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Cryoscopy in polymer solutions : scaling laws and Kauzmann paradox

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SUMMARY : We discuss the melting behavior of the solvent's crystals in linear flexible polymer solutions. Taking into account the Daoud - Jannink (DJ) diagram, and the limit Kauzmann temperature T_K, one gives the cryoscopic laws describing the solid-liquid transition of the solvent, in the different concentration - temperature DJ domains. Finally one explains why, for thermodynamic reasons, below a critical concentration ϕ_K, the solvent can not crystallize. In these systems, the non crystallizable amount of solvent depends of the theta temperature characterizing the polymer-solvent interaction, the Kauzmann temperature and the ratio between the melting enthalpy and the melting temperature of the pure solvent.

Introduction

Polymer - solvent solutions has been extensively studied since half a century (1, 2, 3). Among the macroscopic measurable effects related to the statistical properties of polymer solutions (4, 5), the shift of the solvent's melting temperature was proposed by Orwel (6) as a measure of the polymer-solvent interaction parameter. Recent experimental works show that both the temperature and the melting enthalpy of the solvent are influenced by the presence of polymer chains (7,8). Also in these systems, it has been noted that in certain condition of concentration, a fraction of solvent cannot crystallize even if the glass transition of the system is not regulating the solid-liquid transition as observed in water-hydrophilic polymer systems (8,9).

The aim of this note is to propose a theoretical background taking into account both, advances in polymer solution statistics and the specificity of solid-liquid transition. In this note, one considers only polymer-solvent systems with low glass transition, the polymer chains are linear and neutral and do not crystallize (or crystallize far below the crystallization of the solvent). The system PDMS-cyclohexane obeys these criteria, the crystallization of cyclohexane has been studied by calorimetry and NMR (8,10). In others systems it has been

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shown that the polymer structure would have some influence on the crystallization of the solvent (7, 11).

Theoretical background

In the following, one call, t_m , the reduced shift, $(T_m^0-T_m)/T_m^0$, of the solvent's melting temperature; T_m^0 and T_m being respectively the melting temperatures of the solvent in the pure state and in the solution. The reduced shift is related to the decrease of the solvent's chemical potential in the solution by relation 1a. Osmotic pressure, Π, and the vapor pressure, P, are given by relations 1b,c for comparison purpose (6).

$$t_m = \frac{T_m^0 - T_m}{T_m^0} = -\frac{\Delta\mu_1}{\Delta H_m^0} \text{ (a) ; } \Pi = -\frac{\Delta\mu_1}{\bar{v}_1} \text{ (b) ; } Log\left(\frac{P}{P_0}\right) = \frac{\Delta\mu_1}{RT} \text{ (c)} \qquad (1)$$

$\Delta\mu_1$ is the difference between the chemical potential of the solvent in the solution and in its pure state. ΔH_m^0 is the melting enthalpy of the pure solvent and $\bar{v}_1$ its molar volume. In the following sections, we discuss first the relation (1a) and its modification to take into account the decrease of melting enthalpy while shifting the transition temperature. Then the dependence of the solvent chemical potential decrease with temperature and concentration will be discussed using Daoud - Jannink diagram.

Thermodynamics of melting : the particularity of the solid - liquid transition

During melting there is equilibrium between solvent's crystals and the solution, the Gibbs - Duhem relations for each phases gives after integration :

$$\Delta\mu_1 = \int_{T_m^0}^{T_m} \Delta S_m(T)dT \qquad (2)$$

The lowering of the solvent chemical potential, $\Delta\mu_1$, is due here to the mixing effect, it is to be noted that the chemical potential of pure liquids can be also lowered in the vicinity of an attracting surface. If we assume a constant melting entropy ΔS_m, equation (2) gives the classical relation 1a. However, this assumption is valid only at low shifting of the transition temperature typically $t_m \sim 10^{-2}$. In polymer solutions t_m can reach values of 1 to 2 10^{-1} and one can note that in such conditions the melting enthalpy is respectively 80 and 60% of ΔH_m^0 if one assumes that $\Delta H_m(T_m)$ varies linearly with the melting temperature (8). In confined systems, for example solvents in porous glass (12, 13), it has been shown that the solvent melting enthalpy varies linearly with the temperature and obeys the following relation: $\Delta H_m = \Delta H_m^0 (T_m - T_K)/(T_m^0 - T_K)$, T_K being the Kauzmann temperature where the extrapolated melting entropy vanishes (14). It is to point out that the enthalpy of a pure supercooled liquid varies also linearly with the temperature according to the same relation (15). The Kauzmann temperature of a liquid can be defined as the temperature below which the liquid cannot crystallize, for thermodynamic reasons, obviously before T_K, around Tg the system (confined pure liquid or solution) is frozen and the solvent cannot crystallize for kinetics reasons.

In conclusion the assumption, $\Delta H_m = Cte$, is not verified neither in solution nor in pure liquid confined in small pores. Here one assumes that the change of heat capacity, ΔC_P, at the first order liquid-solid transition is temperature independant :

$$\Delta C_P \cong \frac{\Delta H_m^0}{T_m^0 - T_K} = \frac{\Delta S_m^0}{t_K} = Cte \tag{3}$$

where $t_k = \left(T_m^0 - T_k\right)/T_m^0$. the melting entropy is given by he following classical relation :

$$\Delta S(T) = \frac{\Delta H_m^0}{T_m^0} + \int_{T_m^0}^{T} \frac{\Delta C_P}{T'} dT' \tag{4}$$

combining rel. 2-4, one obtain at a second order in t_m :

$$t_m \cdot \left(\frac{t_m}{2t_k} - 1\right) = \frac{\Delta\mu_1}{\Delta H_m^0} \tag{5}$$

For low shift of the transition temperature, relation (5) gives the classical one (1a) which constitute the first order development in t_m.

The advantage of this last relation compared to the classical one, rel.1a, is that it remains valid even for important shift of the melting temperature. This relation states that solid-liquid transition can never exist thermodynamically below T_K. One can then give thermodynamically a "critical" lowering of the chemical potential at which the melting temperature coincides with T_K :

$$\left(\Delta\mu_1\right)_K \approx -0.5 \cdot t_K \cdot \Delta H_m^0 \tag{6}$$

This corresponds to a certain limiting concentration of polymer above which no liquid - solid transition of the solvent can take place, at this concentration the melting temperature coincides with T_k. In most of the materials, t_K is of the order of 0.5 (16), then the minimum value of the change of the chemical potential shift is $-0{,}25\,\Delta H_m^0$. In order to estimate the critical solvent concentration which corresponds to this value of $(\Delta\mu_1)_K$ and to give expression of the melting temperature shift, one must take into account a statistical model of the polymer solution.

Polymer solution thermodynamics :

It was well established theoretically and experimentally (1-5,17) that the thermodynamic properties of a polymer solution change with both temperature and concentration. The progressive melting of solvent's crystals, in a solution containing polymer chains, involves the changes of those two basic parameters, we should then discuss the melting using such theoretical background.

Figure 1 shows the Daoud - Jannink diagram giving the different domain in temperature and concentration of a linear and flexible polymer solution. Detailed description of the diagram can be found elsewhere (17). Here one is interested in the semi-dilute regime (II), the theta régime (III) and the separation domain (IV). In these domains, the concentration of polymer chain Φ is high enough to produce a measurable shift in the melting depression of the solvent. In these regimes, the scaling laws giving the osmotic pressure, Π, as function of temperature and concentration write :

$$\frac{\Pi}{T} \sim \tau^{l} \cdot \phi^{q} \tag{7}$$

ϕ is the volume fraction of polymer and $\tau = (T - \theta)/\theta$ is the reduced temperature. The value of the exponents in the three considered regimes are given in table 1 :

Table 1. Scaling exponents in the different regimes of a flexible neutral polymer solution.

Domain	**ν**	**q = dν / (dν-1)**	**l**
II	3/5	9/4	3/4
III	1/2	3	0
IV	1/3	q → ∝	0

Using rel. 5,7 and the fact that t_k~0.5 one obtains the following cryoscopic laws in the semi-dilute régime and the theta régime :

$$t_m \sim (\theta_m - t_m)^{3/4} \cdot \phi^{9/4} \qquad \text{regime II} \qquad (8a)$$

$$t_m \sim \phi^{3} \qquad \text{regime III} \qquad (8b)$$

with the reduced temperatures: $\theta_m = (T_m^0 - \theta)/T_m^0$ and $t_m = (T_m^0 - T_m)/T_m^0$.

The crossover between the two behaviors, given by the intersection of the curve $T_m(\phi)$ and the curve $\phi^{**} \sim \tau$, takes place at a concentration around :

$$\phi_m^{**} \sim \left(T_m^0 - \theta\right)/\theta . \qquad (9)$$

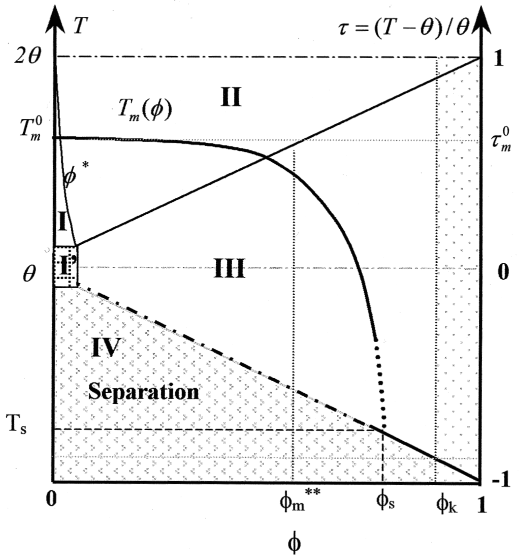

Fig. 1 : Daoud - Jannink diagram giving structural and thermodynamic properties of a neutral flexible polymer solution. The curve T_m gives the evolution of the melting point depression in the semi-dilute and theta regimes.

This concentration is a characteristic parameter of the polymer-solvent system.

The heavy line drawn on the diagram show schematically how the melting temperature T_m change with concentration in these two different domains :

In the semi-dilute regime, the melting temperature of the solvent does not vary conspicuously. In order to compare calorimetric results to osmotic pressure measurements in the semi-dilute régime, one should plot $\Re_{\theta_m}$ versus the volume fraction of polymer in the solution :

$$\Re_{\theta_m} = \frac{t_m}{\left(\theta_m - t_m\right)^{3/4}} \sim \phi^{9/4} \qquad (10)$$

At concentration above ϕ_m^{**} the melting temperature shift is more concentration dependent (rel. 8b). In DSC experiments this effect is observed; the thermograms become extremely large even at low scanning rate (0.6 °C/min). During the progressive melting, a small change in the solution concentration shift notably the melting point. In the theta regime, the large width of the melting DSC peak and the experimental conditions of (low scanning rate) make difficult calorimetric studies on these polymer-solvent solutions. One has applied DSC fractionation method $^{(18)}$ to achieve such experiments in these semi dilute regimes.

Above a polymer fraction ϕ_k that lower the solvent's chemical potential down to the critical value 0.5 t_k ΔH_m^0 (rel.6), no solid-liquid transition can exist thermodynamically. At this concentration, the melting and Kauzmann temperatures of the solvent coincide. In such situation the melting enthalpy vanishes. Since such limit concentration is always in zone III of the diagram, an estimation of such concentration is :

$$\phi_k \cong (0.5 \cdot t_k \cdot \beta)^{1/3} \qquad (11)$$

with t_k~0.5 and $\beta = \Delta H_m^0 / RT_m^0$. For molecular liquid where the melting entropy is about 3/2 R, one get ϕ_k~72%. ϕ_k constitute the thermodynamic limit for the solvent's solid-liquid transition. In figure 1, The dashed part of the T_m curve indicates that this right part of the diagram depend on the characteristic temperatures of the polymer : Crystallization (T_c) and glass transition (T_g)temperatures.

In fact, in many others situations where the glass transition of the polymer is relatively high (hydrophilic polymers), the origin of the non cristallyzable fraction is kinetic; in that case the critical concentration below which the solvent does not crystallize is given by the Tg regulation effect (8-10). If a glass transition line, Tg(ϕ), intercepts the drawn melting line, $T_m(\phi)$, before it reaches the separation zone then the solvent stops crystallizing and this for a kinetic reason.

However if it's not the case ($T_g < T_s$), this fraction of non crystallisable solvent will separate and then crystallize; such behavior has been observed in the system PDMS-Cyclohexane by NMR measurements $^{(10)}$. It can be described mathematically through the exponent q in relation (7) since one have in this region :

$$\phi_k \cong (0.5 \cdot t_k \cdot \beta)^{1/q} \to 1 \quad \text{when } q \to \infty$$

Conclusion and perspectives

In solution of simple liquids, the cryoscopy lowering of the melting temperature is given by rel.5, when the Kauzmann paradox is taken into account ; various experimental facts indicate that the melting enthalpy of a liquid varies linearly with the melting temperature and extrapolates to 0 at the Kauzmann temperature. In polymer solutions using the Daoud -

Jannink expression of the osmotic pressure in the different domains (semi dilute and concentrated), one gives, rel.8, the dependence of the melting solvent depression as function of the theta temperature of the system and of the concentration. In the case analyzed here ($T_g<T_s$), the amount of solvent crystallizing in the system, depends on the relative values of the temperatures, T_m^0, θ, and can never exceed a theoretical value due to existence of the Kauzmann temperature of the liquid. In a forthcoming paper, one will show that the cyclohexane-PDMS system verifies these predictions.

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