NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS, 2016, 7 (1), P. 99–103

Investigation and modeling of evolution of C_{60}/NMP solution UV-Vis spectra

N. Jargalan[1,2], T. V. Tropin[1], M. V. Avdeev[1], V. L. Aksenov[1,3]

[1]Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna, Russia
[2]Institute of Physics and Technology, Mongolian Academy of Sciences, Ulaanbaatar, Mongolia
[3]Petersburg Nuclear Physics Institute, National Research Centre 'Kurchatov Institute',
Gatchina, Russia

narmandah@jinr.ru, ttv@jinr.ru

PACS 78.40.-q, 81.05. ub **DOI 10.17586/2220-8054-2016-7-1-99-103**

The kinetics for the dissolution of fullerene C_{60} in N-methyl-2-pyrrolidone (NMP) solvent are investigated through measurements of the stirring speed and temperature dependence of the UV-Vis absorption spectra. We develop a model for the kinetics of simultaneously occurring processes in the solution, employing a system of simple kinetic equations and obtain the corresponding parameters dependence on preparation conditions. The obtained results will allow one in the future to consider these effects when modeling the slow growth kinetics of large clusters in C_{60}/NMP solutions.

Keywords: kinetics of dissolution, fullerene, N-methyl-2-pyrrolidone, UV-Vis.

Received: 20 November 2015

1. Introduction

Presently, a third allotropic form of carbon, called fullerenes, has attracted the interest of scientists in different areas, due to their unusual properties. Fullerenes are soluble in many various liquids, non-polar, organic, polar etc. Much research is being continuously published on the subject [1–4]. One of the most interesting phenomena studied is the cluster formation of fullerenes C_{60} and C_{70} in solutions. The large, stable clusters were detected in nitrogen containing solvents (aggregates size up to 500 nm) [5–7]. In addition to cluster growth, solvatochromic effects are observed, which are associated with complex formation between fullerene and solvent molecules [7–9].

In our previous work [10], the kinetics of fullerene dissolution were investigated in solvents such as benzene, toluene and N-methyl-2-pyrrolidone (NMP) by UV-Vis spectrometry. As is well known, the stable characteristic absorption peaks (e.g. at $\sim$ 330 nm) disappear for C_{60}/NMP solutions, due to the formation of fullerene-solvent complexes. This fact does not allow one to directly measure the kinetics of dissolution in C_{60}/NMP via spectrophotometry. In the present work, we report new results for the analysis of the evolution kinetics of the UV-Vis spectra of C_{60}/NMP solution during the dissolution process.

2. Materials and methods

Solubility of fullerene C_{60} (Neo-Tech Product, purity $>$ 99.5 %) is 0.89 mg/ml [6] in NMP (Merck, purity $>$ 99.5 %). UV-Vis absorption spectra were obtained using Nanophotometer-P330 spectrometer (wavelength range of 200 – 950 nm, quartz cells with 1 mm light path). For this device, the convenient concentration for direct UV-Vis measurements was obtained to be 0.3 mg/ml. During different runs, the solution was stirred at 4 different speeds (V_s of 0, 100, 200, and 400 rpm), various temperatures were applied (room temperature (25 °C), 50, 60, 75 and 100 °C).

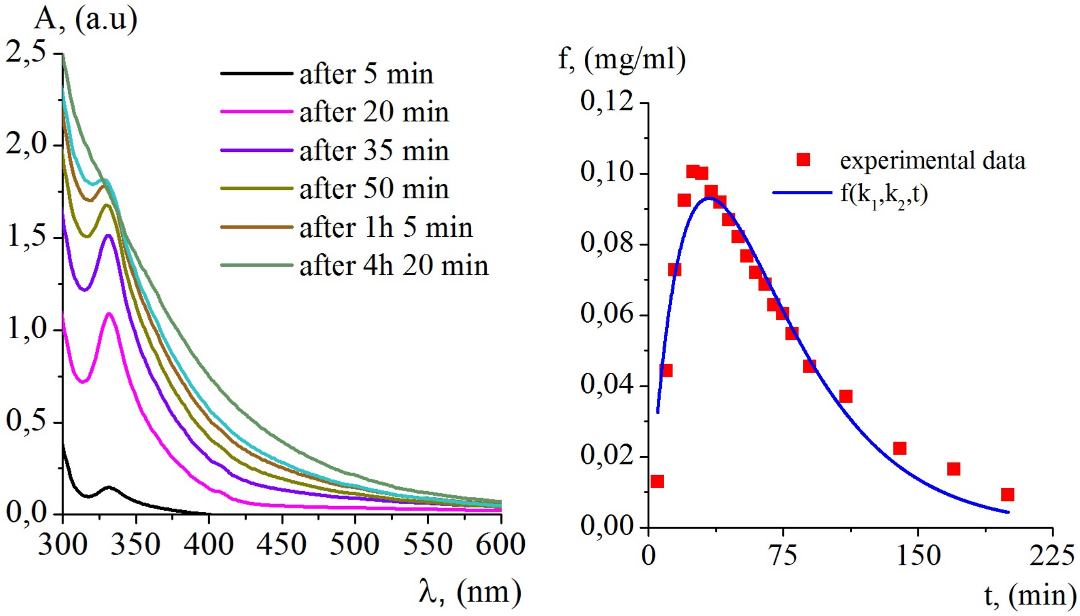
3. Method of UV-Vis spectra analysis

The effect of complex formation in C_{60}/NMP on the UV-Vis spectra permits the direct application of the Lambert-Beer law for evaluating the concentration kinetic curves. Thus, if one aims to extract the proper kinetic parameters, some method must be proposed to account for these phenomena.

The typical well-known evolution of the C_{60}/NMP UV-Vis spectra is presented in Fig. 1a for room temperature and a stirring rate of 400 rpm. To extract the kinetic constants from the measurements, we suppose that the dissolution of fullerene is governed by the Noyes-Whitney equation (with dissolution rate k_1), and that the complex formation proceeds simultaneously (rate of reaction k_2). Thus, a system of kinetic equations can be introduced:

$$\begin{cases} \dfrac{dc(t)}{dt} = k_1(C_s - c(t)), \\ \dfrac{dy(t)}{dt} = k_2(c(t) - y(t)), \end{cases} \tag{1}$$

where $c(t)$ is the concentration of ‘free’ fullerene molecules in the solution (those, that have not yet formed complexes), $y(t)$ – is the concentration of C_{60}-NMP complexes in the system, C_s – is the saturation concentration or the available concentration of C_{60}, if the solution is unsaturated. For the experiments performed, where the initial stage was the addition of fullerene to NMP, the initial conditions for Eqs. (1) should be: $c(0) = y(0) = 0$.



a b

FIG. 1. a – Absorption spectra of C_{60}/NMP for 400 rot/min at room temperature with time, b – Fitting curve for evolution of peak high of C_{60}/NMP for 400 rot/min at room temperature with time

From Fig. 1a, one can see that after all of the fullerene molecules form complexes with NMP in the solution, the UV-Vis spectrum presents a monotonically decreasing curve. The observed peak at $\sim$ 330 nm corresponds to the concentration of 'free' C_{60} molecules. Thus, this peak's height at any moment of time is proportional to $(\varepsilon_1 c(t) - \varepsilon_2 y(t))$, where ε_1 and ε_2 are the absorption coefficients for the 'free' molecules and the complexes, correspondingly. The values of these coefficients are not known, and for the present modeling, we roughly estimate them to be of the same order. This supposition allows one to directly relate the height of the $\sim$ 330 nm peak above the monotonically decreasing type of the UV-Vis spectra to concentration of the 'free' C_{60} molecules, equal to $(c(t) - y(t))$. In Fig. 1b, a typical evolution of the respective peaks height is presented for $T = 25$ °C and $V_s = 400$ rpm. The absorption is normalized to the respective solution concentration, thus it estimates the difference $(c(t) - y(t))$, that can be obtained straight from Eqs. (1):

$$c(t) - y(t) = f(k_1, k_2, t) = \frac{C_s k_1 \left(e^{-k_1 t} - e^{-k_2 t}\right)}{k_2 - k_1}. \tag{2}$$

The quality of the fit of experimental data, presented in Fig. 1b, reflects the applicability of the method proposed. The obtained expression was used for fitting the different experimental curves in order to obtain the values for k_1 and k_2 at various temperatures and stirring rates.

4. Results and discussion

Experimentally, measurements of the absorption spectra were performed apart from the stirred sample. This ensured that the amount of the solution taken for the measurements was small enough to not affect the dissolution kinetics. Measurements were taken at 5, 10, 15, 20, 30, etc. minutes after addition of fullerite soot to the solvent. At high temperatures, especially at $T = 100$ °C the maximum of the dependency of $f(k_1, k_2, t)$, occurs at times prior to 5 minutes, thus only the 'tail' of the evolution was captured and the quality of the fit is well reduced. As can be derived from (2), the maximum of $f(k_1, k_2, t)$ occurs at:

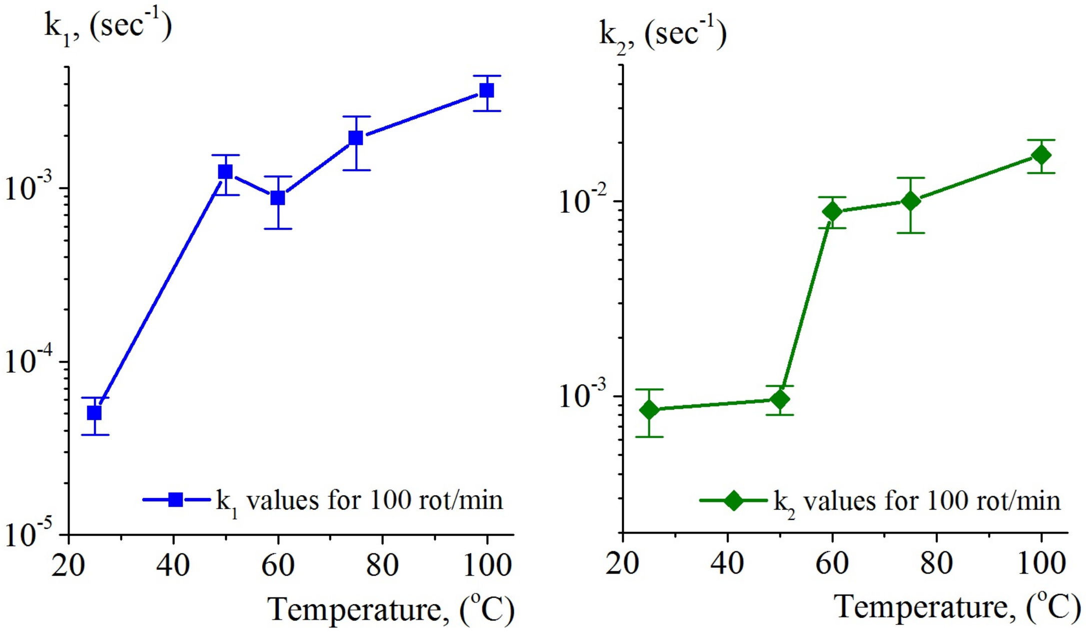
$$t_{\max} = \frac{\log\left(k_1/k_2\right)}{k_1 - k_2}, \tag{3}$$

i.e. must exist for any rate constant values.

From the performed measurements, it can be concluded, that the typical character of dissolution kinetics, accompanied by the complex formation, takes place for any temperature up to 100 °C and stirring rates up to 400 rpm. Yet, for confident estimates of k_1 and k_2 at various points of this range, a series of reproducible measurements would be required. Moreover, after inspection of Eq. (2) one can conclude, that scaled dependencies $f(k_1, k_2, t)$ can be obtained if one replaces k_1 and k_2 values. This fact shows that additional equation or supposition would improve the quality of the model. With respect to this approach, we depict some of the obtained results in Figs. 2 and 3.

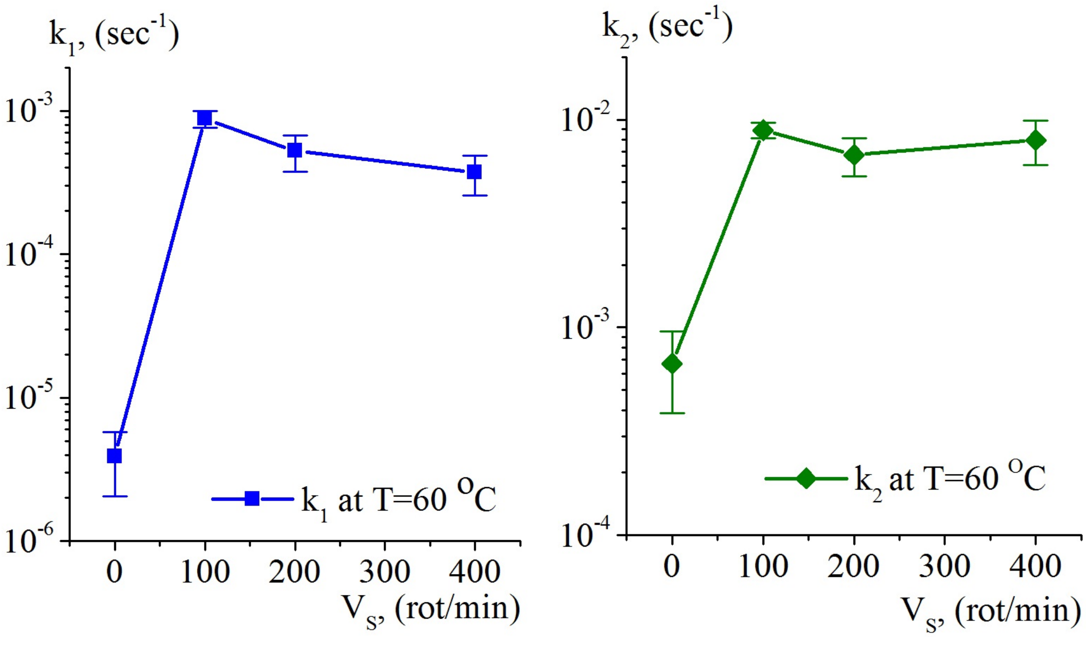
In Fig. 2, typical temperature dependencies of rate constants, introduced in Eqs. (1), are presented for $V_s = 100$ rpm. The expected increase of k_1 and k_2 values with temperature of the Arrhenius type is obtained within experimental error.

The stirring speed dependencies are presented on Fig. 3. Here, we see that the non-stirred solutions tend to dissolve fullerene and form complexes much more slowly than those samples that were subjected to stirring. While the low rate constant values ensure that the peak, similar to the one presented on Fig. 1a, occurs at larger time intervals after initial dissolution, its amplitude, as was observed in the experiments, is very small. Additionally, the solvatochromic effect is not pronounced. For a stirring speed $V_s \geq 100$ rpm, the values of k_1 and k_2 increase by an order of magnitude. As we have obtained, the value of V_s above 100 rpm does not further strongly affect the dissolution character.



a b

FIG. 2. Temperature dependencies of dissolution rate constant k_1 (a), and rate of complex formation k_2 (b) for the stirring speed of C_{60}/NMP solution equal to 100 rot/min



a b

FIG. 3. Stirring speed dependencies of dissolution rate constant k_1 (a), and rate of complex formation k_2 (b) of C_{60}/NMP solution equal at $T = 50$ °C

The obtained values of k_1 and k_2 can also be used in the modeling of cluster growth in the C_{60}/NMP solution. As it was proposed in [11], a model of fullerene aggregation in polar solvents may imply the formation of clusters of C_{60}-solvent molecule complexes. Thus, the kinetic equations developed in [11] directly require one to estimate the rate constant values for a given temperature and other external conditions. As we have obtained here, the approximate values for stirred samples of $k_1 \sim (0.50 \pm 0.15) \cdot 10^{-4}$ s^{-1}, $k_2 \sim (1.0 \pm 0.2) \cdot 10^{-3}$ s^{-1} for room temperature, and $k_1 \sim (0.8 \pm 0.2) \cdot 10^{-3}$ s^{-1}, $k_2 \sim (0.8 \pm 0.2) \cdot 10^{-2}$ s^{-1} for higher temperatures should be used in further theoretical modeling.

5. Conclusions

In the present work, a model for evaluating the C_{60}/NMP dissolution UV-Vis spectra has been proposed, based on the supposition of simultaneous dissolution and complex formation in the solution. The proposed method allows one to estimate the values of the rate constants k_1 and k_2 – the speed of fullerene dissolution, and the rate of new complex formation from the time evolution of the $\sim$ 330 nm peak in the absorption spectra. The dependencies of these parameters on the solution stirring speed and temperature were obtained and presented. Further careful measurements in the emphasized ranges of T and V_s can be performed in order to obtain the $k_1(T, V_s)$ and $k_2(T, V_s)$ dependencies.

Acknowledgements

The work was supported by the Russian Foundation of Basic Research, project No. 14-23-01015. The financial support is gratefully acknowledged.

References

[1] Beck M.T., M'andi G. Solubility of C_{60}. *Fuller. Sci. Technol.*, 1997, **5** (2), P. 291–310.

[2] Avdeev M.V., Aksenov V.L., Tropin T.V. Models of cluster formation and growth in fullerene solutions. *Russ. J. Phys. Chem. A*, 2010, **84**, P. 1273–1283.

[3] Wang C.I., Hua C.C., Chen S.A. Dynamic solvation shell and solubility of C_{60} in organic solvents. *J. Phys. Chem. B*, 2014, **118**, P. 9964–9973.

[4] Meng Z., Hashmi S.M., Elimelech M. Aggregation rate and fractal dimension of fullerene nanoparticles via simultaneous multiangle static and dynamic light scattering measurement. *J. Colloid Interface Sci.*, 2013, **392**, P. 27–33.

[5] Aksenov V.L., Avdeev M.V., et al. Formation of fullerene clusters in the system C_{60}/NMP/water by SANS. *Phys. B: Condens. Matter*, 2006, **385–386**, P. 795–797.

[6] Kyzyma O.A., Bulavin L.A., et al. Aggregation in C_{60}/NMP, C_{60}/NMP/water and C_{60}/NMP/Toluene mixtures. *Fullerenes, Nanotub. Carbon Nanostructures*, 2008, **16**, P. 610–615.

[7] Yevlampieva N.P., Biryulin Y.F., et al. Aggregation of fullerene C_{60} in N-methylpyrrolidone. *Colloids Surfaces A: Physicochem. Eng. Asp.*, 2002, **209**, P. 167–171.

[8] Kyzyma O.A., Korobov M.V., et al. Solvatochromism and fullerene cluster formation in C_{60}/N-methyl-2-pyrrolidone. *Fullerenes, Nanotub. Carbon Nanostructures*, 2010, **18**, P. 458–461.

[9] Kyzyma O.A., Korobov M.V., et al. Aggregate development in C_{60}/N-metyl-2-pyrrolidone solution and its mixture with water as revealed by extraction and mass spectroscopy. *Chem. Phys. Lett.*, 2010, **493**, P. 103–106.

[10] Jargalan N., Tropin T.V., Avdeev M.V., Aksenov V.L. Investigation of the dissolution kinetics of fullerene C_{60} in solvents with different polarities by UV-Vis spectroscopy. *J. Surf. Investig. X-Ray, Synchrotron Neutron Tech.*, 2015, **9**, P. 16–20.

[11] Tropin T.V., Jargalan N., et al. Kinetics of cluster growth in polar solutions of fullerene: Experimental and theoretical study of C_{60}/NMP solution. *J. Mol. Liq.*, 2012, **175**, P. 4–11.