To the Methodology of Phase Transition Temperature Determination in Aqueous Solutions of Thermo-Sensitive Polymers

G.A. Mun[1], I. Moldakhan[2], S.B. Kabdushev[2], B.B. Yermukhambetova[1], R. Shaikhutdinov[1], G.Zh. Yeligbayeva[3]*

[1]Al-Farabi Kazakh National University, 71 Al-Farabi ave., Almaty, Republic of Kazakhstan
[2]Almaty University of Power Engineering and Telecommunications,
126/1 Baitursynova str., Almaty, Kazakhstan
[3]Satbayev University, 22a Satpaev str., Almaty, Kazakhstan

Article info

Abstract

An advanced methodology of phase transition determination in aqueous solutions of thermo-sensitive polymers by using the phase portraits method has been suggested. The methodology allows highly accurate determining the temperature when exactly half of the molecules lose solubility (from the maximum number that can go to another phase state under given conditions). It is shown that since phase transition passes usually in a wide enough temperature interval this indicator should be used as a quantitative parameter that characterizes phase transition process. Additionally, the suggested methodology allows introducing one more quantitative parameter that reflects a sharpness of phase transition. The methodology is verified by an example of phase transitions study in aqueous solutions of thermo-sensitive copolymers based on N-vinylpyrrolidone and vinyl propyl ether.

1. Introduction

Thermo-sensitive polymers are one of the most important classes of hydrophilic macromolecules [1–3]. Study them is of considerable interest both in academic (e.g. in terms of studying the hydrophobic-hydrophilic balance that defines a solubility of the multicomponent composition of copolymer copolymers [4]) and in purely applied aspects. Particularly it is shown in [5, 6] that new systems of information visualization may be implemented based on heat sensitive polymers.

Phase transition experienced by thermo-sensitive polymers at their solution temperature variations is one of the most important properties; such transitions in many works have been studied [1, 5–12]. To date, firmly established that a character of phase transition for various thermo-sensitive polymers can significantly differ. Particularly, a width of a transition area where both macromolecules that have lost a solubility and the ones that

remain in solution coexist significantly varies on a temperature scale from polymer to polymer. The fact that a transition temperature range can quite long lead to certain difficulties related to the phase transition temperature determination. Various kinds of graphic constructions at times used for this purpose lead to noticeable errors and sometimes they are systematic.

It is shown in this work that there is a possibility to develop the methodology of phase transition temperature determination in the thermo-sensitive polymers solutions with high precision based on experimental dependencies of solution turbidity on temperature. This methodology allows also getting the quantitative indicator that reflects «a degree of the heat sensitivity», i.e. how sharp the phase transition is. The methodology is verified by an example of phase transitions study in aqueous solutions of thermo-sensitive copolymers based on N-vinylpyrrolidone (NVP) and vinyl propyl ether (VPE). These copolymers were synthesized in the work [13] early, as well as their temperature-responsive properties have been studied.

*Corresponding author. E-mail: gulzhakh@yandex.ru

2. Experimental part

N-Vinyl-2-pyrrolidone and vinyl propyl ether were purchased from Sigma-Aldrich (UK) and were purified by distillation. 2,20- azobis(isobutyronitrile) (AIBN) were purchased from Acros. AIBN was recrystallized from ethanol before use. Ethanol was purchased from Fisher Scientific (UK) and used without purification.

Copolymers NVP-VPE were synthesized by free radical copolymerization at 60 °C in ethanol solutions. The polymerization was conducted for 26 h with AIBN (0.01 mol/L) used as a radical initiator. Before copolymerization, the monomer mixtures were saturated with argon by bubbling for 10 min. Polymerization was terminated after 26 h by cooling the reaction vials with cold water. The copolymers were purified by dialysis against deionized water (volume 5 L, 20 changes during 4 days) and were recovered by freeze-drying. The copolymer composition was determined by elemental analysis for the content of nitrogen, which is present in NVP only.

3. Methods

The thermo-responsive behavior of NVP-VPE copolymers in aqueous solutions was studied by dynamic light scattering (DLC) at 10–60 °C using a Malvern Zetasizer Nano-S (Malvern Instruments, UK). Each DLS experiment was repeated in triplicate by preparing and analyzing solutions of each polymer sample separately. Dependence of a light scattered by polymer solution on temperature was registered in experiments. This allows acquiring the necessary information about the character of phase transition since it is accompanied by turbidity of the solution and consequently by its ability to efficiently scatter the light.

4. Results and discussion

Figure 1 shows experimentally obtained temperature dependencies of light intensities scattered by NVP-VPE copolymer aqueous solutions at different concentrations (points). Dependence of light intensity scattered by polymer solution on temperature was recorded experimentally. This allows obtaining necessary information about a character of phase transition since the last one is accompanied by turbidity of the solution and, consequently, by its ability to efficiently scatter the light. It is seen that the light scattering intensity grows with
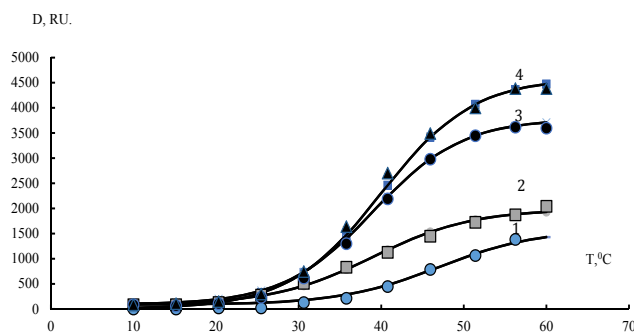

Fig. 1. Temperature dependence of light scattering intensity of aqueous solutions of NVP-VPE copolymer at various concentrations; points – experimental data, solid curves – calculation based on phase portraits; CCPL = 2 (1), 6 (2), 8 (3); 10 mg/ml (4); Copolymer composition, [NVP]:[VPE] = 74,5:25,5 mol.%;

increasing of temperature, when it reaches a certain value close to the phase transition temperature a light scattering sharply rises. The same figure (solid lines) shows the theoretical dependences curves obtained using the technique considered below based on the use of the phase portraits method.

It is seen that a considered copolymer does experience a phase transition, however, it is quite smooth: width of a transition area is about 25 °C.

Figure 2 shows similar dependencies for a case of the water-alcohol mixture.

It can be seen that the presence of ethanol in the solution shifts the hydrophobic-hydrophilic balance and at its high concentrations (30 vol.%) the phase transition is practically not observed.

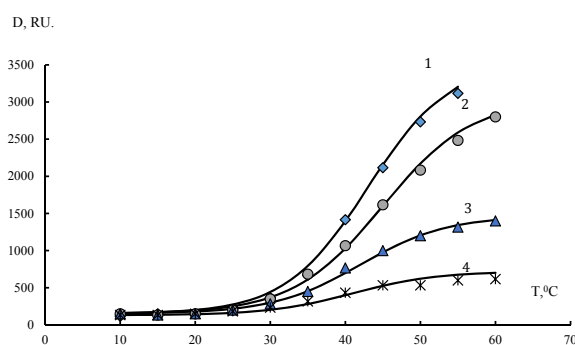Figures 3 and 4 show phase portraits of curves presented in Figs. 1 and 2 respectively.

Fig. 2. Temperature dependence of light scattering intensity of water-alcohol solutions of NVP-VPE copolymer at the various concentrations of ethanol; $C_{Ethanol}$ = 5 (1); 10 (2); 15 (3); 30 vol. % (4); Copolymer composition, [NVP]:[VPE] = 77,5:22,5 mol.%; CCPL = 10 mg/ml; Points – experimental data, solid curves – theoretical calculation based on phase portraits.
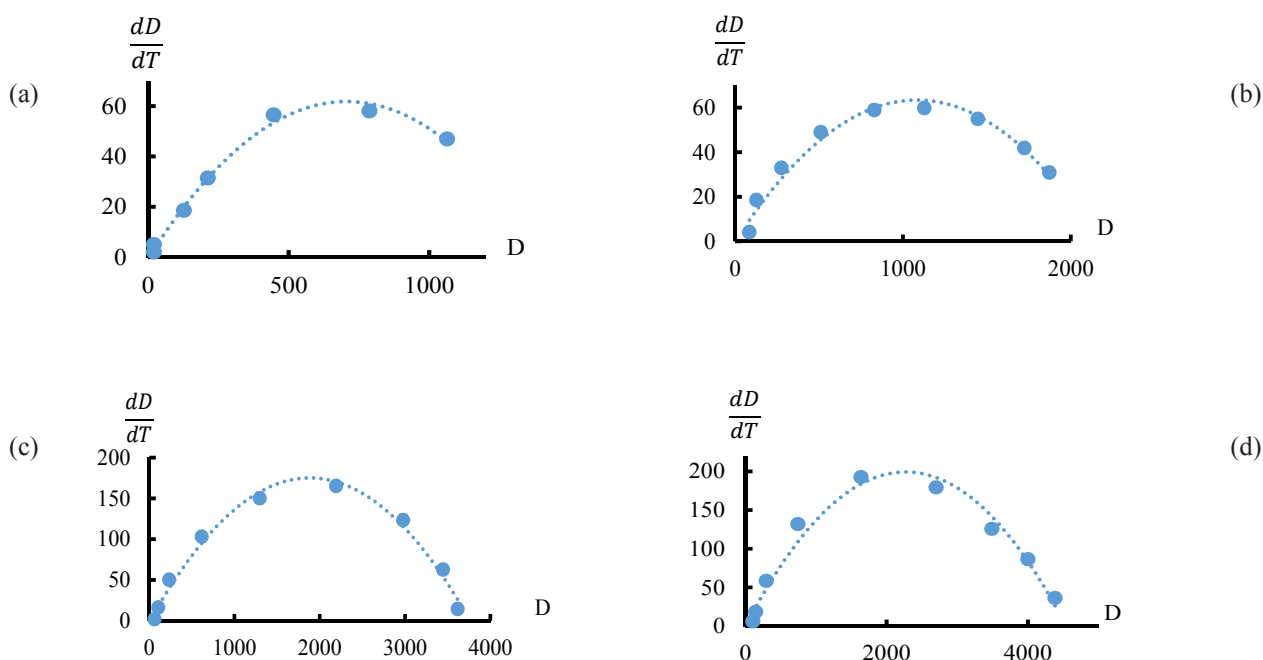
Fig. 3. Phase portraits of curves presented on Fig. 1. Diagrams a)-d) correspond to curves 1–4 in Fig. 1, respectively.
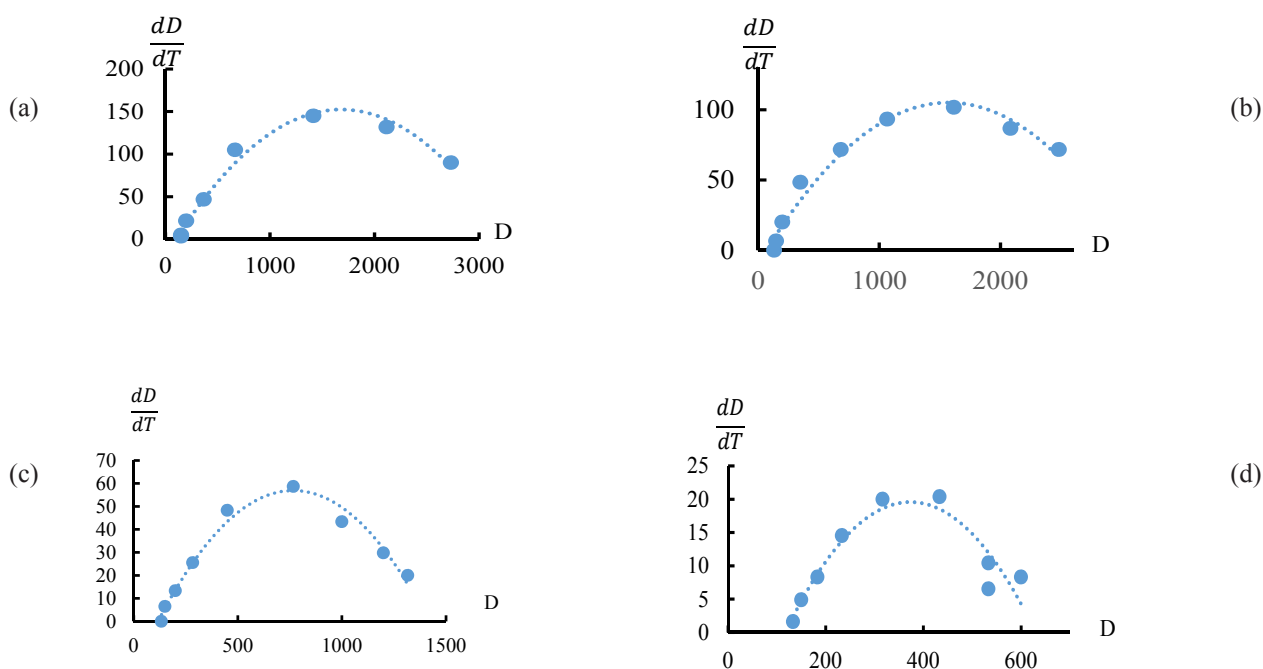

Fig. 4. Phase portraits of curves presented on Fig. 2. Diagrams a)-d) correspond to curves 1–4 in Fig. 2, respectively.

Presented experimental phase portraits are obtained by numerical differentiation using an approximate formula (points in Figs. 3 and 4).

$$\left.\frac{dy}{dx}\right|_n = \frac{1}{10\Delta x}\left(2y_{n+2} + y_{n+1} - y_{n-1} - 2y_{n-2}\right) \quad (1)$$

It is seen that phase portraits of curves presented in Figs. 1 and 2 are described by parabolic dependencies with high accuracy (dashed lines in Figs. 3 and 4).

This suggests that the dependence of the degree of transparency (turbidity) of the solution at the phase transition obeys the following differential equation of the first order.

$$\frac{dD}{dT} = \frac{D^2}{D_0 T_0} - \frac{D}{T_0} \qquad (2)$$

were $\frac{1}{D_0 T_0}$ and $\frac{1}{T_0}$ – coefficients obtained by least squares method at a parabolic approximation of experimentally obtained phase portrait.

Solution of the Eq. (2) has the form:

$$D = \frac{D_0}{1 + \exp\left((T_{ph} - T)/T_0\right)} \qquad (3)$$

where – T_{ph} is a parameter interpreted as a temperature of phase transition

Equation (3) also allows establishing a physical meaning of parameters included in Eq. (2), T_0 – parameter that defines a slope of phase transition, D_0 – extrapolation extremum of optical density.

Dependencies shown in Figs. 1 and 2 as solid curves by Eq. (3) have been calculated. It can be seen that there is a good correspondence between the dependencies obtained by the phase portrait method and the initial experimental data. Parameters of dependencies shown in Figs. 1 and 2 with solid curves are presented in Tables 1 and 2 respectively. Tables show that the suggested method allows determining very small phase transition temperature variations due to changes in polymer concentration in solution or changes in the thermodynamic quality of the medium.

Table 1
Parameters of theoretical dependences for curves of Fig. 1, obtained based on a method of phase portraits

Number of curve	D_0	T_{ph}, °C	T_0, °C
1	1500	47	6
2	1900	39	6
3	3700	39	5.4
4	4600	40	5.6

Table 2
Parameters of theoretical dependences for curves of Fig. 2, obtained based on a method of phase portraits

Number of curve	D_0	T_{ph}, °C	T_0, °C
1	3400	43	5.5
2	2900	45	6.
3	1320	42	5.8
4	590	41	5.6

From the main goal of this work i.e. in terms of determining the temperature of a phase transition, an obtained solution is of interest since it actually corresponds to the logistic curve. Indeed, if put $T = T_{ph}$ in Eq. (3), then a value under sign of exponent will be equal to zero. Respectively, in this case $D = \frac{D_0}{2}$ takes place. In other words, T_{ph} – is a temperature when exactly half of molecules in solution experiences phase transition. This is an exact value that is appropriate to accept as a temperature of phase transition, especially in cases when it is carried out quite smoothly.

Thus, a method of phase portraits allows obtaining simple and reliable approximations of dependencies of solution turbidity on temperature, and it allows determining the characteristic value, which can serve as an effective measure of phase transition temperature with a quite accuracy.

5. Conclusion

Thus, dependencies of the optical density of solution experienced a phase transition on temperature are described by logistic curves. Confirmation of this can be given by the phase portraits method. Namely, the logistic curve corresponds to a parabolic phase portrait, it shows which is shown by the experimental data presented in this work. This fact allows for developing a methodology for accurate estimation of the parameter characterizing the phase transition temperature. Namely, it is appropriate to accept as a temperature of a phase transition the temperature at which exactly half of macromolecules in solution experiences changes in conformation and lose solubility.

References

[1]. G.A. Mun, Z.S. Nurkeeva, B.B. Ermukhambetova, I.K. Nam, V.A. Kan, S.E. Kudaibergenov, *Polym. Advan. Technol.* 10 (1999) 151–156. DOI: 10.1002/(SICI)1099-1581(199903)10:3<151::AID-PAT855>3.0.CO;2-I

[2]. D. Christova, R. Velichkovaq, W. Loos, E.J. Goethals, F. Du Prez, *Polymer* 44 (2003) 2255–2261. DOI: 10.1016/S0032-3861(03)00139-3

[3]. V.V. Khutoryanskiy, T.K. Georgiou. Temperature-Responsive Polymers: Chemistry, Properties and Applications. 2018 John Wiley & Sons Ltd. DOI: 10.1002/9781119157830

[4]. S.A. Dergunov, G.A. Mun, M.A. Dergunov,

I.E. Suleimenov, E. Pinkhassik, *React. Funct. Polym.* 71 (2011) 1129–1136. DOI: 10.1016/j.reactfunctpolym.2011.09.005

[5]. I. Suleimenov, G. Mun, R. Ivlev, S. Panchenko, D. Kaldybekov, *AASRI Procedia* 3 (2012) 577–582. DOI: 10.1016/j.aasri.2012.11.091

[6]. I.E. Suleimenov, S.V. Panchenko, Z. Sedlakova, I.T. Park, *Recent Contributions to Physics* 55 (2015) 114–120.

[7]. T. Shibanuma, T. Aoki, K. Sanui, N. Ogata, A. Kikuchi, Y. Sakurai, T. Okano, *Macromolecules* 33 (2000) 444–450. DOI: 10.1021/ma9915374

[8]. Y. Maeda, T. Nakamura, I. Ikeda, *Macromolecules* 35 (2002) 217–222. DOI: 10.1021/ma011034+

[9]. S. Verbrugghe, A. Laukkanen, V. Aseyev, H. Tenhu, F.M. Winnik, F.E. Du Prez, *Polymer* 44 (2003) 6807–6814. DOI: 10.1016/j.polymer.2003.07.003

[10]. Y.H. Hsu, W.H. Chiang, M.C. Chen, C.S. Chern, H.C. Chiu, *Langmuir* 22 (2006) 6764–6770. DOI: 10.1021/la060229d

[11]. L. Shao, M. Hu, L. Chen, L. Xu, Y. Bi, *React. Funct. Polym.* 72 (2012) 407–413. DOI: 10.1016/j.reactfunctpolym.2012.04.002

[12]. K. Jong, B. Ju, *Colloid Polym. Sci.* 295 (2017) 307–315. DOI: 10.1007/s00396-016-4009-1

[13]. D.E. Zhunuspayev, G.A. Mun, V.V. Khutoryanskiy, *Langmuir* 26 (2010) 7590–7597. DOI: 10.1021/la904403k