Theta temperature of poly(*N*-vinyl pyrrolidone) in water

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The θ temperature of poly(*N*-vinyl pyrrolidone) (PVP) in water has been determined accurately by studying the variation of the cloud points of polymer solutions in the presence of an electrolyte (Na_2CO_3). The cloud point of PVP solutions decreased linearly with electrolyte concentration. The θ temperature was determined by extrapolating the cloud points of dilute solutions to polymer volume fractions of 1. The phase diagram of PVP in water was also constructed by the same procedure over wider polymer concentrations.

(**Keywords: poly(*N*-vinyl pyrrolidone); water; cloud points; phase diagram; theta temperature; cosolute; electrolyte**)

INTRODUCTION

The θ temperature of polymers is a very important parameter for both free and attached chains. At the θ point, the chains assume their unperturbed dimensions and the intermolecular interactions vanish[1,2]. At the same time, segmental interactions become attractive[2].

Determination of the θ temperature is usually implemented by light scattering, and osmotic pressure measurements. Both measurements are based on the fact that the second virial coefficient vanishes at the θ point[1]. More rapid methods use cloud point and turbidity measurements[3–6]. They are based on the observed linearity of the reciprocal cloud point when plotted against the logarithm of the polymer volume fraction (Φ_2). Extrapolation to $\log \Phi_2 = 0$ gives the reciprocal θ temperature. Theoretical justification for this empirical method has been provided by Napper[2].

In this paper we shall report on the θ point of poly(*N*-vinyl pyrrolidone) (PVP). Although, χ values and θ temperatures for PVP in aqueous blends and mixture of solvents have been reported[7–10], there has been no accurate determination of the θ temperature of the polymer in water. Use of cloud point measurements for the determination of the θ point is hindered by the fact that it is located well above the boiling point of water.

It has been known, from the work of Bailey and co-workers[11] and other groups[12], that the cloud point of aqueous poly(ethylene oxide) (PEO) solutions is depressed by the presence of electrolytes (cosolute). This has been argued to be caused by the entropically unfavourable nature of hydration of the PEO with two water molecules per oxyethylene unit. Electrolytes induce salt deficient zones around the PEO molecule which are equally entropically unfavourable. The system reduces its free energy by releasing water molecules from the chain. This in turn causes an increase in the polymer–polymer interactions leading to phase separation. This process offers the possibility for measuring the cloud point of PVP solutions by lowering it below the boiling point of water. To our knowledge, there are only two approximations to the θ temperature of PVP in water available in the literature[13,14]. Molyneux[13] collated literature data extending to the concentrated polymer region (3–10%) for three molecular weights (300, 600 and 1000 kg mol^{-1}) to compute a region for the θ temperature. Meza and Gargallo[14] determined the θ temperature of PVP in Na_2SO_4 solution (0.55 M) by extrapolating to infinite molecular weight (28°C).

In this report, a procedure for the rapid and accurate determination of the θ temperature and phase diagram of aqueous PVP is described.

THERMODYNAMIC BASIS OF THE θ TEMPERATURE DETERMINATION

The theoretical basis of the method for the determination of the θ temperature proposed by Elias[3,4] has been outlined by Napper[2]. It is based on the Flory–Huggins theory[1] derived for moderately concentrated polymer solutions.

Assuming a concentration-independent polymer–solvent parameter (χ_1), $\chi_1'' = \chi_1' = \chi_1$, and a significant difference in the composition of the two phases, Napper showed[2] that:

$$\ln(1 - \Phi_2'') + \Phi_2'' + \chi_1 \Phi_2''^2 = 0 \tag{1}$$

where Φ_2' and Φ_2'' correspond to the volume fraction of polymer in the dilute and concentrated phases, respectively. Rearrangement of this equation gives:

$$\log \Phi_2' = \log[3(\chi_1 - \tfrac{1}{2})] + 3.908r(\chi_1 - \tfrac{1}{2})^2(\chi_1 - \tfrac{2}{3}) \tag{2}$$

where r refers to the number of polymer segments.

The values of χ_1 at the point of incipient phase separation can be readily calculated from equation (2) as a fraction of polymer volume fraction for any given chain length (r). A plot of χ_1 against $\log \Phi_2'$ yields straight lines which extrapolate to a value of 0.5 at $\Phi_2' = 1$. At the same time, Flory[1] has shown that χ_1 is linearly dependent on the reciprocal temperature ($1/T$):

$$\tfrac{1}{2} - \chi_1 = \psi_1(1 - \theta/T) \tag{3}$$

where ψ_1 is the entropy of dilution[1]. This has been confirmed experimentally for the dilute regions[2].

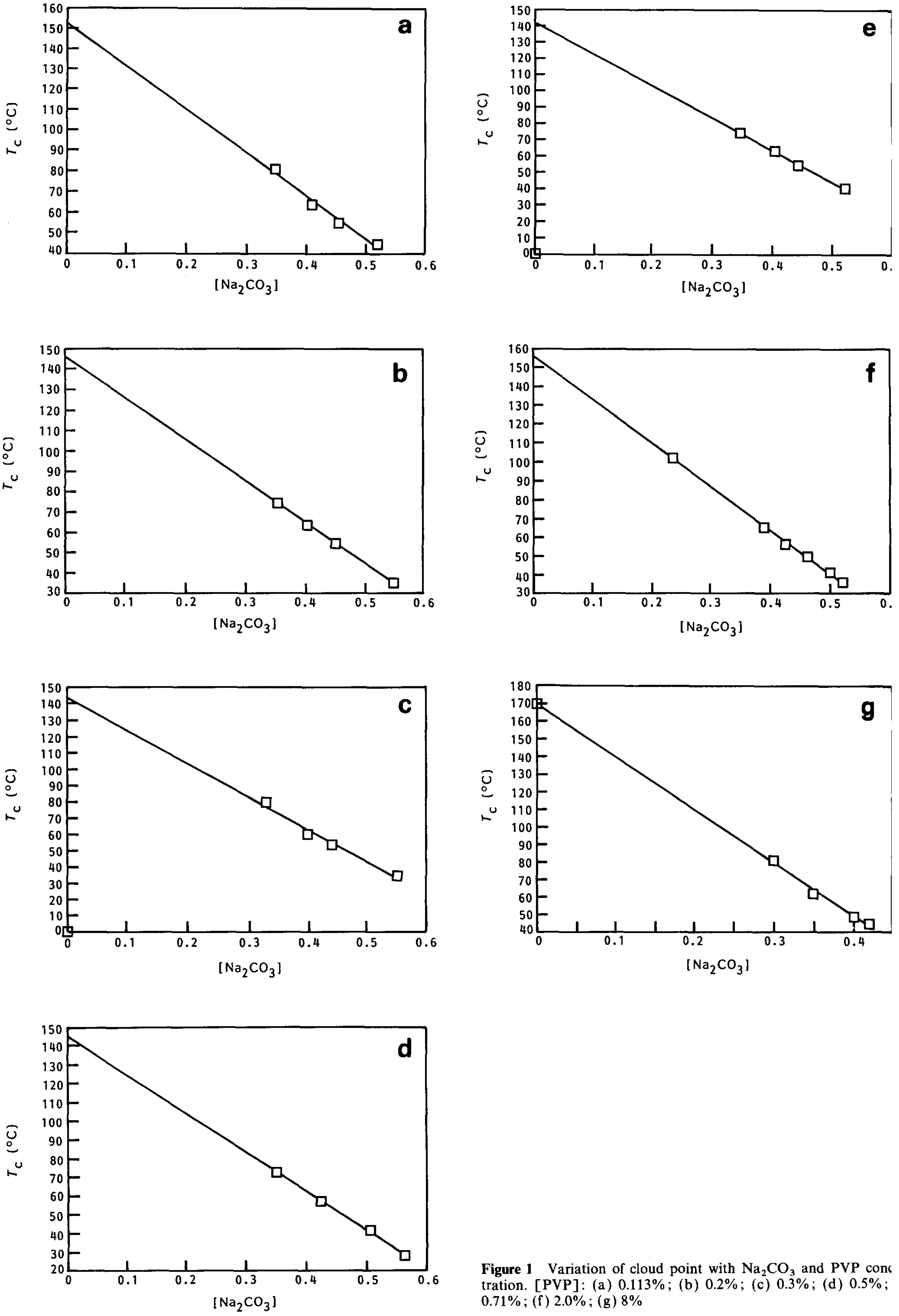

Figure 1 Variation of cloud point with Na_2CO_3 and PVP conc tration. [PVP]: (a) 0.113%; (b) 0.2%; (c) 0.3%; (d) 0.5%; 0.71%; (f) 2.0%; (g) 8%

Table 1 Variation of constant K_s [equation (5)] with Na_2CO_3 concentration (C_s)

C_s ($\times 10^2$) ($g\,ml^{-1}$)	Log C_s	K_s
0.113	−2.947	−211.63
0.200	−2.699	−203.29
0.300	−2.523	−201.26
0.500	−2.149	−205.39
0.710	−2.301	−197.41
2.000	−1.699	−232.53
8.000	−1.097	−301.79

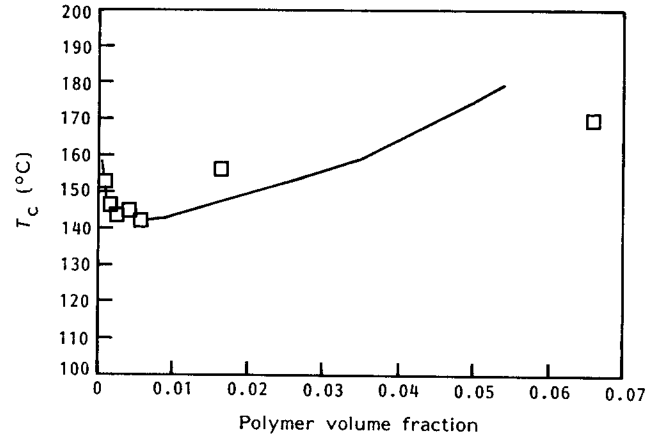

Figure 2 Phase diagram of the PVP–water system

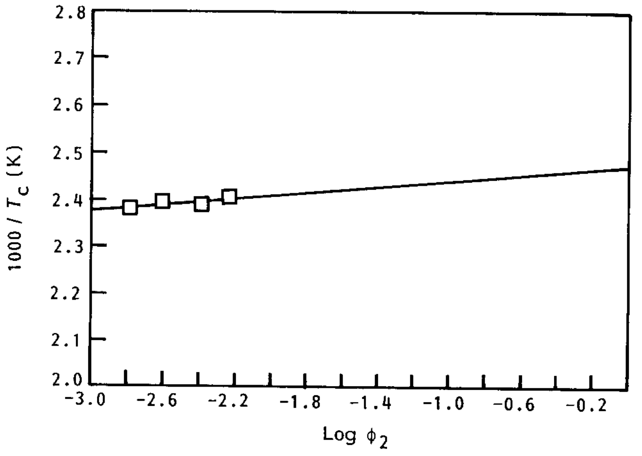

Figure 3 Linear extrapolation of the inverse cloud point *versus* log Φ_2 plot in the dilute region for the determination of the θ temperature

It follows that the temperature corresponding to $\Phi_2' = 1$, and consequently to $\chi_1 = 0.5$, in a plot of inverse phase separation temperature against volume fraction of polymer (Φ_2'), yields the θ temperature.

EXPERIMENTAL

Materials

The PVP, supplied by GAF (K-90), has a molecular weight $\bar{M}_w = 360\ kg\,mol^{-1}$ and intrinsic viscosity $[\eta] = 1.61$ (ref. 15). The polymer was used as received. The electrolyte used was Na_2CO_3 (BDH). Polymer solutions were prepared in deionized water.

Techniques

Cloud points were determined by a custom-made apparatus. Light from an incandescent bulb is split into two beams by means of fibre optics. One beam is passed through a sealed capillary tube containing the sample, while the other goes through another capillary tube containing a suitable reference solution (water). The intensity of the light transmitted through the sample, normalized by the reference beam, is detected by phototransistors and monitored by an X–Y recorder. Sample and reference are heated by resistance windings at a controlled rate of 1°C min^{-1}. The use of capillary tubes ensures rapid heat transfer.

RESULTS AND DISCUSSION

Figure 1 summarizes the variation of the cloud point with increasing Na_2CO_3 and PVP concentrations. The range of polymer concentrations varied from 0.1 to $0.7 \times 10^{-2}\ g\,ml^{-1}$ in the dilute region and up to $8.0 \times 10^{-2}\ g\,ml^{-1}$ in the concentrated region. In all cases, the cloud point of the PVP solution decreased linearly with Na_2CO_3 concentration. This is in agreement with published data on aqueous PEO–cosolute systems and the anticipated increase in the polymer activity (f_n) by the presence of electrolyte as described by the Debye–McAulay equation[16]:

$$\ln f_n = \frac{\beta}{2kT\varepsilon} \sum_i n_i \varepsilon_i / r_i \qquad (4)$$

where β is a constant characteristic of the polymer, ε is the dielectric constant of water and n_i, ε_i and r_i are the number, charge and radius of ions present, respectively.

In all cases, the T_c *versus* Na_2CO_3 concentration behaviour fitted extremely well to a straight line (coefficients of correlation invariably better than 0.999):

$$T_c = T_c^0 + K_s C_s \qquad (5)$$

where T_c^0 is the cloud point in the absence of cosolute and C_s is the cosolute concentration ($g\,ml^{-1}$). The constant K_s describes the efficiency of the electrolyte to depress the cloud point of the polymer solution. *Table 1* summarizes the variation of K_s with increasing polymer concentration. The variation of the absolute value of K_s mirrors a lower critical solution (*LCST*) behaviour, going through a minimum at about $0.7 \times 10^{-2}\ g\,ml^{-1}$ and increasing fast as the polymer solution enters the concentrated regime.

The cloud points of the PVP solutions were in each case determined by extrapolation to $C_s = 0$. *Figure 2* illustrates the variation of the cloud point of the PVP solution with increasing PVP concentration over the whole polymer concentration range. The curve represents a typical *LCST* behaviour. It is interesting to note that the cloud points are invariably well above the boiling point of water. Linear extrapolation of the plot $1/T_c$ *versus* log Φ_2 to log $\Phi_2 = 0$ in the *dilute* region yields a value of 130.5 ± 1°C for the θ temperature (*Figure 3*). This is in the same region as the reported[13,14] approximate value of 140 ± 5°C.

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