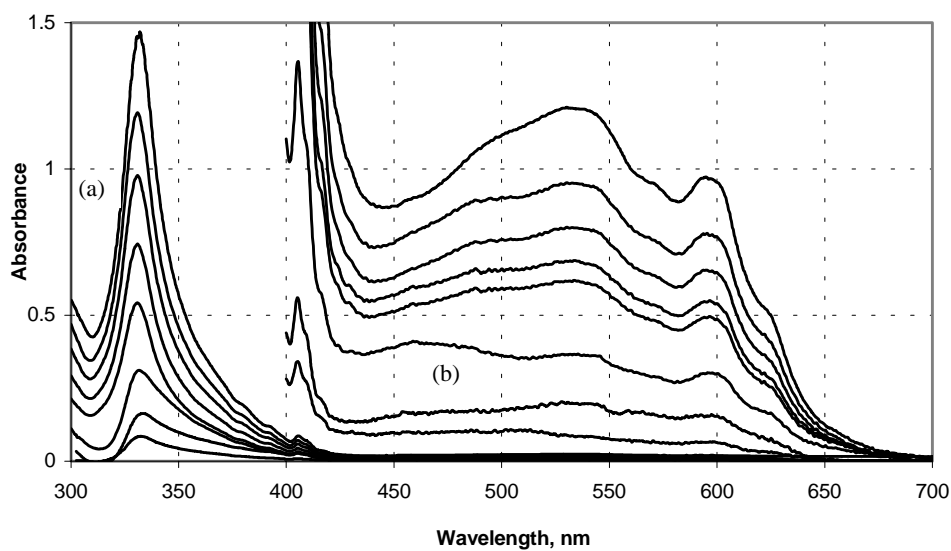
The absorption spectra of  $C_{60}$  were measured in the following solvent mixtures: toluene–acetic acid, toluene–methanol, toluene–acetonitrile, toluene–DMSO, toluene–DMF, pyridine–methanol, pyridine–water. The spectra of some of the mixtures are presented in Figs. 1–3.



**Fig. 1.** UV-vis absorption spectra of  $C_{60}$  in toluene–acetic acid mixtures at different molar fractions of acetic acid (0, 0.1457, 0.2559, 0.3268, 0.4352, 0.5498, 0.7228). (a) 300–700 nm; (b) 400–700 nm region multiplied by a factor of 50 for clarity. Intensities of the band maxima decrease with the increase in the molar fraction of acetic acid.



**Fig. 2.** UV-vis absorption spectra of  $C_{60}$  in toluene–dimethylformamide mixtures at different molar fractions of dimethylformamide (0, 0.2537, 0.4193, 0.5988, 0.7262, 0.8154, 0.8770, 0.9447, 1). (a) 300–700 nm; (b) 400–700 nm region multiplied by a factor of 50 for clarity. Intensities of the band maxima decrease with the increase in the molar fraction of dimethylformamide.



**Fig. 3.** UV-vis absorption spectra of  $C_{60}$  in pyridine–water mixtures at different molar fractions of water (0, 0.2925, 0.3959, 0.4194, 0.4506, 0.5333, 0.6109, 0.6309). (a) 300–700 nm; (b) 400–700 nm region multiplied by a factor of 50 for clarity. Intensities of the band maxima decrease with the increase in the molar fraction of water.

The following absorption bands were used for the analysis (band codes from [5] are used): C:  $3\ ^1T_{1u-1}\ ^1A_g$  (328.4 nm); A<sub>1</sub>:  $1\ ^1T_{1u-1}\ ^1A_g + h_g(8)$  (404.0 nm);  $\delta_1$ :  $1\ ^1T_{2u-1}\ ^1A_g + h_g(8)$  (542.6 nm);  $\gamma_2$ :  $1\ ^1T_{1g-1}\ ^1A_g + h_g(8)$  (598.1 nm) (wavelength in *n*-hexane at room temperature).

These maxima were selected based on experimental considerations: the solubility of fullerene C<sub>60</sub> in toluene is 2.8 mg/mL [45] and in pyridine 0.89 mg/mL [45], which leads to the spectra of rather low intensity. At the low intensities these maxima were the only ones that could be reliably measured. The problem was especially serious with the mixtures in which one of the components was very polar (water, methanol).

The wavelengths of the examined absorption bands are presented in Table 1.

**Table 1.** Absorption band maxima (in nm) of the studied bands (C, A<sub>1</sub>,  $\delta_1$ , and  $\gamma_2$  of C<sub>60</sub> in seven binary solvent mixtures. The molar fraction of the second solvent is denoted by  $x_2$ . The values in brackets are less precise and were left out during the treatment of data

| Solvent mixture      | $x_2$  | C     | A <sub>1</sub> | $\delta_1$ | $\gamma_2$ |
|----------------------|--------|-------|----------------|------------|------------|
| Toluene–acetic acid  | 0.0000 | 335.4 | 406.7          | 535.4      | 596.9      |
|                      | 0.1457 | 334.4 | 406.3          | 534.6      | 596.0      |
|                      | 0.2559 | 333.6 | 406.0          | 535.4      | 595.9      |
|                      | 0.3268 | 333.2 | 405.8          | 534.5      | 595.5      |
|                      | 0.4352 | 332.4 | 405.4          | 534.3      | 595.0      |
|                      | 0.5498 | 331.7 | 405.1          | 534.6      | 594.7      |
|                      | 0.7228 | 330.4 | 404.4          | 534.6      | 594.2      |
| Toluene–methanol     | 0.0000 | 335.4 | 406.7          | 535.4      | 596.9      |
|                      | 0.3485 | 334.4 | 406.5          | 535.2      | 596.8      |
|                      | 0.5460 | 333.9 | 406.1          | 535.4      | 596.4      |
|                      | 0.7154 | 333.1 | 405.8          | 535.3      | 595.4      |
|                      | 0.7987 | 332.4 | 405.5          | 535.6      | 595.4      |
|                      | 0.8439 | 331.7 | 405.3          | 537.6      | 595.3      |
|                      | 0.9156 | 330.9 | 404.9          | 540.2      | 594.2      |
| Toluene–acetonitrile | 0.0000 | 335.4 | 406.7          | 535.4      | 596.9      |
|                      | 0.1098 | 334.7 | 406.6          | 535.2      | 596.7      |
|                      | 0.1746 | 334.5 | 406.5          | 535.1      | 596.8      |
|                      | 0.2912 | 334.2 | 406.3          | 534.9      | 596.6      |
|                      | 0.2943 | 334.0 | 406.3          | 535.0      | 596.4      |
|                      | 0.4136 | 333.5 | 406.0          | 534.9      | 595.4      |
|                      | 0.4417 | 333.6 | 406.1          | 534.9      | 595.9      |
|                      | 0.4792 | 333.5 | 405.9          | 534.8      | 594.7      |
|                      | 0.5602 | 333.1 | 405.7          | 534.6      | 594.3      |
|                      | 0.5819 | 332.9 | 405.8          | (534.6)    | (595.2)    |
|                      | 0.6655 | 332.4 | 405.5          | (534.8)    | (594.1)    |
|                      | 0.7418 | 331.8 | 405.2          | 532.9      | 594.2      |
|                      | 0.7424 | 332.0 | 405.3          | 533.1      | 594.0      |
|                      | 0.7809 | 331.4 | 404.9          | 533.3      | 593.3      |
|                      | 0.7901 | 331.6 | 405.1          | 533.0      | 592.4      |
| 0.8100               | 331.1  | 404.9 | 531.9          | 593.1      |            |
| 0.8149               | 331.0  | 404.8 | 532.7          | 592.9      |            |



Table 1 continued

| Solvent mixture             | $x_2$  | C       | A <sub>1</sub> | $\delta_1$ | $\gamma_2$ |
|-----------------------------|--------|---------|----------------|------------|------------|
|                             | 0.8353 | 330.9   | 404.6          | –          | 592.6      |
|                             | 0.8573 | 331.2   | 404.7          | –          | 592.0      |
|                             | 0.8780 | 330.5   | 404.5          | 532.0      | 591.1      |
|                             | 0.9306 | (330.9) | 404.4          | –          | 589.6      |
| Toluene–dimethyl sulphoxide | 0.0000 | 335.4   | 406.7          | 535.4      | 596.9      |
|                             | 0.2134 | 334.2   | 405.9          | 535.8      | 596.0      |
|                             | 0.4117 | 334.0   | 405.8          | 535.8      | 596.1      |
|                             | 0.6984 | 333.6   | 405.7          | 535.4      | 596.2      |
|                             | 0.8614 | 332.9   | 405.2          | 531.0      | 597.4      |
|                             | 0.9150 | 332.6   | 404.8          | 530.6      | 598.9      |
|                             | 0.9514 | 331.9   | 403.9          | 526.0      | 600.2      |
| Toluene–dimethylformamide   | 0.0000 | 335.4   | 406.7          | 535.4      | 596.9      |
|                             | 0.2537 | 334.5   | 406.4          | 530.4      | 596.2      |
|                             | 0.4193 | 333.8   | 406.2          | 528.9      | 595.8      |
|                             | 0.4315 | 334.0   | 406.2          | 528.4      | 595.4      |
|                             | 0.5988 | 333.0   | 405.9          | 525.8      | 595.0      |
|                             | 0.6471 | 332.9   | 405.8          | –          | 594.9      |
|                             | 0.6671 | 332.4   | 405.6          | –          | 594.5      |
|                             | 0.7262 | 332.2   | 405.7          | 525.1      | 594.5      |
|                             | 0.8154 | 331.5   | 405.4          | –          | 593.0      |
|                             | 0.8411 | 331.9   | 405.4          | –          | 593.4      |
|                             | 0.8539 | 331.7   | 405.5          | –          | 592.9      |
|                             | 0.8770 | 331.2   | 405.2          | –          | 592.3      |
|                             | 0.9154 | 328.8   | 405.0          | –          | 592.1      |
|                             | 0.9447 | 329.6   | 405.1          | –          | –          |
|                             | 1.0000 | 326.7   | 404.7          | –          | –          |
| Pyridine–methanol           | 0.0000 | 330.0   | 405.7          | 532.3      | 595.1      |
|                             | 0.1319 | 329.6   | 405.5          | 531.4      | 594.8      |
|                             | 0.2613 | 329.3   | 405.3          | 530.2      | 594.7      |
|                             | 0.4143 | 329.0   | 405.0          | 527.8      | 594.6      |
|                             | 0.6118 | 328.3   | 404.5          | 527.9      | 594.0      |
|                             | 0.7528 | 327.3   | 404.0          | 529.0      | 593.8      |
|                             | 0.8248 | 326.9   | 403.7          | 529.7      | 593.4      |
|                             | 0.8893 | 326.5   | 403.4          | 529.3      | 590.9      |
|                             | 0.9418 | 325.8   | 403.0          | –          | –          |
|                             | 0.9763 | 325.3   | 403.0          | –          | –          |
| Pyridine–water              | 0.0000 | 330.0   | 405.7          | 532.3      | 595.1      |
|                             | 0.2925 | 330.9   | (405.7)        | 532.9      | 595.6      |
|                             | 0.3177 | 330.9   | (405.6)        | 533.4      | 595.9      |
|                             | 0.3384 | 331.2   | 405.4          | 533.4      | 595.9      |
|                             | 0.3959 | 330.8   | 405.5          | 533.5      | 596.0      |
|                             | 0.4194 | 330.8   | 405.5          | 533.5      | 596.4      |
|                             | 0.4506 | 331.3   | 405.5          | 533.9      | 596.2      |
|                             | 0.4935 | 331.8   | 405.5          | 533.8      | 596.2      |
|                             | 0.5333 | 331.5   | 405.4          | 534.5      | 596.6      |
|                             | 0.6109 | (333.2) | 405.2          | 535.0      | 597.0      |
|                             | 0.6309 | 332.4   | 405.2          | –          | (597.8)    |

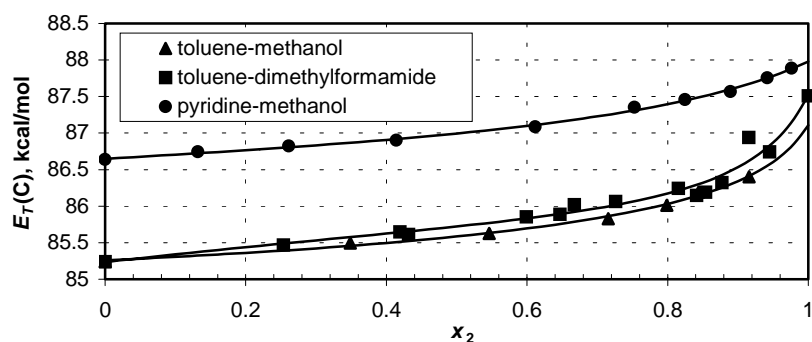
– Data missing because the intensity of the absorption band was too low to find the maximum.

Examination of the spectra for several systems reveals that distortions arise when the mole fraction  $x$  of the more polar components increases. Various agglomeration processes of  $C_{60}$  have been proposed as the reason for these phenomena [46]. In such cases the treatment of the data in terms of Eq. 10 cannot be done in a reasonable way. Such spectra were left out during the data treatment process.

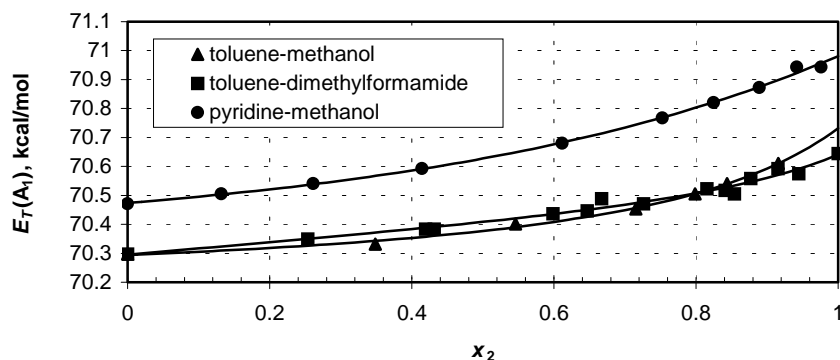
These effects are particularly noticeable for the two longer-wavelength maxima. Thus in the mixtures of toluene with acetonitrile, DMSO, and DMF the  $\delta_1$  maximum practically disappears. The effect is especially dramatic in the mixture of toluene and DMF: even the  $\gamma_2$  maximum almost disappears.

Practically in all the systems the measurement of the wavelength of the  $\delta_1$  and  $\gamma_2$  maxima posed a significant problem and in fact could not be done satisfactorily over the whole range of  $x$ . Therefore, we limit the application of the preferential solvation model to the bands C and  $A_1$ .

The results of the analysis of the spectra in terms of Eq. 10 are presented in Table 2 and Figs. 4 and 5.



**Fig. 4.** Some typical results of the data treatment of the C band. The molar fraction of the second solvent is denoted by  $x_2$ .



**Fig. 5.** Some typical results of the data treatment of the  $A_1$  band. The molar fraction of the second solvent is denoted by  $x_2$ .

**Table 2.** Parameters of the binary mixtures derived from the treatment of the data in terms of Eq. 10. The parameters on the lines denoted by  $C'$  and  $A_1'$  were derived using simultaneous treatment of both bands (SD – standard deviation of regression;  $n$  – number of data points)

| Solvent 1 | Solvent 2    | Band   | $E_{T1}$ | $E_{T2}$ | $E_{T12}$ | $f_{2/1}$ | $f_{12/1}$ | SD    | $n$ |
|-----------|--------------|--------|----------|----------|-----------|-----------|------------|-------|-----|
| Toluene   | Acetic acid  | C      | 85.2     | 88.9     | 86.7      | 0.039     | 1.22       | 0.014 | 7   |
|           |              | $A_1$  | 70.3     | 71.5     | 70.8      | 0.040     | 0.99       | 0.007 | 7   |
|           |              | $C'$   | 85.2     | 88.8     | 86.7      | 0.041     | 1.21       | 0.008 | 14  |
|           |              | $A_1'$ | 70.3     | 72.1     | 70.7      | *         | *          | *     | *   |
| Toluene   | Methanol     | C      | 85.3     | 87.1     | 86.2      | 0.031     | 0.49       | 0.053 | 7   |
|           |              | $A_1$  | 70.3     | 70.7     | 70.6      | 0.030     | 0.36       | 0.011 | 7   |
|           |              | $C'$   | 85.2     | 87.1     | 86.2      | 0.026     | 0.49       | 0.028 | 14  |
|           |              | $A_1'$ | 70.3     | 70.9     | 70.5      | *         | *          | *     | *   |
| Toluene   | Acetonitrile | C      | 85.3     | 88.1     | 86.6      | 0.011     | 0.60       | 0.049 | 20  |
|           |              | $A_1$  | 70.3     | 70.6     | 70.9      | 0.013     | 0.26       | 0.015 | 21  |
|           |              | $C'$   | 85.2     | 87.7     | 86.6      | 0.010     | 0.65       | 0.039 | 41  |
|           |              | $A_1'$ | 70.3     | 71.2     | 70.7      | *         | *          | *     | *   |
| Toluene   | DMSO         | C      | 85.2     | 86.7     | 85.6      | 0.59      | 12.3       | 0.025 | 7   |
|           |              | $A_1$  | 70.3     | 76.4     | 70.4      | 0.22      | 68.5       | 0.010 | 7   |
|           |              | $C'$   | 85.2     | 87.1     | 85.6      | 0.34      | 12.2       | 0.023 | 14  |
|           |              | $A_1'$ | 70.3     | 71.4     | 70.4      | *         | *          | *     | *   |
| Toluene   | DMF          | C      | 85.2     | 87.5     | 85.8      | 0.17      | 1.96       | 0.131 | 15  |
|           |              | $A_1$  | 70.3     | 70.6     | 70.4      | 0.31      | 1.56       | 0.017 | 15  |
|           |              | $C'$   | 85.2     | 87.5     | 85.9      | 0.14      | 1.62       | 0.087 | 30  |
|           |              | $A_1'$ | 70.3     | 70.7     | 70.5      | *         | *          | *     | *   |
| Pyridine  | Methanol     | C      | 86.6     | 88.0     | 87.0      | 0.36      | 1.60       | 0.031 | 10  |
|           |              | $A_1$  | 70.5     | 71.0     | 70.6      | 0.43      | 1.27       | 0.011 | 10  |
|           |              | $C'$   | 86.6     | 88.0     | 87.0      | 0.36      | 1.59       | 0.021 | 20  |
|           |              | $A_1'$ | 70.5     | 71.0     | 70.7      | *         | *          | *     | *   |
| Pyridine  | Water        | C      | 86.6     | 80.7     | 85.7      | 0.021     | 0.51       | 0.082 | 10  |
|           |              | $A_1$  | 70.5     | 71.9     | 70.6      | 0.021     | 0.46       | 0.016 | 9   |
|           |              | $C'$   | 86.6     | 81.3     | 85.7      | 0.020     | 0.54       | 0.052 | 19  |
|           |              | $A_1'$ | 70.5     | 71.8     | 70.6      | *         | *          | *     | *   |

\* These parameters are identical for the corresponding  $C'$  and  $A_1'$ .

## DISCUSSION

Some macroscopic and microscopic properties of the pure solvents used to prepare the mixtures are given in Table 3.

It has been shown that solvent effects on the UV-vis spectrum of a polar molecule depend on the polarity of the ground and excited state of the molecule [14–17, 33]. In the case when both the ground state and the excited state of a molecule are nonpolar, a bathochromic shift is generally observed for the corresponding absorption band upon going from a less polarizable solvent to a more polarizable one [14–17].

These findings are supported by our results. Indeed, in all mixtures but one there was a bathochromic shift upon going from a less polarizable mixture to a more polarizable mixture. The preferential solvation of  $C_{60}$  in the solvent mixtures is reflected by the  $f_{2/1}$  and  $f_{12/1}$  coefficients for the mixtures. In the mixtures of toluene with solvents of high polarity and low polarizability,  $f_{2/1}$  is significantly less than unity. This is an evidence of strong preferential solvation of  $C_{60}$  by toluene. The value of  $f_{12/1}$  is generally less than or around unity. In the mixtures of pyridine with polar solvents the same trend holds for  $f_{2/1}$ .

The trends in  $f_{2/1}$  and  $f_{12/1}$  are easily rationalized on the basis of the parameters in Table 3. It is clear that  $C_{60}$  – a nonpolar and highly polarizable molecule – is preferentially solvated by solvents with high polarizability. This is really the case: the solvent shell around  $C_{60}$  contains preferentially toluene and pyridine. On the other hand, there seems to be practically no dependence of the  $f_{2/1}$  value on the hydrogen bond donicity of the solvent; for example, the  $f_{2/1}$  values in the systems toluene–acetonitrile and toluene–methanol are very similar, although the hydrogen bond donor properties of acetonitrile and methanol are dramatically different.

In order to be of chemical significance, the  $f_{2/1}$  and  $f_{12/1}$  coefficients derived from the treatment of different absorption bands must coincide. Examination of

**Table 3.** Properties of the solvents studied

| Solvent      | $\epsilon_r^a$ | $\mu(10^{-30}\text{Cm})^a$ | $n_D^a$ | $\pi^{*b}$ | $\beta^b$           | $\alpha^b$ | $E_T(30)^c$         |
|--------------|----------------|----------------------------|---------|------------|---------------------|------------|---------------------|
| Toluene      | 2.38           | 1.0                        | 1.4969  | 0.54       | 0.11                | 0.00       | 33.9                |
| Pyridine     | 12.91          | 7.9                        | 1.5102  | 0.87       | 0.64                | 0.00       | 40.5                |
| DMF          | 36.71          | 10.8                       | 1.4305  | 0.88       | 0.69                | 0.00       | 43.2                |
| DMSO         | 46.45          | 13.5                       | 1.4793  | 1.00       | 0.76                | 0.00       | 45.1                |
| Acetonitrile | 35.94          | 11.8                       | 1.3441  | 0.75       | 0.31                | 0.19       | 45.6                |
| Methanol     | 32.66          | 5.7                        | 1.3284  | 0.60       | (0.62) <sup>d</sup> | 0.93       | 55.4                |
| Water        | 78.30          | 5.9                        | 1.3330  | 1.09       | (0.18) <sup>d</sup> | 1.17       | 63.1                |
| Acetic acid  | 6.17           | 5.6                        | 1.3719  | 0.64       | –                   | 1.12       | (51.7) <sup>d</sup> |

<sup>a</sup> Data on dielectric constant (at 25 °C), dipole moment, and refractive index from [15]. <sup>b</sup> Data on  $\pi^*$ ,  $\beta$ , and  $\alpha$  from [47]. <sup>c</sup> Data on  $E_T(30)$  from [17]. <sup>d</sup> Data in parentheses are less certain.

Table 2 reveals that, given the very narrow ranges of the solvatochromic shifts and the difficulties in finding the exact positions of the absorption maxima, the  $f_{2/1}$  and  $f_{12/1}$  derived for the same system independently from the bands C and A<sub>1</sub> agree reasonably well.

In order to get more reliable estimates of  $f_{2/1}$  and  $f_{12/1}$  they were also derived for each system using simultaneously both the C and A<sub>1</sub> absorption bands. In that case the  $f$  coefficients were kept common for the two bands, while the  $E_T$  parameters were varied separately. The results are presented in Table 2. As can be seen, these values agree well with the ones derived independently.

The excited states of C<sub>60</sub> were also investigated using the ZINDO method. These computations yield the excitation energies and dipole and quadrupole moments of the excited states. The dipole moments of the excited states were found to be very low: they did not exceed 0.015 debyes. It is, therefore, not surprising that the positions of the transition maxima are quite insensitive to the changes in the polarity of the medium as well as to the characteristics of the specific solvation capacity of its components.

It can be concluded that, at least formally, the preferential solvation model is applicable for the description of the solvatochromic shifts of the UV-vis spectrum of fullerene C<sub>60</sub>.

## CONCLUSIONS

The appearance of the UV-vis spectra of fullerene C<sub>60</sub> was found to be influenced by the composition of the solvent mixture, as revealed by the study of the position of four absorption bands. The solvent-induced shifts of the absorption maxima were generally in the range of several nanometers, the longest being 10.3 nm in the mixture of toluene and dimethylformamide.

Analysis of the data in terms of the preferential solvation model of Rosés et al. [18] revealed that, compared to more polar solvents of the mixtures, fullerene was strongly preferentially solvated by toluene and pyridine. The selective solvation model was found to be applicable to the description of the solvatochromism of C<sub>60</sub> in binary solvent mixtures, at least formally.

No simple scheme of relationships between the shifts of the absorption maxima and the properties of the solvents could be found. Particularly interesting solvent effects – significant changes in the shape of the spectrum – were found in the mixtures toluene–DMF and pyridine–water.

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## **Fullereeni C<sub>60</sub> solvatokromism solvendisegudes: eelissolvatatsiooni mudel**

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On uuritud fullereeni C<sub>60</sub> neeldumisspektreid vahemikus 300–700 nm binaarsetes solvendisegudes (tolueen–äädikhape, tolueen–metanool, tolueen–atsetonitriil, tolueen–dimetüülsulfoksiid, tolueen–dimetüülformamiid, püridiin–metanool ja püridiin–vesi).

Et fullereeni C<sub>60</sub> spektri kuju sõltub solvendisegu koostisest, selgitati selle mõju nelja neeldumisjoone (C, A<sub>1</sub>,  $\delta_1$  ja  $\gamma_2$ ) asukohale. Saadud andmeid töödeldi eelissolvatatsiooni mudeli raames. Leiti, et tolueen ja püridiin solvateerivad fullereeni C<sub>60</sub> tunduvalt intensiivsemalt kui segude polaarsemad komponendid. Mudel on vähemalt formaalselt sobiv kirjeldama fullereeni C<sub>60</sub> solvatokromismi. Iseäranis huvitavad solvendiefektid – suured muutused spektrite kujus – ilmnesid süsteemides tolueen–dimetüülformamiid ja püridiin–vesi.