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Lower critical solution temperature and hydrophobic hydration in aqueous polymer solutions

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Abstract: Phase diagrams of aqueous solutions of poly(N-vinyl caprolactam) (PVCL), N-vinyl caprolactam copolymer with vinylamine (3.8 mol%) (CP(VCL-VA)), and poly(N-vinyl propylacetamide) (PVPA) were shown to be binodal curves with lower critical solution temperatures (LCST) in the range 304–313.5 K and critical concentrations in the range of 0.02–0.08 polymer weight fraction. Aqueous solutions of N-vinyl caprolactam copolymer with N-vinyl pyrrolidone (80 mol%) (CP(VCL-VP)) remained homogeneous in the entire region of the liquid state of water. The enthalpy of mixing with water of PVPA and CP(VCL-VP) was negative and the curve was concave over the entire range of composition at 298 and 308 K. The excessive heat capacity and partial heat capacity at infinite dilution of PVPA were positive, proving the hydrophobic character of hydration of this polymer. In contrast, these parameters were negative for CP(VCL-VP), revealing hydrophilic hydration. Hydrophilic hydration was predominant in solutions which were homogeneous over a wide temperature range, whereas hydrophobic hydration predominated in solution of polymers with LCST.

Key words: Poly(N-vinyl caprolactam) – poly(N-vinyl propylacetamide) – lower critical solution temperature – thermodynamics of polymer hydration

Introduction

The interest in the properties of water and aqueous solutions of nonelectrolytes stems from the need to understand the role which water plays in the stability and interactions of biological macromolecules [1]. Frank and Evans were first to clearly elucidate the effect of dissolved molecules and ions on the structure of water [2]. They revealed the decrease in entropy which takes place when nonpolar gases dissolve in water. This is connected with structural organization of water molecules and the formation of "microscopic icebergs," as the authors nicknamed these structures. These ideas were further developed in the concept of hydrophobic hydration which takes place on dissolution of any molecule with a hydrophobic moiety in water [3, 4]. The solubility of hydrophobic substances such as nonpolar gases and alkanes in water is negligible. However, if organic molecule contains some polar hydrophilic groups together with hydrophobic groups, it may be completely soluble in water at room temperature. Heating of such homogeneous solutions may cause phase separation which is characterized by a phase diagram with a lower critical solution temperature (LCST). The relationship of LCST to hydrophobic hydration has been examined in the literature [5–12].

The most well-known polymer system having a LCST is polyethylene glycol (PEG) - water, which has been discussed in detail by Kjellander and Florin [5]. The pronounced solubility of PEG in water compared to other polyesters is the result of the conformity of the distance between ester oxygen atoms in the PEG chain to the distance between oxygen atoms in the delicate structure of water. This conformity of the distances permits PEG molecules to be incorporated into the structure of water. The hydrophobic hydration of methylene groups accompanied this incorporation. The authors analyzed the literature data on phase diagrams and thermodynamics of PEG dissolution in water and concluded that the LCST in this system is caused by hydrophobic hydration. The negative signs of both the enthalpy and the entropy of PEG mixing with water were used as criteria of hydrophobic hydration [5]. However, negative values of these thermodynamic functions are known to occur both during hydrophilic and hydrophobic hydration, though for different reasons [4].

We consider the thermodynamic analysis presented in ref. [6] to be more correct. The sign of excessive heat capacity (C_{P2^∞}) and the sign of the derivative of heat capacity with respect to temperature ($\delta C_P^E/\delta T$) were used as criteria of the hydrophobic hydration. These criteria are of empirical character and cannot be deduced directly from the present statistical theories of aqueous solutions [6–9]. Nevertheless, it has been widely used for the determination of the hydration type [4, 6, 10] and was shown by us to be valid for nitrogen-containing vinyl polymers [11–13]. C_{P2^∞} is negative for dilute solutions of poly(1-vinylazoles) [11] and $C_{P2^\infty} \gg 0$ for aqueous solutions of poly(N-vinyl caprolactam) [12, 13]. It was concluded that these data represent a predominance of hydrophylic hydration in the first case and hydrophobic hydration in the second case.

The intention of this work was to elucidate the relationship of LCST in aqueous solutions of vinyl polymers to the predominant type of hydration.

Materials and methods

Polymers (Table 1) were synthesized as described previously [14, 15]. The content of amino groups in the copolymer of vinyl caprolactam with vinylamine (CP(VCL-VA)) was determined by potentiometric titration [15]. The structure of the copolymer of vinyl caprolactam with vinylpyrrolidone (CP(VCL-VP)) was deduced from IR-spectra of a dried film according to [13]. The amorphous nature of the polymer structures was confirmed by x-ray analysis. Prior to use the polymers were dried at 298 K and ≈ 100 Pa up to a constant weight.

All polymers are completely soluble in water at room temperature. On heating only CP(VCL-VP) was miscible with water at all temperatures up to boiling. Phase separation occurred in aqueous solutions of all the other polymers on heating.

The enthalpy of polymer mixing with water per g of polymer was determined at different temperatures according to [16]. The enthalpy of polymer dissolution (ΔH_{dis}) in excess solvent and the enthalpy of dilution (δH_{dil}) per g of polymer in predissolved polymer solutions with various polymer weight fractions (ω_2) were measured using Calvet-type calorimeter with 10 ml cell and sensitivity 0.032 V/W. The accuracy of measurements was ± 2%. The enthalpy of mixing per g of solution was calculated as:

$$\Delta H_m = \omega_2(\Delta H_{\mathrm{dis}} - \Delta H_{\mathrm{dil}}) . \qquad (1)$$

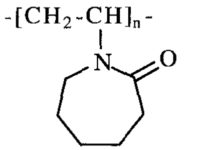
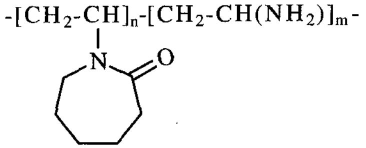
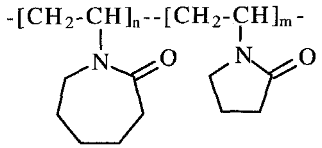
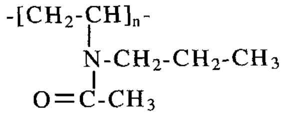
The heat capacities of dilute aqueous solutions were determined using a Calvet-type calorimeter with a 100 ml cell and sensitivity 0.22 V/W according to [17]. Dilute polymer solution was placed in the sample cell and an equal amount of pure water was placed in the reference cell. A constant heat power was applied simultaneously to both cells using an electric heater. The curve of the heat evolution was monitored. The area under the curve is proportional to the difference of heat capacities of the cells. The proportional coefficient was determined by placing different amounts of water in the sample and reference cell. The accuracy of the measurements was ± 0.1%.

Results and Discussion

The phase diagrams of PVCL PVPA and CP(VCL-VA) solutions presented in Fig. 1 are binodials with LCST. The corresponding values of the critical temperatures and concentrations are given in Table 1. The critical concentrations were rather small, and are typical for polymer solutions. CP(VCL-VP) was as soluble at all temperatures as poly(vinylpyrrolidone) itself.

Figure 2 presents the dependencies of ΔH_m on the composition of the polymer solution obtained at two temperatures for PVPA and CP(VCL-VP). The mixing was exothermic in all cases showing no difference between the system with LCST and the completely mixible one. Using these data

Table 1. Properties of polymers

Polymer	Formula	Specific viscosity $[\eta]$ at 25°C, dl/g	Viscosity-average molecular weight	Lower critical solution temperature, K	Critical concentration, weight fraction	Limited heat capacity at infinite dilution J/g K
Poly(N-vinyl caprolactam), PVCL, MW 500 000		0.602	470 000[a]	304.0	0.04	160
Copolymer of N-vinyl caprolactam with vinylamine, CP(VCL-VA)		0.323	160 000[a]	308.8	0.08	140
Copolymer of N-vinyl caprolactam with N-vinylpyrrolidone, CP(VCL-VP)		0.120	8 000[b]	no phase separation	—	3.5
Poly(N-vinyl propylacetamide), PVPA	 $-[CH_2-CH]_n-$ $N-CH_2-CH_2-CH_3$ $O=C-CH_3$	0.290	30 000[b]	313.5	0.02	70

[a] The molecular weight was calculated using the equation $[\eta] = 3.5\ 10^{-4}\ \bar{M}_W^{0.57}$ [21]

[b] The molecular weight was calculated using the equation $[\eta] = 3.5\ 10^{-4}\ \bar{M}_W^{0.65}$ [22]

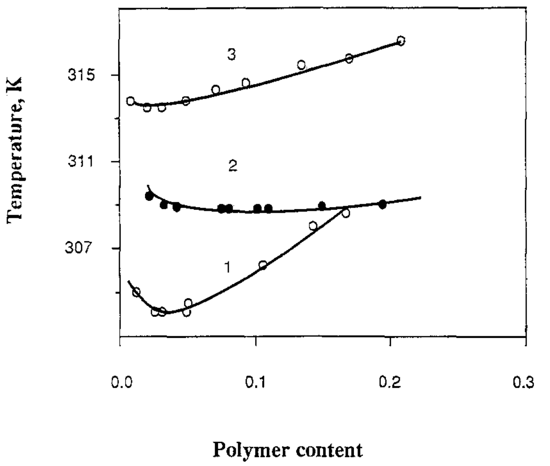


Fig. 1. Equilibrium temperature-composition diagram for PVCL (1), CP(VCL-VA) (2) and PVPA (3).

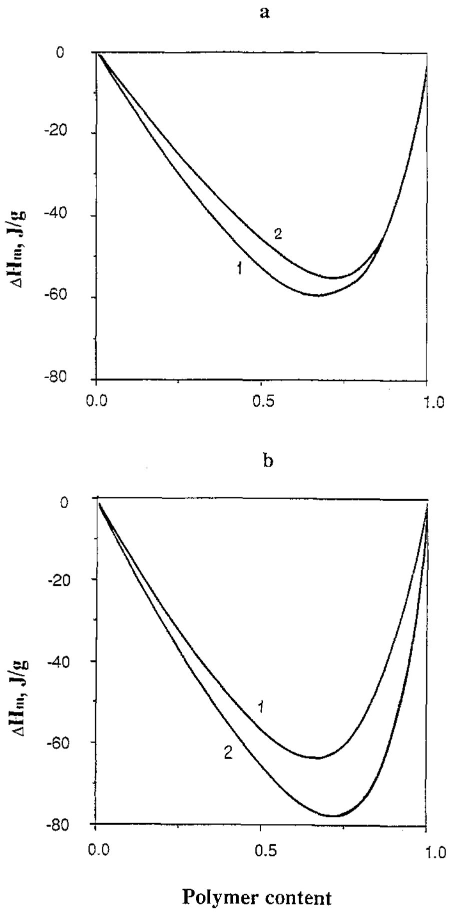


Fig. 2. Enthalpy of mixing (ΔH_m)-composition for PVPA (a) and CP(VCL-VP) (b) at 298 (1) and 308 (2) K.

the average C_P^E values for 298–308 K range were calculated over the entire composition range according to:

$$C_P^E = \frac{H^E(T_2) - H^E(T_1)}{T_2 - T_1} \tag{2}$$

C_P^E was negative for *CP*(VCL-VP), which is water-soluble at all temperatures; and positive for PVPA, a polymer with a LCST (Fig. 3).

The dependence of heat capacity on the concentration of dilute polymer solutions at 298 K is presented in Fig. 4. Heat capacity of CP(VCL-VP) solutions was less than that of pure water and its dependence on concentration had a minimum. In contrast,C_P for aqueous solutions of the other three polymers was higher than that of pure water and the dependence on concentration had a maximum.

For a dilute solution

$$C_P = C_{P1}{}^{\infty}\omega_1 + C_{P2}{}^{\infty}\omega_2 \,, \tag{3}$$

where ω_1 and ω_2 are the partial weight fractions of water and polymer and $C_{P1}{}^{\infty}$ and $C_{P2}{}^{\infty}$ are partial heat capacities of water and polymer at infinite dilution, the former value being equal to the heat capacity of pure water, $C_{PH_2O}{}^{298} = 4.18$ J/g K [18].

Taking into account $\omega_1 + \omega_2 = 1$, one obtains:

$$C_P = C_{PH_2O}{}^{298} + (C_{P2}{}^{\infty} - C_{PH_2O}{}^{298})\omega_2 \,, \tag{4}$$

which is a linear equation with an origin at 4.18 J/g K. The approximation of the initial part

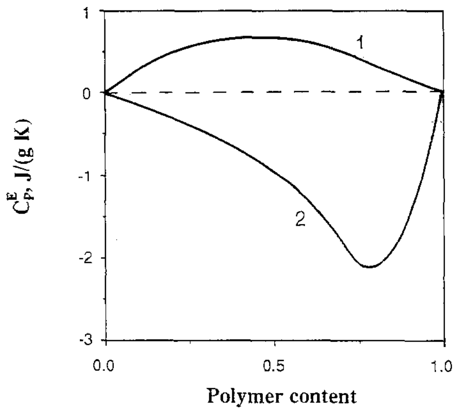


Fig. 3. Average excessive heat capacity (C_P^E)-composition curves for PVPA (1) and CP(VCL-VP) (2) at 298–308 K.

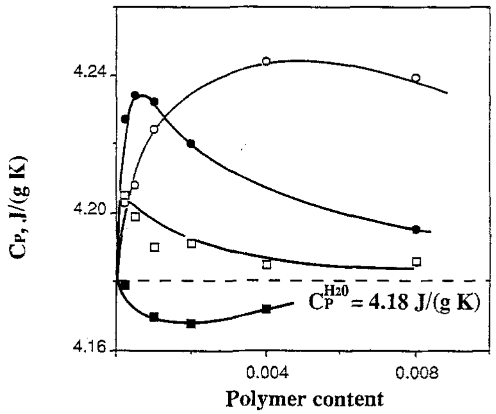


Fig. 4. Heat capacity (C_P)-composition curves for dilute solutions of PVCL (●), CP(VCL-VA) (○), PVPA (□), and CP(VCL-VP) (■) at 298 K.

of the curves of Fig. 4 with the straight line resulted in the $C_{P2}\infty$ values given in Table 1.

As well as C_P^E, $C_{P2}\infty$ is also negative for CP(VCL-VP), which is soluble at all temperatures, and positive for polymers with LCST. Thus, the sign of C_P^E and $C_{P2}\infty$ can be taken as a valid criterium for distinguishing hydrophilic and hydrophobic hydration in aqueous solutions of nonionic polymers.

Most of the polymers can be considered as consisting of hydrophilic and hydrophobic moieties. Thus, the only hydrophobic or the only hydrophilic hydration is quite rare. One can speak only about the predominance of the hydration type.

The hydrophilic hydration is predominant in aqueous solutions of CP(VCL-VP) containing 80 mol% of pyrrolidone links, and poly(1-vinylazoles) [10]. These polymers are complete mixible with water at all temperatures and no phase separation takes place.

The hydrophobic hydration is predominant in aqueous solutions of PVCL, PVPA, and CP(VCL-VA), water being a poor solvent for these polymers. The mixing of PVCL, PVPA, and CP(VCL-VA) with water at temperatures lower that LCST is possible only due to hydrophobic hydration, which stabilizes water and, consequently, solution structure [19]. Upon increasing temperature, water "icebergs" are destroyed, structure is destabilized, and phase separation takes place.

The poor quality of a solvent as such i.e., $G^E > 0$, does not entail complete impossibility of dissolution. Phase separation occurs only when $G^E \approx 0.5$ RT [20]. This happens at LCST.

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