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## Experimental study of polymer interactions in a bad solvent

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**Résumé.** — Les interactions entre chaînes polymériques dans un mauvais solvant (polystyrène-cyclohexane à des températures plus petites que 35 °C) ont été étudiées en utilisant des mesures d'intensité de lumière diffusée. Les résultats obtenus, dans des solutions diluées, montrent que la concentration de demixion,  $C_D$ , est reliée au second coefficient du viriel,  $A_2$ , de la pression osmotique. Les variables réduites à utiliser pour avoir une courbe universelle ne sont pas celles prédites par les théories de champ moyen ou de loi d'échelle. Il est trouvé empiriquement que  $C_D/C_c$  et  $A_2/A_2^c$  sont fonction de  $\frac{T_c - T}{T_c} \times M_w^{0,31}$ .  $M_w$  est la masse moléculaire,  $C_c$  et  $A_2^c$  sont respectivement la concentration critique et le second coefficient du viriel à la température critique  $T_c$ .

**Abstract.** — The interactions between polymer chains in a bad solvent (polystyrene-cyclohexane at temperatures lower than 35 °C) was studied using light scattering intensity measurements. The results obtained in dilute solutions show that the demixing concentration  $C_D$  is related to the second virial coefficient  $A_2$  of the osmotic pressure. Using the reduced variables predicted by mean-field or scaling theories the demixion curves are dependent on  $M_w$ , the molecular weight. Empirically, it is found that  $C_D/C_c$  and  $A_2/A_2^c$  are only functions of  $\frac{T_c - T}{T_c} \times M_w^{0,31}$ .  $C_c$  and  $A_2^c$  are the critical concentration and the second virial coefficient at the critical temperature  $T_c$ .

### 1. Introduction.

In a polymeric system of linear and flexible chains diluted in a bad solvent, attractive interactions can be strong enough to induce a phase separation in the solution. Among the two coexisting phases one is diluted while the other is more concentrated in the chain concentration. The phase diagram (Fig. 1), temperature  $T$  versus concentration  $C$ , presents a completely forbidden range of concentrations limited by a coexistence curve and with a critical point  $(T_c, C_c)$  at its maximum (UCST). Above  $T_c$  and in the vicinity of  $T_c$  [1, 2], intermolecular interactions are, within a mean field framework, directly related to intramolecular interactions. These interactions govern the deswelling of an isolated chain which has been extensively studied and is well described, at first order, by existing theories. The purpose of this paper is to analyse intermolecular interactions, whatever the temperature and the molecular weight, in the very dilute regime ( $C \ll C_c$ ). Experiments are performed on polys-

tyrene-cyclohexane system with chain molecular weight  $M_w$  ranging from  $1.71 \times 10^5$  to  $2.06 \times 10^7$  daltons, over a temperature domain from 10 °C to 35 °C, corresponding to a bad solvent situation. Using light scattering measurements [3], two quantities are determined: the demixing concentration  $C_D$  and the inverse of the osmotic compressibility  $C \frac{\partial \pi}{\partial C}$ . The demixing concentration  $C_D$ , in the dilute phase ( $C_D \ll C_c$ ) of the coexistence curve, is a function of temperature and molecular weight:

$$C_D = f(T, M_w). \quad (1)$$

The coexisting conditions are defined by equalizing the chemical potential and the osmotic pressure in the two coexisting phases. The inverse of the osmotic compressibility of the dilute solution is given by:

$$\frac{C}{RT} \frac{\partial \Pi}{\partial C} = \frac{C}{M_w} + 2 A_2 C^2 \quad (2)$$

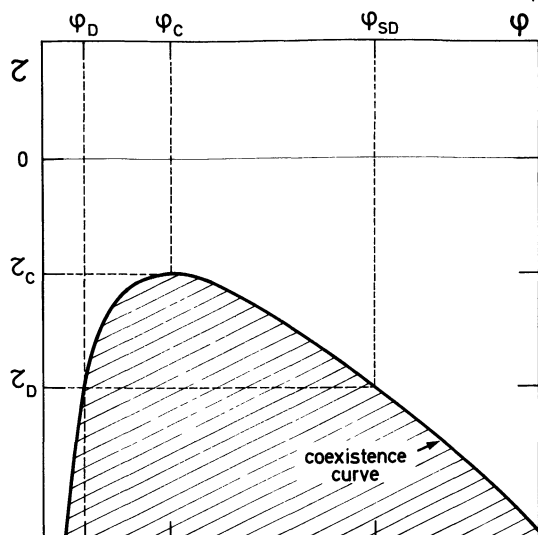


Fig. 1. — Phase diagram  $(\tau, \varphi)$  of a polymeric system. Full line corresponds to the coexistence curve.  $\tau_c$  and  $\varphi_c$  represent the coordinates of the critical point. The dashed area is the forbidden region. At the reduced temperature  $\tau_D$  the two coexisting phases have the concentration  $\varphi_D$  and  $\varphi_{SD}$ .

$\Pi$  being the osmotic pressure of the solution,  $A_2$  the second virial coefficient between chains <sup>(1)</sup>,  $C$  the weight concentration of polymer per unit volume and  $R$  the perfect gas constant.

In these bad solvent conditions the attractive interactions, corresponding to a negative  $A_2$ , progressively increase as the temperature decreases down to the demixion occurrence. We present here a comparative discussion of the two quantities  $A_2$  and  $C_D$  measured on the same molecular weights samples. By light scattering experiments, for each molecular weight, at a given temperature, using samples having different concentration we determine  $A_2$ . Using one sample having a given concentration, decreasing the temperature, step by step, we determine the demixing temperature  $T_D$ . For  $T > T_D$ , the transmitted intensity is a constant while it deeply decreases as the temperature decreases for  $T < T_D$ . Experimental details are given in reference [4] and in the thesis of one of the authors (R. P.) [3] where the apparati and data analysis used are extensively described.

The effective  $\theta$  temperature of the system, at which attractive and repulsive interactions compensate is experimentally determined by two methods :

— either as the temperature where  $A_2$  is equal to zero.

<sup>(1)</sup> The second virial of the osmotic pressure  $A_2$  is in fact an effective second virial coefficient between statistical units of two different chains.

— or as the infinite molecular weight extrapolation of the critical demixing temperature  $T_c$ .

Experimentally the second method leads to a slightly lower  $\theta$  temperature than the first method ( $\Delta\theta \approx 1^\circ\text{C}$ ) [3]. The direct determination of  $\theta$  from the  $A_2$  measurements is preferred here as no extrapolation of the measurements is required ( $\theta = 35^\circ\text{C}$  for our system). No molecular weight dependence (from  $2.4 \times 10^4$  to  $6.77 \times 10^6$ ) is found experimentally for the  $\theta$  temperature.

## 2. Theory.

From scaling arguments [5], as well as from a mean field approach, a description of the interactions in bad solvent leads to the relations :

$$C_D/C_c = g(\tau_D/\tau_c) \quad (3)$$

$$(A_2/A_2^c)_{c \rightarrow 0} = h(\tau/\tau_c) \quad (4)$$

where  $\tau$  is the relative temperature defined as <sup>(2)</sup> :  $\tau = \frac{T - \theta}{T}$ .  $A_2^c$  and  $\tau_c$  are the respective values of  $A_2$  and  $\tau$  at  $T = T_c$  and  $\tau_D$  is the value of  $\tau$  in the demixing conditions. With this formalism the quantities  $C_D/C_c$  and  $A_2/A_2^c$  are functions of only one reduced variable  $\tau/\tau_c$ .

In order to determine the orders of magnitude of the interactions involved, a mean field approach is used. An expression of the free energy  $F$  per unit volume, of a polymer solvent system has been proposed [1, 2] <sup>(3)</sup>.

$$\frac{F}{kT} = \underbrace{\frac{\varphi}{N} \ln \varphi}_{(a)} + \underbrace{\frac{1}{2} v \varphi^2 + \frac{1}{6} w \varphi^3}_{(b)} \quad (5)$$

$k$  is the Boltzmann constant.  $N$  is the number of statistical units of mass  $m$  in a chain :  $N = M_w/mN_a$ ,  $N_a$  is Avogadro's number.  $\varphi$  is the number of statistical units in a unit volume of the solution :  $\varphi = C/m$ . Part (a) of  $F/kT$  is the translational free energy of the chains in the solvent. Part (b) of  $F/kT$  is the free energy of interactions between the statistical units, these being regarded as a Van der Waals gas.  $v$  and  $w$  are the second and third virial coefficients between statistical units [6, 7].  $v$ , as  $A_2$ , is equal to zero at the  $\theta$

<sup>(2)</sup> The Flory definition of  $\tau = \left(\frac{T - \theta}{T}\right)$  differs from the definition used in phase transitions physics  $\tau = \left(\frac{T - \theta}{\theta}\right)$ .

As far as  $\tau \ll 1$ , these two definitions are close to each other.

<sup>(3)</sup> The complete Flory-Huggins equation leads to expression 5, providing that  $\varphi \ll 1$  and thus  $N \gg 1$ .

temperature [1] and is proportional to the relative temperature  $\tau$ ; the proportionality factor  $b = v/\tau$  is a constant.  $w$  is weakly temperature dependent and is often taken to be a constant [2, 7].

This expression of the free energy leads to the coordinates  $(\varphi_c, \tau_c)$  (see Fig. 1) of the critical point using  $\frac{\partial^2 F}{\partial \varphi^2} = \frac{\partial^3 F}{\partial \varphi^3} = 0$

$$\varphi_c = \frac{1}{\sqrt{wN}} \quad \tau_c = -\frac{2}{b} \sqrt{\frac{w}{N}}. \quad (6)$$

On the coexistence curve (Fig. 1) the two phases ( $\varphi_D$  and  $\varphi_{SD}$ ) coexisting at the same temperature ( $\tau_D$ ) have identical chemical potential  $\left(\frac{\partial F}{\partial \varphi}\right)$  and identical osmotic pressures  $\left(\pi = \varphi^2 \frac{\partial (F/\varphi)}{\partial \varphi}\right)$ :

$$\frac{\pi}{kT} = \frac{\varphi}{N} + \frac{1}{2} v \varphi^2 + \frac{1}{3} w \varphi^3. \quad (7)$$

Far from the critical point ( $\varphi_D \ll \varphi_c \ll \varphi_{SD}$ ) these identities lead to [3]:

$$\frac{1}{N} \ln \left[ \varphi_D \cdot \left( \frac{2w}{-3v} \right) \right] = -\frac{3v^2}{8w}. \quad (8)$$

Then  $\varphi_D \sqrt{N}$  is function only of  $\tau \sqrt{N}$ , in agreement with relation (3). One must note that  $\varphi_D/\varphi_c \propto \varphi_D \sqrt{N}$  and  $\tau/\tau_c \propto \tau \sqrt{N}$ . Using experimental quantities this can be written as:

$$C_D \sqrt{M_W} = g(\tau \sqrt{M_W}). \quad (9)$$

This theory leads to coexistence curves independent of molecular weight if the variables  $C_D \sqrt{M_W}$  and  $\tau \sqrt{M_W}$  are used. For the second virial coefficient  $A_2$ , formula (4) may be justified by the following argument. In the good solvent situation it is experimentally verified [8] that:

$$A_2 M_W C_T^* \approx 1 \quad (10)$$

and that:

$$A_2 \sqrt{M_W} \approx \frac{1}{C_T^* \sqrt{M_W}} = f(\tau \sqrt{M_W}) \quad (11)$$

where  $C_T^*$  is the overlap concentration at the temperature  $T$ . Since  $C_T^* \approx C_c$ , relation (4) corresponds to an extension of relation (11) for  $T < \theta$ .

So this mean field description, as well as scaling, would lead to representations of coexistence curves and interactions between chains on single master curves, whatever the temperature and the molecular weight. The reduced variable would be  $\tau \sqrt{M_W}$ . It must be pointed out that  $\tau \sqrt{M_W}$  is also the reduced variable of expansion factors of an isolated chain.

### 3. Experimental results and discussion.

**3.1 INTRAMOLECULAR INTERACTIONS.** — In the so-called  $\theta$  domain [9] ( $|\tau \sqrt{M_W}| \leq 10$ ) where mean field theory can be applied, the osmotic compressibility measured by elastic light scattering allows both  $v$  in the dilute regime ( $C \ll C_\theta^*$ ) and  $w$  in the semi-dilute regime ( $C \gg C_\theta^*$ ,  $T = \theta$ ) to be determined.

In the dilute regime,  $\frac{\partial \pi}{\partial C}$  is found to be a linear function of concentration. In the  $\theta$  domain,  $A_2$  is experimentally independent of  $M_W$  and proportional to  $\tau$  for  $T \geq \theta$  and for  $T \leq \theta$  if  $|\tau| \leq 2 \times 10^{-2}$  (see Fig. 2). This agrees with the mean field description:  $A_2$ , the second virial coefficient between chains is directly proportional to  $v$  the second virial coefficient between statistical units. This leads experimentally to:

$$\frac{v}{m^2 N_a} = 5 \times 10^{-3} \tau \text{ (cm}^3 \times \text{mole/g}^2\text{)}. \quad (12)$$

From this expression one can deduce the Yamakawa excluded volume parameter [3, 10]:  $z = 8.10^{-3} \times \tau \sqrt{M_W}$ . This agrees with the  $z$  value deduced, for example, from the expansion factor of the intrinsic viscosity measured in the  $\theta$  domain [11, 12]:

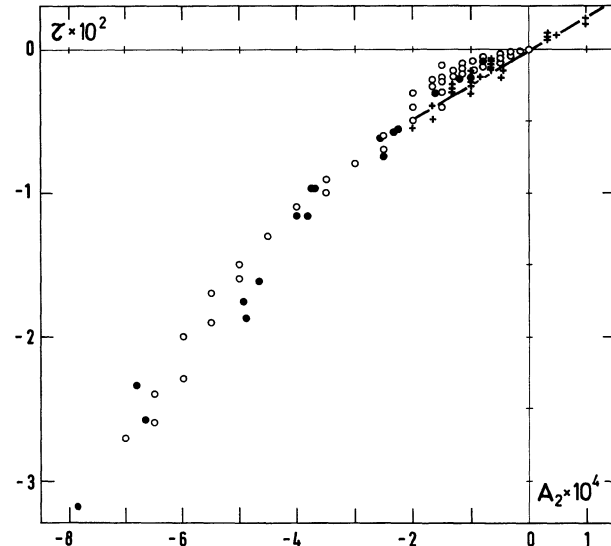


Fig. 2. — Second virial coefficient of the osmotic pressure ( $A_2$  (cm<sup>3</sup> × mole/g<sup>2</sup>)) versus the relative temperature  $\tau$  the  $\theta$  domain ( $|\tau \sqrt{M_W}| \leq 10$ ) +: measurements from references [14, 21, 28, 29] for  $1.3 \times 10^5 \leq M_W \leq 5.7 \times 10^7$ ; O: measurements for  $2.4 \times 10^4 \leq M_W \leq 6.77 \times 10^6$  (see appendix 1). The absolute accuracy on  $A_2$  is smaller than  $5 \times 10^{-5}$  cm<sup>3</sup> · mole/g<sup>2</sup>; ●: correspond to the quantity  $-\frac{1.4}{M_W C_c}$ , plotted versus  $\tau_c$ , as determined from references [18-20]. The straight line corresponds to relation (12).

$z = 7 \times 10^{-3} \times \tau \sqrt{M_w}$ . For our system  $z$  is experimentally the reduced variable of the expansion factor of isolated chain inside and outside the  $\theta$  domain for both  $T \geq \theta$  and  $T \leq \theta$  [9, 11, 13-15]. The intrachain interaction is thus experimentally only a function of the reduced variable  $\tau \sqrt{M_w}$  whatever the temperature and the molecular weight. It must be noticed in figure 2 that for the lower values of  $\tau$ ,  $A_2$  determinations in the  $\theta$  domain deviate from expression (12).

In the semi-dilute regime, at the  $\theta$  temperature,  $\partial\pi/\partial C$  is experimentally proportional to  $C^2$  [4]. This leads to a determination of  $W$  [3] which is found to be independent of  $M_w$ :

$$\frac{W}{m^3 N_a} = 1.25 \times 10^{-3} (\text{cm}^6 \times \text{mole}/\text{g}^3). \quad (13)$$

From this experimental determination a value of  $y$  may be derived:  $y \approx 10^{-2}$ .  $y$  is the three body interaction coefficient of the modified Flory equation for the deswelling of an isolated chain (4). A comparison between experimental expansion factors and the modified Flory equation [3, 11], in the collapsed regime, leads to higher  $y$  values ( $0.1 \leq y \leq 1$ ). On the contrary a comparison between experimental expansion factors and a tricritical model [16] in the vicinity of  $\theta$  is in good agreement with determination (13) of the three body interaction.

**3.2. COMPARISON WITH THEORETICAL PREDICTIONS.** — Substituting experimental values (12) and (13) for  $\nu$  and  $w$ , determined in  $\theta$  domain, in (6) and (8) gives:

$$\tau_c = -14/\sqrt{M_w} \quad C_c = 28/\sqrt{M_w} \quad (\text{g}/\text{cm}^3)$$

$$1/M_w \cdot \ln\left(\frac{C_D}{-6\tau_D}\right) = -7.5 \times 10^{-3} \tau_D^2. \quad (14)$$

These numerical values are to be compared with the experimental determinations of  $\tau_c$  and  $C_c$  of the system. From the literature [18-22], it is found that (5) (see Fig. 3a):

(4) If the modified Flory equation for expansion factor  $\alpha$  is written as [17]:

$$\alpha^5 - \alpha^3 - y/\alpha^3 \sim z$$

one obtains  $y \approx (9 \pm 2) \times 10^{-3}$ , using relations [3]  $w = 3yl^6$  and  $R_g^{\theta^2} = \frac{l^2}{6} \left(\frac{M_w}{mN_a}\right)$ ;  $l$  is the length of the statistical unit and  $R_g^{\theta}$ , the radius of gyration at the  $\theta$  temperature, equal to  $0.29 \times \sqrt{M_w}$  (Å) for PS-cyclohexane (mean value from literature measurements).

(5) As previously mentioned  $T_c(M_w \rightarrow \infty) = 34.0 \pm 0.2$  (°C) is not equal to the temperature where  $A_2$  is experimentally equal to zero ( $35 \pm 0.5$  °C).

$$\frac{10^3}{T_c(\text{K})} = 3.256 \times \left[1 + \frac{(14.6 \pm 0.2)}{\sqrt{M_w}}\right] \quad (15)$$

which agrees with (14). On the contrary one can see in figure 3b that relation (14) is not verified for  $C_c$  and that:

$$C_c = 6.8 \times M_w^{-0.38 \pm 0.01} (\text{g}/\text{cm}^3). \quad (16)$$

If the mean field description predicts a satisfactory value of  $\tau_c$  it only gives an order of magnitude for  $C_c$ . The molecular weight dependence (Eq. (16)) would imply a molecular weight dependence of  $w$  in the model; this is in opposition with the experimental observation (13).

The relation  $\tau_c \sim M_w^{-0.5}$  and  $C_c \sim M_w^{-0.38}$ , obtained

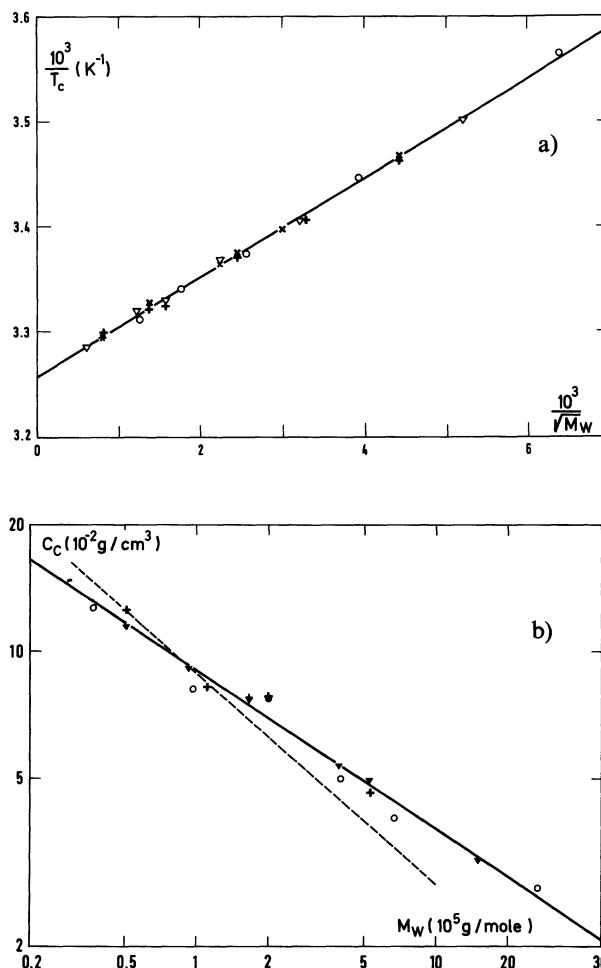


Fig. 3. — Variation of the critical coordinates as a function of the molecular weight. Fig. 3a:  $T_c^{-1}$  versus  $M_w^{-1/2}$  for the polystyrene-cyclohexane system. Symbols: +, ∇, ×, O, \* correspond to references [18 to 22] respectively. Fig. 3b:  $C_c$  versus  $M_w$  in log-log scale for polystyrene-cyclohexane system: ∇ reference [18]; O reference [19]; + reference [20]. The full line corresponds to  $C_c = 6.8 \times M_w^{-0.38} (\text{g}/\text{cm}^3)$  and the dashed line to  $C_c = 28/\sqrt{M_w} (\text{g}/\text{cm}^3)$ .

for polystyrene-cyclohexane system, may well be more general as they remain valid [3] for a different system : polystyrene-methylcyclohexane, which was extensively studied experimentally in the vicinity of the critical point [23].

A tricritical theory [24] has been proposed to describe the concentration effects in  $\theta$  solvents. It leads to logarithmic corrections to the mean field expressions. Providing a proportionality between the boundaries of the diluted  $\theta$  regime and the critical point coordinates, the tricritical effect is a weak correction for  $\tau_c$  ( $\tau_c \propto N^{-1/2} \cdot (\ln N)^{-3/2}$ ) and a stronger correction for  $C_c$  ( $C_c \propto N^{-1/2} \cdot (\ln N)^{+1/2}$ ). This effect could explain the discrepancy between the meanfield theory (6) and experimental results (15), (16).

If  $C_c$  is not well described by the mean field formalism, a strong observation is that  $A_2^c$  and  $\frac{1}{M_w C_c}$  are experimentally found to be of the same order of magnitude (see Fig. 4) :

$$MA_2^c C_c = -1.4. \quad (17)$$

The two physical magnitudes  $A_2^c$  and  $C_c$ , quantities both related to interchain interactions, deviate together from the mean field behaviour (straight line in Fig. 2) for relative temperatures  $\tau \leq -2 \times 10^{-2}$ . In good solvents,  $A_2$  is proportional to  $R_g^3/M_w^2$ ,  $R_g$  being the radius of gyration of an isolated chain. An interesting comparison would be to plot also  $R_g^3/M_w^2$  in figure 2. Unfortunately no  $R_g$  measurements are available, for PS-cyclohexane system, in the range of  $\tau$  where the second virial coefficient deviates from expression (12).

Considering now the coexistence curve, far from the

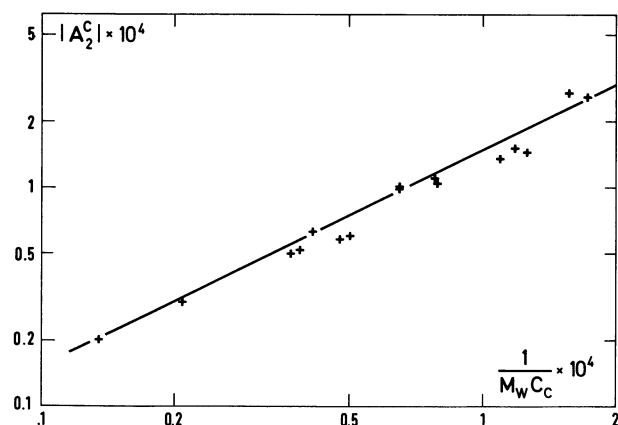


Fig. 4. —  $A_2^c$  versus  $\frac{1}{M_w C_c}$  in log-log scale.  $C_c$  measurements from references [18-20] and  $A_2^c$  are interpolated through measurements of the present work. The straight line corresponds to the law  $A_2^c = -1.4 (M_w C_c)^{-0.99 \pm 0.04}$ .

critical conditions, a comparison is given in figure 5 between mean field predictions ( $2^d$ -part of formula (14)) and experimental determinations. The mean field description gives only a good order of magnitude for  $C_D$ , but with molecular weight distortions. Thus  $C_c \sqrt{M_w}$ ,  $C_D \sqrt{M_w}$  and  $A_2 \sqrt{M_w}$  are not functions of the single reduced variable  $\tau \sqrt{M_w}$ . This is not surprising because a mean field description is not strictly valid either in the vicinity of the critical point or in the dilute regime : it neglects the concentration fluctuations.

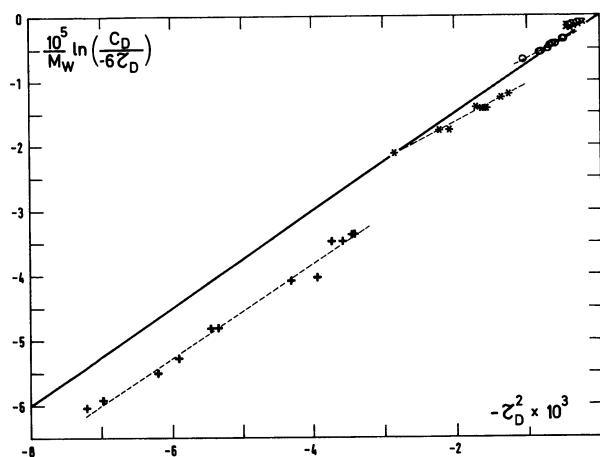


Fig. 5. — Experimental phase diagram  $\frac{1}{M_w} \ln \left( \frac{C_D}{-6 \tau_D} \right)$  versus  $-\tau_D^2$ . The absolute accuracy on  $\tau_D$  is 0.5 °C and  $C_D$  determination better than 2 %. The molecular weight symbols are : +  $1.71 \times 10^5$ ; \*  $4.22 \times 10^5$ ;  $\circ$   $1.26 \times 10^6$ ;  $\times$   $3.84 \times 10^6$ ;  $\nabla$   $6.77 \times 10^6$ . The straight line corresponds to the mean field calculation (formula (14)). Dashed lines have been drawn just to have a visual guide.

### 3.3 ANALYSIS OF THE INTERCHAIN INTERACTIONS.

— In this section we shall try to find the reduced parameter of interchain interactions. First of all one may go back to relations (3) and (4), using only experimental determinations of the various critical quantities (formulae (15), (16), (17)). In figure 6,  $C_D/C_c$  and  $A_2/A_2^c$  are plotted <sup>(6)</sup> versus  $\tau/\tau_c$  : a systematic splitting with  $M_w$  subsists for the two quantities in these representations.

A second attempt is shown in figure 7. If  $\tau/\tau_c$  is neither the reduced variable of  $C_D/C_c$  nor of  $A_2/A_2^c$ , on the contrary the quantity  $C_D/C_c$  is only function of

<sup>(6)</sup> It must be noted that owing to (15) the reduced quantity  $\tau/\tau_c$  is proportional to  $\tau \sqrt{M_w}$ .

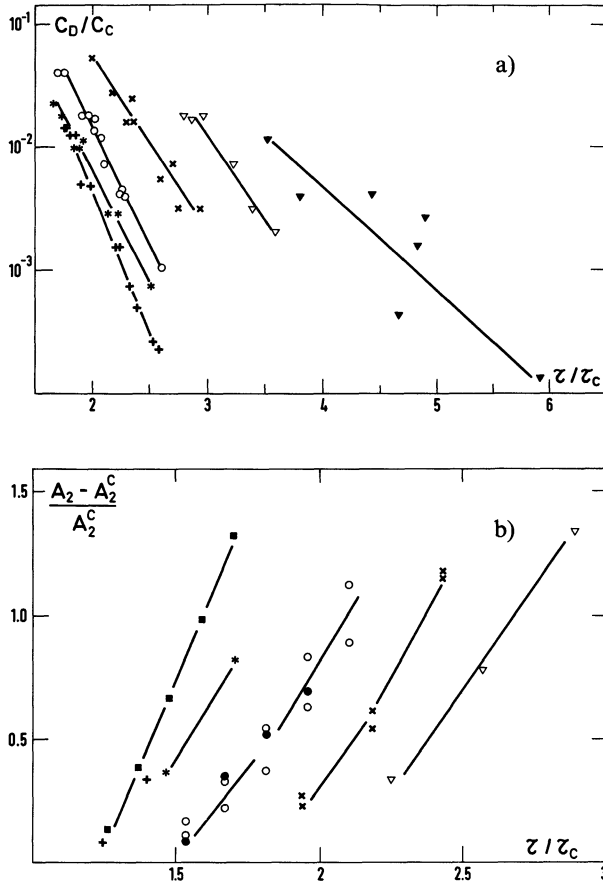


Fig. 6. — Mean field universal coordinates for demixion curve and second virial coefficient. Fig. 6a : Semi-logarithmic plot of  $C_D/C_c$  versus  $\tau/\tau_c$ . Fig. 6b : Linear plot of  $\left(\frac{A_2}{A_2^c} - 1\right)$  versus  $\tau/\tau_c$ .

For molecular weight symbols see figure 5. The meaning of the other symbols is :  $\blacktriangledown M_w = 2.06 \times 10^7$ ,  $\blacksquare M_w = 1.71 \times 10^5$ ,  $\bullet M_w = 1.26 \times 10^6$ .  $\blacksquare$  and  $\bullet$  correspond to  $A_2$  determination from quasi elastic light scattering measurements [3, 9] (see appendix 2 and 3). Full lines have been drawn just to have a visual guide.

$A_2/A_2^c$ . The empirical relation between  $A_2$  and  $C_D$  (7) is :

$$\frac{C_D}{C_c} = 2.5 \times 10^{-2} \left( \frac{A_2 - A_2^c}{A_2^c} \right)^{-1}. \quad (18)$$

If in the critical conditions, the quantity  $M_w A_2^c C_c$  is equal to  $-1.4$ , on the contrary, far from the critical conditions ( $C_D/C_c < 2.5 \times 10^{-2}$ ) it becomes :

(7) Simultaneous determinations of both  $A_2$  and  $C_D$  ( $C_D \ll C_c$ ) for a given  $M_w$  is only possible in a narrow temperature range.

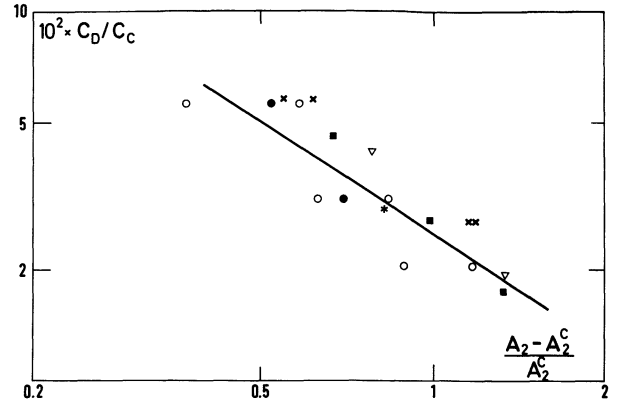


Fig. 7. — Log-log plot of  $C_D/C_c$  versus  $\frac{A_2 - A_2^c}{A_2^c}$ . For molecular weight symbols see figure 6. The straight line corresponds to relation (18). For a given  $M_w$  and a given  $T$ ,  $\frac{A_2 - A_2^c}{A_2^c}$  is the measured quantity and  $C_D/C_c$  are interpolated values or extrapolated values for  $\tau - \tau_c \leq \tau_c/4$ .

$$M_w A_2 C_D = -4 \times 10^{-2}. \quad (19)$$

This relation shows that, even in the vicinity of the coexistence curve, the low concentration expansion of the osmotic pressure (relation (2)) is valid. The molecular weight independent relation (18) between  $A_2/A_2^c$  and  $C_D/C_c$  means that the interactions between chains are really the physical cause of demixion.

In a third attempt, we shall consider the system to be a critical binary mixture. For mixtures of identical size molecules, the analysis of the phase diagram is done using a reduced temperature  $\varepsilon = \frac{T_c - T}{T_c}$  which meas-

ures the relative distance to the critical temperature  $T_c$ . For mixtures of different size molecules, the difference in size must be compensated by a function of the molecular weight [25]. In order to determine this function, the reduced temperature  $\varepsilon$  is plotted as a function of molecular weight at a given reduced concentration  $C_D/C_c$  (see Fig. 8). It is found that, over two decades of molecular weight,  $\varepsilon$  is proportional to  $M_w^{-0.31 \pm 0.04}$ .

Indeed  $\varepsilon \times M_w^{0.31}$  is the reduced variable of both quantities  $C_D/C_c$  and  $A_2/A_2^c$  (see Fig. 9). The dilute side of the coexistence curve (Fig. 9a) has an exponential behaviour :

$$C_D/C_c = 0.15 \times \exp(-3.5 \times \varepsilon M_w^{0.31}). \quad (20)$$

In figure 9b the analytical expression of  $C_D$  (20) transformed into an analytical expression for  $A_2$  through relation (18) is a good extension of the

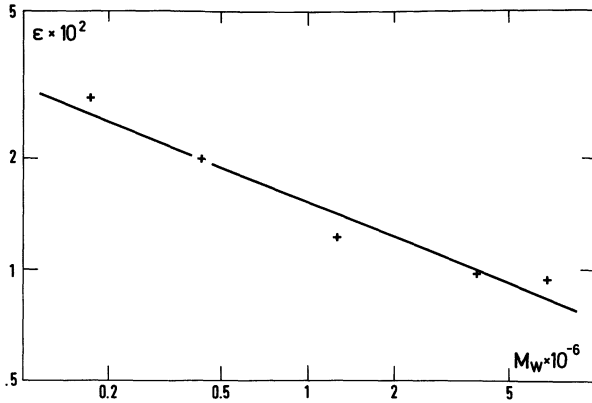


Fig. 8. — Log-log plot of  $\varepsilon = \frac{T_c - T_D}{T_c}$  versus  $M_w$  for  $C_D/C_c = 3.2 \times 10^{-3}$ . The straight line is the best fit  $\varepsilon = 1.1 \times M_w^{-0.31 \pm 0.04}$ .

$A_2$  measurements. A second virial coefficient of the osmotic pressure, between chains, which is an exponential function of temperature, qualitatively agrees with a description of the dilute polymeric solution in bad solvent as a Van der Waals gas of independent statistical links [26].

Two points must be noted. First, expansion factors of isolated chain plotted versus  $\varepsilon M_w^{0.31}$  exhibit a wide molecular weight dependence which does not exist versus  $\tau \sqrt{M_w}$ . Secondly, Sanchez [27] has reanalysed the coexistence measurements from reference [23] obtained with the system polystyrene-methylcyclohexane, in the vicinity of the critical point, over a range of molecular weights:  $1.02 \times 10^4 \leq M_w \leq 7.19 \times 10^5$ . A symmetrization of the two sides of the coexistence curves, with respect to the critical conditions was carried out, using two specific reduced variables. One of these,  $\varepsilon M_w^{0.31}$  is identical to that obtained here from  $A_2$  and  $C_D$  measurements. Thus  $\varepsilon M_w^{0.31}$  is the reduced variable of the coexistence curves both near to and far from the critical point.

**4. Conclusion.**

In bad solvents, expansion factors and interchain interactions do not scale with the same reduced variable. For polystyrene-cyclohexane system expansion factors of an isolated chain may be described as functions of the single variable  $\tau \sqrt{M_w}$ , during the evolution towards collapse [3, 9, 11, 14, 15] and in the collapsed state [3, 11]. A mean field approach then allows a qualitative description for expansion factor variations to be obtained but gives only an estimation of the interchain interactions.

A coherent description is obtained for interactions between chains in diluted solutions: the second virial

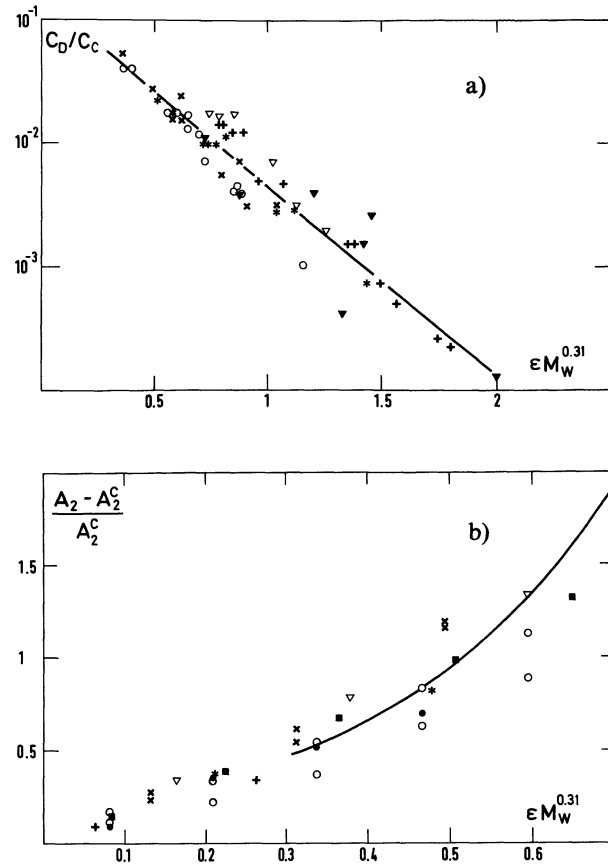


Fig. 9. — Universal coordinates for demixion curve and second virial coefficient. Fig. 9a: Semi-logarithmic plot of  $C_D/C_c$  versus  $\varepsilon M_w^{0.31}$ . The straight line is the best fit (relation 20). Fig. 9b: Linear plot of  $\left(\frac{A_2 - A_2^c}{A_2^c}\right)$  versus  $\varepsilon M_w^{0.31}$ . The full line is  $\frac{A_2 - A_2^c}{A_2^c} = 0.16 \times \exp(3.5 \times \varepsilon M_w^{0.31})$ . For symbols see figure 6.

coefficient of osmotic pressure is related to the coexistence curve  $\left(\frac{A_2 - A_2^c}{A_2^c} = 2.5 \times 10^{-2} \frac{C_c}{C_D}\right)$ . Demixion,

which occurs owing to the thermodynamic interactions between chains, may be described with the same reduced variable in the vicinity of the critical point and in the very dilute range where  $C_D/C_c$  and  $A_2/A_2^c$  are only functions of  $\left(\frac{T - T_c}{T_c}\right) M_w^{0.31} = \varepsilon M_w^{0.31}$ . The reduced variable  $\varepsilon M_w^{0.31}$  seems to be quite general as it is obtained :

- from two different polymeric systems,
- from different physical quantities:  $A_2$  and  $C_D$ ,
- from measurements both near to and far from the critical point,



— using various samples of various polydispersity  
 $\left(1.01 \leq \frac{M_w}{M_n} \leq 1.2\right)$  over a wide range of molecular  
 weights ( $10^5 \leq M_w \leq 10^7$ ).

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#### Appendix 1

Experimental values of the second virial coefficient  $A_2$  ( $A_2 < 0$ ) expressed in  $10^{-5} \text{ cm}^3 \cdot \text{mole/g}^2$  for  $\tau_c \leq \tau \leq 0$ .

$M_w \backslash -\tau \times 10^{-2}$	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5	6	6.5	7
$2.4 \times 10^4$	0	0	-1	-3	-6	-8	-10	-11	-13	-16	-19	-23	-26	
$4.39 \times 10^4$	-1	-2	-3	-5	-7	-8	-10	-11	-13	-15	-17	-20	-24	-27
$8.2 \times 10^4$	-1	-2	-3	-4	-6	-8	-9	-11	-13	-16				
$1.71 \times 10^5$	-1	-2	-4	-5	-6	-8	-10							
$4.22 \times 10^5$	-1	-2	-3	-4	-6									
$2.16 \times 10^6$	-0.6	-1.3	-2.1											
$3.84 \times 10^6$	-0.4	-0.9												
$6.77 \times 10^6$	-0.3	-0.9												

#### Appendix 2

Experimental values of the phase diagram in the dilute regime.

$M_w = 1.71 \times 10^5$		$M_w = 4.22 \times 10^5$		$M_w = 1.26 \times 10^6$	
$T_D$ (°C)	$C_D$ (g/cm <sup>3</sup> )	$T_D$ (°C)	$C_D$ (g/cm <sup>3</sup> )	$T_D$ (°C)	$C_D$ (g/cm <sup>3</sup> )
18	$1.07 \times 10^{-3}$	24.4	$1.16 \times 10^{-3}$	28.4	$1.43 \times 10^{-3}$
17.9	$1.07 \times 10^{-3}$	24	$9.43 \times 10^{-4}$	28.3	$1.43 \times 10^{-3}$
17.6	$9.21 \times 10^{-4}$	23.3	$5.22 \times 10^{-4}$	27.7	$6.28 \times 10^{-4}$
17.25	$9.22 \times 10^{-4}$	23.2	$5.22 \times 10^{-4}$	27.5	$6.28 \times 10^{-4}$
16.8	$3.68 \times 10^{-4}$	23	$5.22 \times 10^{-4}$	27.3	$6.02 \times 10^{-4}$
16	$3.53 \times 10^{-4}$	22.75	$5.88 \times 10^{-4}$	27.3	$4.76 \times 10^{-4}$
14	$1.14 \times 10^{-4}$	21.55	$1.49 \times 10^{-4}$	27.1	$4.16 \times 10^{-4}$
13.8	$1.14 \times 10^{-4}$	21.1	$1.49 \times 10^{-4}$	27	$2.55 \times 10^{-4}$
13	$5.56 \times 10^{-5}$	19.4	$3.84 \times 10^{-4}$	26.5	$1.45 \times 10^{-4}$
12.5	$3.75 \times 10^{-5}$			26.45	$1.59 \times 10^{-4}$
11.25	$1.97 \times 10^{-5}$			26.4	$1.38 \times 10^{-4}$
10.85	$1.69 \times 10^{-5}$			25.3	$3.66 \times 10^{-5}$

$M_w = 3.84 \times 10^6$		$M_w = 6.77 \times 10^6$		$M_w = 2.06 \times 10^7$	
$T_D$ (°C)	$C_D$ (g/cm <sup>3</sup> )	$T_D$ (°C)	$C_D$ (g/cm <sup>3</sup> )	$T_D$ (°C)	$C_D$ (g/cm <sup>3</sup> )
30.4	$1.23 \times 10^{-3}$	30.15	$3.22 \times 10^{-4}$	31.35	$1.35 \times 10^{-4}$
30	$6.43 \times 10^{-4}$	30.05	$3.04 \times 10^{-4}$	31.1	$4.63 \times 10^{-5}$
29.75	$3.62 \times 10^{-4}$	29.9	$3.22 \times 10^{-4}$	30.55	$4.79 \times 10^{-5}$
29.65	$5.65 \times 10^{-4}$	29.5	$1.31 \times 10^{-4}$	30.35	$5.08 \times 10^{-6}$
29.65	$3.62 \times 10^{-4}$	29.25	$5.68 \times 10^{-5}$	30.2	$1.87 \times 10^{-5}$
29.15	$1.27 \times 10^{-4}$	28.95	$3.64 \times 10^{-5}$	30.15	$3.15 \times 10^{-5}$
28.95	$1.66 \times 10^{-4}$			29.25	$1.55 \times 10^{-6}$
28.85	$7.15 \times 10^{-5}$				
28.5	$7.15 \times 10^{-5}$				

### Appendix 3

Experimental values of the reduced second virial coefficient :  $(A_2 - A_2^c)/A_2^c$  for  $\tau \leq \tau_c$ .

$M_w$	$T$ (°C)	$(A_2 - A_2^c)/A_2^c$
$1.71 \times 10^5$	23.15	0.08
	23	0.13 (*)
	22	0.38 (*)
	21.75	0.33
	21	0.66 (*)
	20	0.98 (*)
	19	1.32 (*)
$4.22 \times 10^6$	26	0.36
	24.5	0.82
$1.26 \times 10^6$	29.5	0.11-0.17-0.09 (*)
	29	0.22-0.33-0.35 (*)
	28.5	0.37-0.58-0.52 (*)
	28	0.63-0.83-0.69 (*)
	27.5	0.89-1.17
$3.84 \times 10^6$	31	0.27-0.23
	30.5	0.55-0.61
	30	1.19-1.15
$6.77 \times 10^6$	31.5	0.33
	31	0.78
	30.5	1.33

(\*) Values deduced from quasielastic light scattering measurements.

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