Notes

The Θ Point of Polymer Solutions

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During discussion at the ninth IUPAC microsymposium on macromolecules in Prague, it was to be noted that considerable confusion has come to surround the Θ point concept for polymer solutions since its introduction by Flory.[2] The source of this confusion rests in the variety of definitions which have been applied to the term Θ *point*. Such definitions are not in general equivalent, although they may become so for special models. The general concensus of opinion at the microsymposium regarded the Θ point as the solution analog of the *Boyle point* in gases. However, according to the best nomenclature, there is not one single Boyle point for a gas but rather a line in pressure (p), volume (V), temperature (T) space whose points are called Boyle points.[3]

We find the analogy with gases useful. Figure 1 shows a plot of the compressibility factor $Z = p/\rho RT$ (where ρ is the density, or reciprocal volume of the gas) against the reduced temperature (T/T_c) and reduced density (ρ/ρ_e). This plot (based on the theory of corresponding states) fits the noble gases well,[4] but its general features reflect the properties of any gas. Three loci may be considered to relate to notions of "ideal" behavior of a real gas. Mathematically, they may be described through a use of the virial expansion

$$Z = 1 + \rho A_2(T) + \rho^2 A_3(T) + \ldots \tag{1}$$

The first locus

$$Z - 1 = \rho\{A_2(T) + \rho A_3(T) + \ldots\} = 0 \tag{2}$$

has two branches

$$\text{(A)} \qquad \rho = 0, Z = 1 \tag{3}$$

and

$$\text{(B)} \qquad A_2(T) + \rho A_3(T) + \ldots = 0, Z = 1 \tag{4}$$

The branch A corresponds with the notion that "all gases are perfect in the limit $\rho \rightarrow 0$." *Along the line B*, the gas "behaves as if it were perfect" in the sense that it obeys the relationship $pV = RT$ (or $p = \rho RT$).

The second locus, C, is called the locus of Boyle points,[3] because in the neighborhood of C, Boyle's law (pV = constant at fixed temperature) is obeyed, although the constant is not necessarily RT. Thus

$$\text{(C)} \qquad [\partial(p\rho^{-1})/\partial\rho]_T = 0$$

or

$$A_2(T) + 2\rho A_3(T) + 3\rho^2 A_4(T) + \ldots = 0 \tag{5}$$

The third locus is the isotherm for $T = T_B$, where T_B is the temperature defined by

$$\text{(D)} \qquad A_2(T_B) = 0 \tag{6}$$

In general, the gas is not perfect in any sense along this locus.

All three loci have in common the branch point, E, of the first. Some authors have used the term "Boyle point" in the sense of a "point" on the temperature scale, rather than a point in the (Z, ρ, T) space of Figure 1. The term *Boyle temperature* is to be preferred for this purpose and it is the temperature T_B defined by (6). The point E (Figure 1) is then the only *Boyle point* whose temperature is T_B. At E, $\rho = 0$.

The analogy with polymer solutions is developed by replacing $p/\rho RT$ in eq 1 by $-\Delta\mu_0/\phi RT$ and ρ by ϕ, where $\Delta\mu_0$ is the chemical potential of mixing for the solvent and ϕ is the volume fraction of polymer. The virial expansion has coefficients which depend on molecular weight

$$Z = 1/M_n + A_2(T, M_n)\phi + A_3(T, M_n)\phi^2 + \ldots \tag{7}$$

Analogously to the gas case, the first of the three loci is again branched

$$\phi\{A_2(T, M) + A_3(T, M)\phi + \ldots\} = 0 \tag{8}$$

because either

$$\text{(A)} \qquad \phi = 0, Z = 1/M_n \tag{9}$$

or

$$\text{(B)} \qquad A_2(T, M_n) + A_3(T, M_n)\phi = \ldots = 0, Z = 1/M_n \tag{10}$$

The analog of the Boyle point locus is

$$\text{(C)} \qquad [\partial(-\Delta\mu_0\phi^{-1})/\partial\phi]_T = 0$$

or

$$A_2(T, M_n) + 2A_3(T, M_n)\phi + 3A_4(T, M_n)\phi^2 + \ldots = 0 \tag{11}$$

This is the locus of minima in the usual isothermal osmotic pressure plots of π/ϕ *vs.* ϕ.

Finally, the third locus is the isotherm, for a fixed molecular weight, for which the second virial coefficient is zero

$$\text{(D)} \qquad A_2(T, M_n) = 0 \tag{12}$$

As in the case of a gas, this does not correspond in general to ideal behavior of the solution. Again all three loci have in common the branch point E of the first.

If the Θ point is to be the solution analog of the Boyle point for a gas, then any point on the locus C may be called a Θ point. The term "Θ point" has again been used in the sense of a "point" on the temperature scale. This is better termed Θ temperature, and it is that temperature defined by eq 12.

We understand that Flory prefers to confine the Θ prefix to a use in the limiting case $M_n \rightarrow \infty$. With this we concur and in conclusion we would suggest the following as definitions.

(1) The Θ *temperature* for a polymer–solvent system at a given pressure is that temperature at which the second virial

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[2] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

[3] See, *e.g.*, J. S. Rowlinson, "Encyclopedia of Physics," Vol. 12, Springer-Verlag, Berlin, 1958, p 20.

[4] J. S. Rowlinson, *Trans. Faraday Soc.*, **51**, 1317 (1955).

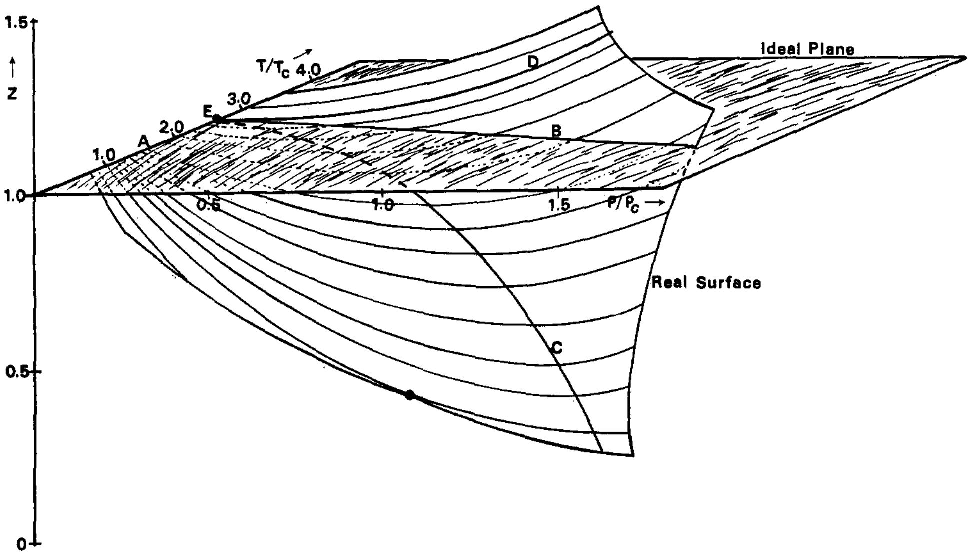

Figure 1. Compressibility factor (Z), reduced temperature, reduced density surface for a real gas, constructed from data given in ref 4.

coefficient is zero in the limit of infinite molecular weight. That is, the temperature T_Θ defined by

$$A_2(T_\Theta, \infty) = 0 \qquad (13)$$

(2) A Θ *point* of a polymer solution at a given pressure is any point on the locus

$$A_2(T, \infty) + 2A_3(T, \infty)\phi + 3A_4(T, \infty)\phi^2 + \ldots = 0 \qquad (14)$$

that is, the locus of minima in isothermal osmotic pressure plots (π/ϕ *vs.* ϕ) for the limit of infinite molecular weight. The only Θ point which occurs at the Θ temperature is then the point E (*cf.* Figure 1) at which $\phi = 0$ and eq 13 and 14 both apply.

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Polymerization of 1,6-Anhydro-2,3,5-tri-*O*-benzyl-α-D-galactofuranose

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Polysaccharides and their derivatives have been of great interest to chemists over the past century because of their abundance in nature as well as their possible important applications in biological, immunological, and medical fields.[1] However, the chemical synthesis of a limited number of high molecular weight stereoregular polysaccharides[2–5] has only recently been successfully carried out. Stereoregular [1→6]-α-D-glycopyranans have been synthesized by cationic polymerization of 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glycopyranoses[2–5] followed by debenzylation with sodium in liquid ammonia. In order to extend the scope of the synthetic method to a new ring system and explore the possibility of chemical synthesis of a stereoregular [1→6]-glycofuranan, we have attempted to polymerize 1,6-anhydro-2,3,5-tri-*O*-benzyl-α-D-galactofuranose.

The monomer, 1,6-anhydro-2,3,5-tri-*O*-benzyl-α-D-galactofuranose, was prepared by conventional benzylation of 1,6-anhydro-2,3,5-tri-*O*-acetyl-α-D-galactofuranose[6] (mp 79–80°, $[\alpha]^{25}\mathrm{D}$ 144.9° [c 1, $CHCl_3$]). The latter was obtained by pyrolysis of D-galactose under reduced pressure (~15 mm), followed by separation of levogalactosan and acetylation. The crude monomer mixture from benzylation was carefully steam distilled, dried, and purified by passing through a neutral alumina column. The structure of the syrupy monomer ($[\alpha]^{25}\mathrm{D}$ +60.7° [c 0.6, $CHCl_3$]) was confirmed by nmr, ir, tlc, and carbon and hydrogen analysis. (*Anal.* Calcd: C, 75.00; H, 6.48. Found: C, 74.93; H 6.58.) The nmr spectrum of the monomer had a singlet at δ 7.33 (15 H, aromatic protons), a doublet at 5.32 (1 H, J = 4.3 cps, anomeric proton) and multiplets in the region of 4.66–3.71 (12 H). The infrared spectrum of the monomer showed no evidence of hydroxyl groups.

Polymerizations of 1,6-anhydro-2,3,5-tri-*O*-benzyl-α-D-galactofuranose were carried out in anhydrous methylene chloride using a high-vacuum technique.[3] Phosphorus pentafluoride and boron trifluoride etherate were used as catalysts. The results are shown in Table I.

Phosphorus pentafluoride did not cause polymerization at −78°, and most of the monomer was recovered unchanged. However, as the temperature of polymerization was increased from −78 to −30°, the yield of polymer (no. 2 and 3) increased. No significant difference in specific rotation between polymers 2 and 3 was observed, since the product from No. 2 might be contaminated with a small amount of monomer. When the polymerization was carried out at 0°, the specific rotation of the product became positive. Boron trifluoride etherate, a Lewis acid catalyst which caused stereospecific polymerization in the 1,6-anhydroglycopyranan series at temperatures from −20 to 25°, failed to polymerize the monomer at 0°.

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