

PRESSURE PERTURBATION CALORIMETRY OF POLY(ETHYLENE) GLYCOL SOLUTIONS IN WATER

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The physico-chemical properties of poly(ethylene) glycol solutions in water have been studied with use of pressure perturbation calorimetry. The three PEGs of average molecular mass (M_r) 6000, 10000, 20000 were used. The concentration of polymers was changed in the range 0–30% mass per volume (w/v%). On the basis of VP-DSC measurements with use of PPC technique the dependencies of thermal expansion coefficient (α) and excess specific heat capacity ($C_{p,exc}$) on temperature were determined for PEG–water solutions.

Keywords: $C_{p,exc}$ determination, DSC, polyethylene glycol, pressure perturbation calorimetry

Introduction

Many compounds have a role in the altering water structure and are responsible for the peculiar and large effects in the protein solutions [1–4]. Aqueous polymer solutions have found several applications, because of their use in two phase aqueous systems, to separate, purify or crystallize biological products in biocompatible surroundings [5–7]. Polymers such as poly(ethylene) glycol (PEG) and poly(ethylene oxide) (PEO) are two of the most popular of these compounds and because of its physical and chemical properties – with large range of applications [8, 9]. Many experiments carried out with different technical instrumentations (X-ray, viscosity, density, etc.) are reported in the literature [10–12]. Unfortunately the absence of chromophore groups in the molecular structure does not determine any utility with optical determinations. On the contrary, volumetric properties of PEG's solutions can be measured by a calorimetric technique, the pressure perturbation calorimetry (PPC) [13, 14].

The main aim of this work is to present some preliminary studies directed to physical and chemical properties of three PEG of average molecular mass (6000, 10000, 20000 M_r) in water solutions with use of PPC technique.

The pressure perturbation calorimetry – some theoretical aspects. Taking in consideration the Maxwell's equations:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V; \quad \left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T; \quad \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

and

$$TdS = C_V dT + T\left(\frac{\partial P}{\partial T_V}\right)dV;$$

$$TdS = C_P dT - T\left(\frac{\partial V}{\partial T_P}\right)dP$$

from the second law of thermodynamics

$$dS = \frac{dQ_{rev}}{T} \quad (1)$$

where dS is the entropy change, dQ_{rev} is the heat change at T temperature.

Differentiating with respect to pressure at constant temperature then gives

$$\left(\frac{\partial Q_{rev}}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T \quad (2)$$

using the Maxwell relations

$$\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P \quad (3)$$

substituting Eq. (3) into Eq. (2) gives

$$\left(\frac{\partial Q_{rev}}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P = -TV\alpha \quad (4)$$

where V is the volume and α is the coefficient of thermal expansion, $(1/V)(\partial V/\partial T)_P$.

Integration of Eq. (4) at constant temperature over a short pressure range ΔP leads to

$$Q_{rev} = -TV\alpha\Delta P$$

where V and α are considered constant with small pressure change.

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Experimental

Materials and methods

Polyethylene glycols (PEG) 6000, 10000 (Fluka) and 20000 (Polysciences Inc.) were used as received, without further purification methods. The average molecular mass of polymers were checked with use of mass spectrometry method. The calorimetric measurements were conducted in citrate buffer solutions of pH=3.00 in the temperature range from 0 to 100°C with the constant scan rate of 1°C min⁻¹. The PEG concentration was changed in the range 0–30% w/v where w/v corresponds to the ratio of PEG mass in grams per volume unit expressed in percents.

The DSC measurements of PEG solutions in pH=3.00 were made using differential scanning calorimeter VP-DSC Microcal (MicroCal LLC, Northampton, MA, US) [15]. All calorimetric measurements were made differentially with water-buffer solutions as references in order to observe only PEG influence on its water solutions a result of pressure and temperature changes. The obtained data (not shown) are in agreement, indicating that the measurement and the analysis of results are in accord with the recommendation for DSC experiments reported by Hinz *et al.* [16].

Results and discussion

The experimental results of heat capacity determination for PEG 6000 and 20000 in water solutions as a function of increasing temperature, up to the 75 psi are presented in Fig. 1.

On the basis of received heat capacity dependencies evaluated from VP-DSC data the thermal expansion

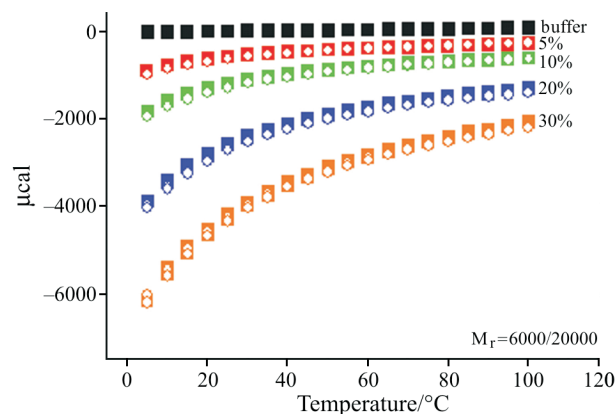


Fig. 1 Experimental heats resulting from pressure increase of 75 psi for PEG 6000 (filled squares) and PEG 20000 (open circles) solutions at different mass/mass% in citrate buffer 50 mM, pH=3.00

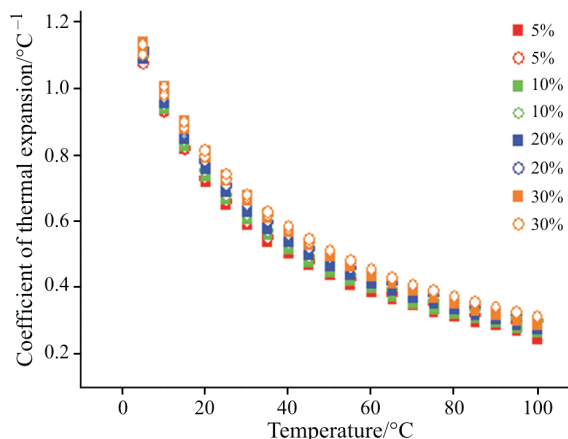


Fig. 2 Calculated values of coefficient of thermal expansion α obtained from experimental PPC heats for PEG 6000 (filled squares) and PEG 20000 (open circles) solutions at different mass/mass% in citrate buffer 50 mM, pH=3.00

coefficient (α) was calculated for the solutions used. The dependence of α as a function of temperature in different PEG 6000 and 20000 is presented in Fig. 2.

The heat capacity C_p dependences at normal pressure of PEG 6000, 10000 and 20000 on temperature received in DSC experiments are presented in Fig. 3.

As it could be noticed, no difference curve run has been observed for different molecular mass of polymers used.

In Fig. 4 the heat capacity (C_p) of PEG 6000 buffered solutions dependence on temperature is presented.

The C_p curves follows to the 30% of PEG concentration line up to a temperature at which a drastic deviation take place. This temperature of this deviation point is dependent on the PEG's concentration.

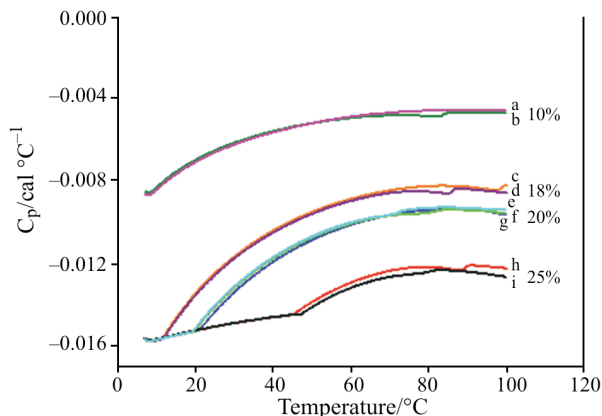


Fig. 3 Temperature dependence of the excess specific heat capacity of different molecular mass PEG solutions at different concentration mass/mass% in citrate buffer 50 mM, pH=3.00; a, d, e, i – PEG 6000; f – PEG 10000; b, c, g, h – PEG 20000

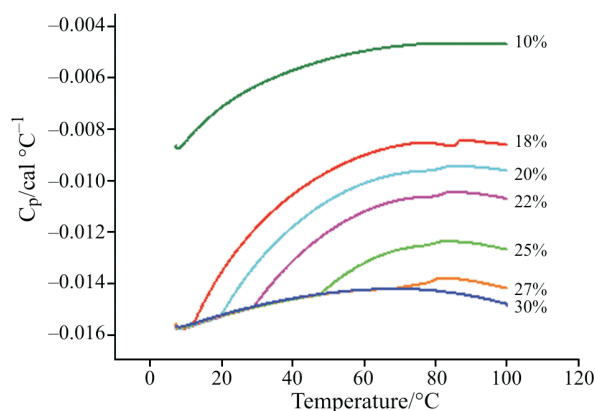


Fig. 4 Temperature dependence of the excess specific heat capacity of PEG 6000 solutions at different concentration mass/mass% in citrate buffer 50 mM, pH=3.00

The thermal expansion coefficient (α) does not show any effect on the PEG molecular mass or its concentration. On the contrary, some changes of changes in calorimetrically determined dependencies of heat capacities on temperature and concentration of PEG solutions were observed. The concentration-dependent curves, presented in Fig. 4 are changing, following to the 30% of PEG concentration. This observation could indicate that there is some effect of melting. In spite of this fact the other curves (Fig. 3) show different values of inflection point on C_p dependences on temperature and PEG molecular mass and concentration. That suggest that there is the effect of molecular mass and concentration of polymer used. Our investigations were performed at a very low scan rate. Therefore, regarding received DSC plots of C_p dependence on temperature for PEG solutions, it is highly probable that there is a phase-transition at 'critical' concentration of polymer. This phase change is supposed to be gel-transition. At high polymer concentration and at low temperature PEG solutions are rather similar to gel phases. Increasing the temperature, or lowering the concentration of PEG – it is possible to observe the phase transition.

Conclusions

DSC experiments suggest that the temperature increase or the concentration decrease of PEG solution determine different 'states'. The change of the 'states' occurs in a very small range of temperature ($\sim 1^\circ\text{C}$). The light scattering values indicate that no aggregation phenomena are presents. PPC measurements follow a monotonic behaviour therefore the thermal expansion coefficient α does not show any drastic variation as it was observed by ΔC_p values.

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Images

