Energetics of phase separation in aqueous solutions of poly(vinyl methyl ether)

Valerij Y. Grinberg [a, *], Tatiana V. Burova [a], Natalia V. Grinberg [a], Alexander S. Dubovik [b], Alexander A. Senin [c], Sergey A. Potekhin [c], Igor Y. Erukhimovich [a]

[a] A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov St. 28, 119991 Moscow, Russian Federation
[b] N.M. Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, Kosygin St. 4, 119991 Moscow, Russian Federation
[c] Institute of Protein Research, Russian Academy of Sciences, Institutskaya St. 4, Pushchino, Moscow Region 142290, Russian Federation

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ABSTRACT

Phase separation in aqueous solutions of poly(vinyl methyl ether) was first investigated by high-sensitivity differential scanning calorimetry at normal and high pressures. Thermograms of the phase separation had two singular points: a binodal point ($T_{t,1}$) and a point of the three phases coexistence ($T_{t,2}$). At normal pressure the temperature $T_{t,1}$ decreased slightly and the temperature $T_{t,2}$ was constant ($36.8 \pm 0.1°C$) upon increasing the polymer concentration from 0.01 to 0.25%. The transition enthalpy and heat capacity increment did not depend on the polymer concentration ($\Delta_t h = 88.0 \pm 1.2$ J g^{-1}; $\Delta_t c_p = -1.0 \pm 0.1$ J g^{-1} K^{-1}). The calorimetric experiments at high pressures were carried out up to pressure 170 MPa in the range of polymer concentrations 0.1–1.1%. When pressure increased the temperature $T_{t,1}$ dropped by 10 °C, the temperature $T_{t,2}$ increased by 15 °C, the total transition enthalpy reduced 1.5 fold and the transition heat capacity increment remained virtually unchanged. These data reveal that the sequential phase transitions, which the diluted aqueous solutions of poly(vinyl methyl ether) undergo upon heating, have different nature.

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1. Introduction

Amphiphilic polymers are a special class of high-molecular compounds capable of self-organization in aqueous solutions upon heating [1–4]. Examples of such a self-organization are represented by conformational coil-globule transitions, phase or microphase separation, micelle formation and gelation. These phenomena are of great practical interest, especially for solution of various biomedical problems from the directed transport of drugs to controled cell adhesion, enzymatic activity and gene expression [5,6]. Thus, elucidation of principles and mechanisms of the self-organization of aqueous solutions of amphiphilic polymers is an important problem of polymer science. A substantial progress in this direction can be achieved as a result of detailed thermodynamic analysis of conformational and phase transitions of amphiphilic polymers in aqueous medium by obtaining new experimental data in a wide range of temperatures and pressures.

Such an analysis is possible only on the basis of calorimetric data on energetics of these transitions at various pressures, including the region of very high pressures (of the order of hundreds of MPa).

The transition energetics can be evaluated by means of high-sensitivity differential scanning calorimetry (HS-DSC) [7–11]. This experimental approach makes it possible to carry out precise calorimetric measurements with microheterogeneous polymer systems at rather low polymer concentrations and heating rates. Under these conditions, the artefacts related to kinetic effects and sedimentation instability of the polymer dispersions are minimized. Therefore, in addition to measurements of the transition temperature and enthalpy HS-DSC provides precise determination of values of the partial heat capacity of polymer before and after the phase transition, i.e. the transition heat capacity increment. These data involve a valuable information on local structure of macromolecules in the coexisting phases. With exact values of the transition temperature, enthalpy and heat capacity increment it is possible to calculate temperature dependences of the transition enthalpy, entropy and free energy. Their analysis enables quantitative comparison of contributions of hydrophobic effect and van-der-Waals interactions into driving forces of the transition.

* Corresponding author.
E-mail address: grinberg@ineos.ac.ru (V.Y. Grinberg).

Recently, we have shown using PNIPAM as a typical example that precise calorimetric data on energetics of phase separation of aqueous solutions of thermoresponsive polymers can be obtained at high pressures up to about 200 MPa [12]. Simultaneous determination of temperature, enthalpy and width of the phase transition at different pressures gives information on changes in the volume characteristics of a polymer and in the phase diagram of the system. These features provide a basis for more detailed consideration of thermodynamics and mechanism of the phase separation.

The manifested potential of HS-DSC at high pressures opens in fact a new direction in physical chemistry of polymers [13]. A goal of this direction is the development of adequate thermodynamic models of self-organization of amphiphilic macromolecules taking into account the transition volume effects. Accumulation of the complementary data on energetics and volume parameters of various types of macromolecular self-organization allows one to track correlations between the structure of a macromolecule in the "organized" state and the change in its volume in the course of self-organization. On the base of these correlations the semiempirical models linking structural, energetic and volume parameters of amphiphilic macromolecules could be developed.
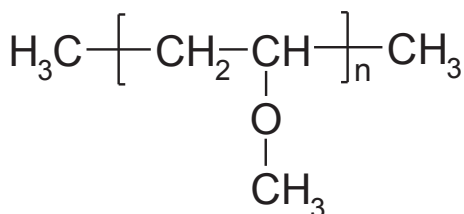
In this paper we present results of a first precise calorimetric study of phase separation in diluted aqueous solutions of poly(vinyl methyl ether), PVME (Scheme 1), at normal and high pressures. The characteristic temperatures, enthalpy and heat capacity increment of the phase separation transition were determined as functions of the polymer concentration and pressure. The dependences of the transition temperatures on pressure were approximately analysed in therms of the Clausius−Clayperon equation. This approach allowed determination of signs of the partial volume increments of the polymer associated with sequential phase transitions, which the system undergoes in the course of the phase separation. The information obtained indicates a significant difference in the nature of these transitions.

2. Experimental

2.1. Materials

Poly(vinyl methyl ether), PVME, was purchased from "Sigma-Aldridge" (USA) as 50% aqueous solution and used after an additional purification by the thermoprecipitation procedure [14]. The PVME solution was diluted by water to a concentration of 10%. The solution was heated at a phase separation temperature (45 °C) for 3 h. The phases were separated by centrifugation at ~200,000 g for 1 h (Hitachi Centrifuge 70P72). The concentrated phase was diluted to a concentration of 13.7% and used as a stock solution of the polymer. The intrinsic viscosity of the polymer, $[\eta] = 51 \pm 2$ cm^3 g^{-1} was determined in tetrahydrofuran at 25 °C. The molecular weight of PVME, $M_\eta = 1.0 \times 10^5$, was calculated by the Mark−Houwink equation $[\eta] = 0.0226 M^{0.67}$[15].

Polymer solutions for calorimetric measurements were prepared by dilution of the stock PVME solution (13.7%) with water by weight. A polymer concentration in the obtained solutions was controlled by dry residue after drying at 105 °C overnight.

2.2. Methods

Calorimetric measurements at normal pressure were carried out with a differential adiabatic scanning microcalorimeter DASM-4 (NPO "Biopribor", Pushchino, Russia) at a heating rate of 1.0 K min^{-1}. Experiments at high pressures were performed with the differential scanning microcalorimeter of high pressure SCAL-3H (Institute of Protein Research, Pushchino, Russia) also at a heating rate of 1.0 K min^{-1}. The measurement part of SCAL-3H is similar to that of the scanning calorimeter SCAL-1 [16]. The measuring and reference cells of the calorimeter are made of glass. A useful volume of the cell is 0.3 mL. The calorimeter allows measurements at a heating rate from 0.1 to 2 K min^{-1} and a pressure up to about 200 MPa in the temperature range 10−100 °C. The amount of the sample in the cell was corrected for changes in the density of the solution with increasing pressure. The density of water as a function of temperature and pressure was used for the instrument calibration. Changes in the cell volume due to changes in pressure and temperature were not taken into account because of their negligibility. Measurements of pressure were performed by means of a reference gauge taking into account a ratio of cross-section squares of the inner and outer pistons in the pressure booster. Processing of the thermograms and determination of the phase transition parameters: temperatures $T_{t,1}$ and $T_{t,2}$, total enthalpy $\Delta_t h$ and total heat capacity increment $\Delta_t c_p$, were carried out with a proprietary computer program Nairta 2 (A.N. Nesmeyanov Institute of Organoelement Compounds) using the standard protocols of high-sensitivity differential scanning calorimetry [17].

The cloud points of PVME solutions were visually determined upon heating with a constant rate of 1.0 K min^{-1}.

3. Results and discussion

3.1. Phase separation of aqueous solutions of PVME at normal pressure

The phase behavior of aqueous solutions of PVME is very unusual. The phase diagram of this system has two low critical solution points and probably a line of coexistence of three liquid phases (Fig. 1). When the PVME-Water system with a relatively low polymer content is heated it is possible to anticipate consequent changes in its phase state: at a temperature of crossing the binodal line ($T_{t,1}$) and at a temperature of crossing the line of coexistence of three phases ($T_{t,2}$). These temperatures correspond to the initial point of the thermogram of phase separation and its maximum, respectively [18].

The known data on calorimetry of phase separation of aqueous solutions of PVME were obtained at normal pressure for rather high polymer concentrations using relatively low-sensitivity instruments [18,19]. It seemed necessary to supplement them with precise data for diluted solutions of the polymer.

This study was conducted for different PVME concentrations from 0.1 to 2.5 mg mL^{-1} (0.01−0.25%). The primary calorimetric data were obtained as temperature dependences of apparent partial heat capacity of the polymer. An example of such a dependence is given in Fig. 2. This dependence possesses two singular points: an initial point of the peak (1) as a breakpoint and a maximum point (2). The temperature of the initial point practically coincides with the cloud point temperature. According to the data of Schäfer-Soenen et al. [18] the temperature of the initial point and the peak maximum temperature were accepted as the binodal temperature $T_{t,1}$ and the temperature of coexistence of three phases $T_{t,2}$

Scheme 1. Chemical structure of poly(vinyl methyl ether).