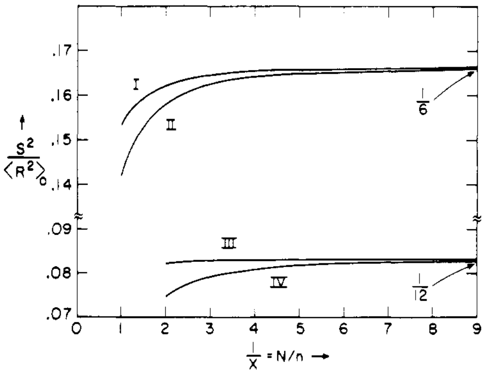

Figure 1. The square ratio of the radius of gyration and the open-chain end-to-end distance as a function of $1/x$. (I and II) radius of gyration for open chains, $2\tau = 1.1$ and $2\tau = 2\nu$, respectively; (III and IV) radius of gyration for rings, $2\tau = 1.025$ and $2\tau = 2\nu$, respectively.

$$\begin{aligned}\langle r_{ij}^2\rangle_r &= |i-j|^{2\tau}\left(1-\frac{|i-j|}{N}\right)n^{2\nu-2\tau} \\ &\qquad |i-j| \le n \\ &= |i-j|\left(1-\frac{|i-j|}{N}\right)n^{2\nu-1} \\ &\qquad |i-j| > n\end{aligned} \tag{4}$$

The result for S_r^2 is

$$\frac{S_r^2}{\langle R^2\rangle_0} = \frac{1}{12} + \left(\frac{1}{2\tau+1} - \frac{1}{2}\right)x^2 + \left(\frac{1}{3} - \frac{1}{2\tau+2}\right)x^3 \tag{5}$$

Other reasonable choices for $\langle r_{ij}^2\rangle_r$ in the region $|i-j| \le n$ are possible, but $S_r^2/\langle R^2\rangle_0$ will only differ by terms of order $(2\tau - 1)x^3$. In particular, note that eq 4 is not symmetric about $(N/2)$ in the region $|i-j| \le n$. We adopt this form rather than the symmetric form which would be obtained by raising the second factor to the (2τ) power for the following three reasons. First, the present form is continuous at $|i-j| = n$. Second, for $x < 1/2$, the two arcs of the ring $|i-j|$ and $[N - |i-j|]$ have different lengths relative to n when $|i-j| \le n$ and accordingly will feel the influence of excluded volume differently. Finally, the only discrepancy arises near $x = 1/2$ where a symmetric form would be preferred, but this is where the form for $|i-j| > n$ is questionable. As indicated, a change in functional form has only a minor effect on the numerical values presented below.

The value of τ may be chosen in a variety of ways, e.g., to match the enumeration results of Rapaport[6] for the dilute case $x = 1/2$. This leads to $2\tau = 1.025$. In Figure 1 the ratio $S_r^2/\langle R^2\rangle_0$ is plotted vs. $1/x$ for the choices $2\tau = 1.025$ and $2\tau = 2\nu = 6/5$. We see that the concentration dependence for $2\tau = 1.025$ is much less than that exhibited for the choice $\tau = \nu$. However, the uncertainty in Rapaport's enumeration work does not exclude values of 2τ which are larger, up to about $2\tau = 1.1$.

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Huggins Coefficients in Heterodisperse Solutions of Macromolecules

F. A. H. PEETERS and A. J. STAVERMAN*

Gorlaeus Laboratoria, Rijksuniversiteit Leiden,
Leiden, The Netherlands. *Received April 27, 1977*

In 1942 Huggins[1] proposed the following expression for the viscosity of a solution of macromolecules

$$\eta = \eta_0(1 + [\eta]c + K[\eta]^2c^2) \tag{1a}$$

where η and η_0 are the viscosities of the solution and the solvent, respectively, c is the mass concentration of the solute,

$$[\eta] = \lim_{c\to 0}\frac{\eta - \eta_0}{\eta_0 c}$$

is the intrinsic viscosity of the solute, and K is the Huggins coefficient. Equation 1a is more than a formal expansion of η with respect to c. By the introduction of the factor $[\eta]^2$ in the coefficient of c^2, the remaining Huggins coefficient may be expected to provide information about the interactions between the macromolecules.

This can be seen from considering Einstein's equation for the viscosity of a solution of hard spheres. The viscosity depends on the volume fraction ϕ only

$$\eta = \eta_0(1 + 2.5\phi + k\phi^2) \tag{1b}$$

Since k in (1b) can be calculated for hard spheres and the volume of the macromolecule is expressed by $[\eta]$, the effect of introducing the factor $[\eta]^2$ in the coefficient of c^2 in eq 1b is to obtain a Huggins coefficient K which can be compared with a theoretical value for hard spheres. Since the second-order terms in both (1a) and (1b) represent the interactions between the solute molecules, comparison between the experimental Huggins coefficients and those calculated for hard spheres gives not only an insight in the hydrodynamic interaction between the macromolecules, that is in the "hardness" and the interpenetration of the spheres, but reveals also the occurrence of specific thermodynamic interactions, if the latter are present.

Experimentally Huggins coefficients have been determined for many different polymer–solvent systems. In solutions without strong association the values range from 0.5 to 0.7 and are nearly independent of molecular weight. They depend on the branching and the stiffness of the macromolecules and are sensitive to specific interactions.

Theoretical calculations of k and K yield different results. For random coil polymers under theta conditions the result of the calculations depends strongly on the models used for the interpenetration of the macromolecules, the draining, and the segment distribution. Besides, for hard spheres the effect of the correlation between the positions of the particles in a shear field gives rise to different results.

Some results compiled from the literature are given in Table I.

For hard spheres the calculations of Peterson and Fixman appear the most reliable; for deformable and interpenetrable coils the results of Sakai can be used with some confidence.

For a dilute ternary system we can write in analogy to (1)

$$\eta = \eta_0\{1 + [\eta]_1c_1 + [\eta]_2c_2 + K_1[\eta]_1^2c_1^2 + K_2[\eta]_2^2c_2^2 + 2K_{12}[\eta]_1[\eta]_2c_1c_2\} \tag{2}$$

where the symbols need no explanation. The coefficient K_{12} is often[12–16] called the "interaction coefficient", but incorrectly.

If we call the total polymer concentration c and the intrinsic viscosity of the mixture $[\eta]_m$ we have

$$c = c_1 + c_2; \quad [\eta]_m c = [\eta]_1c_1 + [\eta]_2c_2, \tag{3a}$$

Table I
Theoretical Huggins Coefficients for Binary Solutions

Author(s)	Hard spheres	Theta solutions
Riseman and Ullman[2]		0.6
Vand[3]	0.6438	
Saito[4]		0.4; 0.6; 1.0
Brinkman[5]	0.76	
Yamakawa[6]		0.5
Peterson and Fixman[7]	0.6909	0.894
Sakai[8]		0.523
Batchelor and Green[9]	1.22	
Freed and Edwards[10]		0.7574
Felderhof[11]	0.400	

and

$$K_m{}^{id}[\eta]_m{}^2c^2 = K_1[\eta]_1{}^2c_1{}^2 + K_2[\eta]_2{}^2c_2{}^2 + 2(K_1K_2)^{1/2}\cdot[\eta]_1[\eta]_2c_1c_2 \quad (3b)$$

where $K_m{}^{id}$ is defined[12] as "the ideal Huggins coefficient" or the Huggins coefficient for ideal mixtures, which turns (2) into

$$\eta = \eta_0\{1 + [\eta]_mc + (K_m{}^{id} + \delta)[\eta]_m{}^2c^2\} \quad (4a)$$

with

$$\delta[\eta]_m{}^2c^2 = 2c_1c_2[\eta]_1[\eta]_2\{K_{12} - (K_1K_2)^{1/2}\} \quad (4b)$$

The experimental Huggins coefficient is then $K_m{}^{exptl} = K_m{}^{id} + \delta$. In ideal[12] mixtures $\delta = 0$ and $K_{12} = (K_1K_2)^{1/2}$ Budtov et al.[16] give a somewhat more restricted definition of such solutions.

Expressed in volume fractions the equation for the viscosity of the ternary solution becomes

$$\eta = \eta_0\{1 + 2.5(\phi_1 + \phi_2) + k_1\phi_1{}^2 + k_2\phi_2{}^2 + 2k_{12}\phi_1\phi_2\} \quad (5)$$

Again we call the solution "ideal" in case $k_{12} = (k_1k_2)^{1/2}$. In that case the viscosity increment by the solute depends on the total volume fraction only and the contribution of the hydrodynamic interaction to this increment is considered to be additive.

Starting from the hard-sphere model of Peterson and Fixman we have calculated the coefficients k_1, k_2, and k_{12} in order to investigate to what extent mixtures of hard spheres may be expected theoretically to behave as ideal mixtures.

The following assumptions have been made: (1) applicability of the linearized Navier-Stokes equation; (2) incompressibility of the liquid; (3) absence of slip along the surface of the spheres; (4) at large distances from the spheres the perturbations of velocity and pressure caused by the spheres vanish; (5) the spheres are large enough to allow the liquid to be considered as a continuum and the Brownian movement to be neglected; (6) gradients of velocity are constant over distances of the order of sphere diameter; (7) the spheres are distributed at random in space; (8) collisions and associations are neglected.

Especially the assumptions 5 to 8 deserve scrutiny.

Since for hard spheres k does not depend on the size of them we find using this model the same value for k_1 and k_2. The calculation yields $k_1 = k_2 = 4.3178$, a result already found by Peterson and Fixman.

Extending their procedure to mixtures of spheres of different size we have calculated k_{12}. Details of the calculations will be published elsewhere. Here we give the results. It is found that k_{12} contains a term depending on ϵ, the ratio of the radii.

We can rewrite (5)

$$\eta = \eta_0\{1 + 2.5\phi + 4.3178\phi^2\} + \eta_0\Lambda(\epsilon)\phi_1\phi_2 \quad (6a)$$

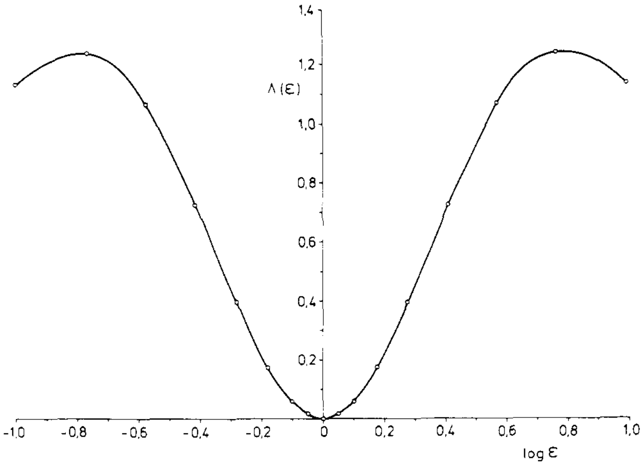

Figure 1.

or more shortly

$$\eta = \eta(\phi) + \eta^E \quad (6b)$$

where η^E is the excess viscosity increment due to the heterogeneity of the solute.

$$\eta^E = \eta_0\Lambda(\epsilon)\phi_1\phi_2$$

η^E represents the nonadditive part of the viscosity increment. The function $\Lambda(\epsilon)$ was calculated for a number of ϵ values (see Figure 1). Obviously for $\epsilon = 1$, $\Lambda(\epsilon) = 0$, since in that case the viscosity must be additive. For $\epsilon \neq 1$, $\Lambda(1/\epsilon) = \Lambda(\epsilon) > 0$ and passes through a maximum of about 1.25 at $\epsilon = 6$. For large values of ϵ the results become less reliable on account of the limitations of the model in question. For $\phi_1 = \phi_2$ the contribution of η^E to η reaches a maximum and attains a value of over 7% of the term in ϕ^2 for $\epsilon = 6$. Such an effect should be measurable. Although a number of experimental Huggins coefficients in ternary macromolecular solutions have been reported in the literature,[12–16] the requirements that the solute components be homologous and the solution at theta temperature are not always fulfilled. The accuracy claimed by Budtov et al.,[16] who observe ideal behavior in a single case, is insufficient to check our eq 6.

In order to allow comparison with experimental quantities for mixtures of homologous macromolecules in solution we write (6a) in the form (4a) and find at the theta temperature, where the effective radius is proportional to the square-rooted molecular weight and also to the intrinsic viscosity, with $c_1 = \lambda c$ and $c_2 = (1 - \lambda)c$ $(0 \leq \lambda \leq 1)$, using (3a) and remembering that in the hard-sphere model $2.5\phi_i = [\eta]_ic_i$

$$\delta = \frac{\Lambda(\epsilon)}{6.25}\frac{\lambda(1-\lambda)\epsilon}{\{1 + (\epsilon - 1)\lambda\}^2} \quad (7)$$

with

$$\epsilon = [\eta]_1/[\eta]_2$$

The dispersion effect is a maximum for $\lambda = 1/(\epsilon + 1)$.

Conclusion

From a theoretical calculation of the Huggins coefficient for mixtures of hard spheres of different size it follows that deviations from additivity up to 7% of the coefficient may be expected on purely hydrodynamic grounds.

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On Polymer Mixture Thermodynamics†

R. KONINGSVELD*[1a] and R. F. T. STEPTO[1b]

Central Laboratory, DMS, Geleen, The Netherlands, and the Department of Polymer and Fibre Science, UMIST, Manchester, UK.

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The object of this note is to draw attention to an important relationship which exists between certain parameters in two different considerations of the entropy change involved in the mixing of two polymers. On one hand, we extend Silberberg's treatment of polymer solutions[2] which yields the original Flory–Huggins[3,4] entropy of mixing expression upon the introduction of a simplifying assumption. Second, we consider Huggins' recent refinement of the theory which deals with entropy changes involved in the variation of the immediate surroundings of a polymer segment when the composition of the solution is changed.[5–7]

Extending Silberberg's treatment to a mixture of two polymolecular homopolymers 1 and 2 we can write for the total number of configurations Ω_{1+2}:

$$\Omega_{1+2} = \frac{\left(\sum_i N_{1i}m_{1i} + \sum_j N_{2j}m_{2j}\right)!}{\prod_i (\mathrm{N}_{1i}!) \prod_j (\mathrm{N}_{2j}!)} \times \prod_i (V_{1i}{*}(\phi_1)/V)^{N_{1i}(m_{1i}-1)} \prod_j (V_{2j}{*}(\phi_2)/V)^{N_{2j}(m_{2j}-1)} \qquad (1)$$

where N_{1i} and N_{2j} are the numbers of molecules of species i in polymer 1 and species j in polymer 2. The relative chain lengths m_{1i} and m_{2j} are measured in arbitrary units; with polymer solutions the size of the solvent molecules usually serves as a yard stick. The "parametric" volume V^* was introduced by Silberberg to correct for the gross overestimation of the number of configurations involved in the term containing the factorials. Once the first segment of a polymer chain is placed somewhere in the total volume V, the volume available to any of the next $(m - 1)$ segments is restricted to a parametric volume V^* surrounding the preceding segment. Silberberg shows that assuming V^* to be independent of the composition of the mixture leads to an entropy of mixing expression identical with the original Flory–Huggins equation.[2]

We prefer to retain a possible concentration dependence and derive the free enthalpy (Gibbs free energy) of mixing ΔG_ϕ per mole of polymer segments in the usual way, adding to the entropy terms a Van Laar-type heat of mixing, $g\phi_1\phi_2$:

$$\Delta G_\phi/RT = \sum_i \phi_{1i}m_{1i}^{-1} \ln \phi_{1i} + \sum_j \phi_{2j}m_{2j}^{-1} \ln \phi_{2j} + g\phi_1\phi_2 - \sum_i \phi_{1i}(1 - m_{1i}^{-1}) \ln \tau_{1i} - \sum_j \phi_{2j}(1 - m_{2j}^{-1}) \ln \tau_{2\mathrm{j}} \qquad (2)$$

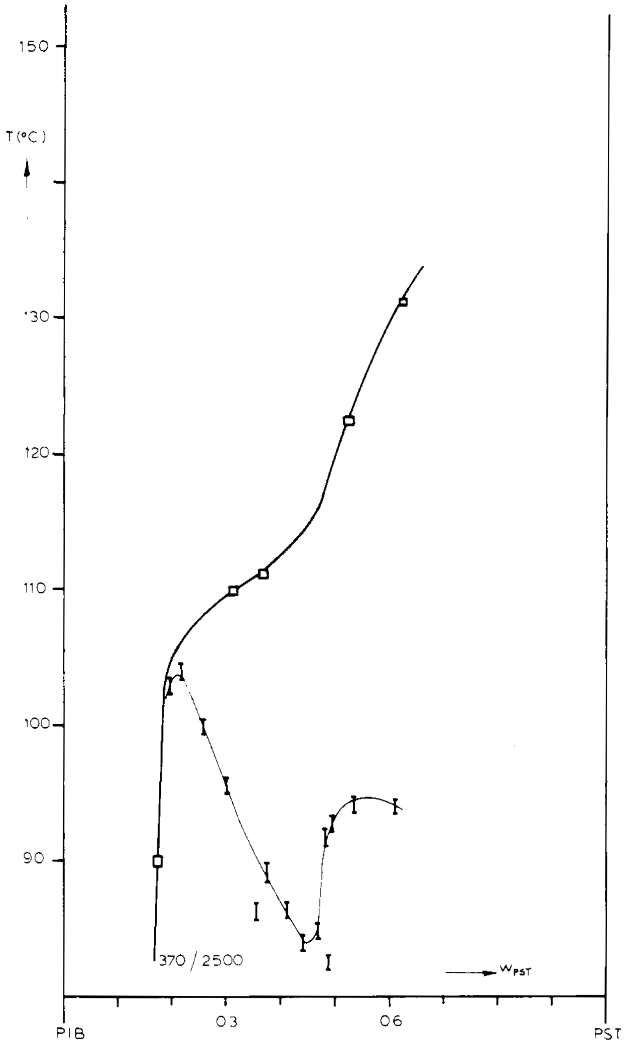

Figure 1. Cloud-point curve (□) and spinodal (by pulse induced critical scattering[14,15]) (I) for a polyisobutylene/polystyrene system (molecular weights indicated); w_{pst} is the weight fraction of polystyrene.

where ϕ denotes a volume fraction ($\Sigma_l\phi_{kl} = \phi_k$, the volume fraction of whole polymer k), τ_{kl} stands for $V_{kl}{*}\,(\phi_k)/V_{kl}{*}\,(1)$, and RT has its usual meaning. Silberberg's simplifying assumption ($\tau_{kl} = 1$) reduces eq 2 to the original Flory–Huggins expression for a mixture of two polymolecular polymers (the first three terms on the rhs).

For reasons outlined below it seems useful to compare eq 2 with Huggins' more recent expressions[5–7] in which he, like Flory et al.,[8–10] introduces the interacting surfaces of the segments. It is thus possible to allow for a disparity between the interacting surfaces (volumes) of segments 1 and 2. This considerably relaxes the rigidity of the original lattice model (one and the same coordination number for both types of segment), and, i.e., appears to accommodate the experimentally well-known concentration dependence of the interaction parameter g.[11] Huggins' considerations[5,6] lead to an expression for g which, for random mixing, reads

$$g = \beta\,[1 - (1 - \rho)\phi_2]^{-1} = \beta Q^{-1} \qquad (3)$$

Here, $\rho = (\sigma_2/\sigma_1)/(v_2/v_1)$, with σ_k and v_k the contact area and molecular volume, respectively, of the segments of polymer k, and $\beta = \sigma_2\Delta\epsilon/2RT$, with $\Delta\epsilon$ = the interchange energy (cf. ref 5 and 6). Equation 3 is used below for relating g to T when

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† Dedicated to Dr. Maurice L. Huggins on the occasion of his 80th birthday.