If $\beta\varphi$ is much smaller than f_0 (although β may be comparable to f_0[11]), then eq 3 is reduced to the familiar exponential form

$$D/D_0 \cong \exp(B\beta\varphi/f_0^2) \cong \exp(ac) \qquad (5)$$

We now examine the condition which may lead to the linear dependence of D on concentration. It is perhaps worthwhile to recall that the exponential term, $\exp(-B/f)$, in eq 1 is derived from counting the number of ways of redistributing the free volume packets within the system. As long as we utilize the concept of large-scale redistribution of free volume and allow f to change with φ, the final equation for D/D_0 will always contain an exponential term of φ or its related functions. However, if we begin with the mechanism of type-A Fickian diffusion, *i.e.*, localized, activated jumps into neighboring preexisting cavities, the jump frequency is simply proportional to the number of the preexisting cavities. If we further assume that the cavity size increases linearly with φ, with the same proportional constant applicable to all cavities, then the size distribution function (see the figure in ref 8) simply shifts linearly toward larger sizes. The number of cavities larger than a certain critical size will increase linearly with φ for small values of φ, and so will the diffusion coefficient.

In conclusion, the diffusion of organic molecules in oriented crystalline polymers affords a useful tool for understanding the state of the amorphous segments. We have also uncovered a case where the diffusion coefficient increases linearly with concentration. It is believed that this type of concentration dependence has not been reported previously.

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Gas Chromatographic Determination of Thermodynamic Properties of Polymer Solutions

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ABSTRACT: The gas chromatographic technique of elution on a concentration plateau of solvent in a carrier gas, reported by Conder and Purnell, is used to determine the solubility isotherms of selected hydrocarbons in amorphous polymers. This technique, adapted for the first time to a polymeric stationary phase, permits the calculation of vapor–polymer equilibrium ratios and polymer–solvent interaction parameters over a wide range of composition, including pure polymer. The following results are reported for polystyrene in benzene at 120°, K (equilibrium ratio in pure polymer) = 4.92 and χ (interaction parameter) = 0.325; for high-density polyethylene in n-decane at 185°, K = 3.94 and χ = 0.12.

In a recent note,[2] Patterson, *et al.*, discuss the use of gas chromatography (gc) data to calculate the thermodynamic properties of polymer–solvent systems, and they derive equations for calculating the activity coefficient, the activity coefficient rationalized by weight fraction, and the interaction parameter. Because of the assumptions they use, their equations and procedure are valid only for systems containing an infinitesimal amount of the low molecular weight solvent. We have now found that a gc apparatus can be employed to measure the thermodynamic properties of polymer solutions with up to about 50 vol % solvent in the carrier gas.

The technique used is based on theoretical relationships that were developed by Conder and Purnell[3] and then used by them to calculate activity coefficients for such low molecular weight systems as n-hexane in squalane and n-heptane in di-n-nonyl phthalate at gas concentrations ranging from zero to 70 mol %.[4]

The key relationship is between the measured gc variables and the solubility of the volatile component per unit mass of polymer in the stationary phase[5]

$$q(P) = \frac{1}{V_1}\int_0^{y_0} j\,\frac{(V_R - V_M)}{1 - \psi}\,dc \qquad (1)$$

where q is the solubility in moles per gram at the mean column pressure P in atmospheres, j is a correction for gas compressibility, and V_1 is the mass of the stationary polymer phase in grams. The difference between retention volumes of the solvent and air, $V_R - V_M$, is corrected for ψ, the mole fraction of solvent in the gas above the polymer, and then is integrated over the solvent concentration c in the gas up to a value determined by y_0, the mole fraction composition of the carrier gas at the outlet. Equation 1 defines a solubility isotherm and provides the basic information for calculating the vapor–polymer equilibrium ratio and the interaction parameter over a range of composition. The experimental apparatus and procedure will be described in a separate publication.[6]

One equilibrium ratio commonly used in work with polymers is the following

$$K = \frac{P_2}{P_2^0 w_2} = \frac{P\psi}{P_2^0 w_2} \qquad (2)$$

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[1] (a) Amoco Chemicals; (b) Standard Oil Co.

[2] D. Patterson, Y. B. Tewari, H. P. Schreiber, and J. E. Guillet, *Macromolecules*, 4, 356 (1971).

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where P_2^0 is the vapor pressure of pure solvent at the column temperature and P_2 is its partial pressure above the polymer. The weight fraction of solvent in the polymer phase is

$$w_2 = \frac{qM_2}{1 + qM_2} \tag{3}$$

where M_2 is the solvent molecular weight. Since the activity a_2 is P_2/P_2^0, K is identical with a_2/w_2, the activity coefficient rationalized by weight fraction. This definition of K obviates the need to know the polymer molecular weight and has other advantages discussed by Patterson, *et al.*[2]

With the application of eq 1–3, the gc apparatus need not be operated only at infinite dilution. The solvent can be eluted on a concentration plateau of the same solvent added to the carrier gas, as described by Conder and Purnell.[5,7] The polymer coating on the solid support must be uniform and thin enough so that phase equilibrium is achieved as elution proceeds.[6] Either absorption on the support must be negligible or a suitable correction must be made. Finally, dispersion of the elution peaks will generally require a small correction to the retention time measured at peak maximum. With these precautions, the data will be representative of equilibrium conditions. This ability to acquire thermodynamic data over a range of solution compositions permits a much more exacting test of any solution theory such as the Flory–Huggins,[8] the Maron,[9] or the free volume[10] theories. Specifically, the polymer–solvent interaction parameter χ is one of the important variables in each of these theories which can be calculated as a function of composition from the K values. Only data covering a range of composition can reveal the functional form of χ.

The Flory–Huggins equation is usually used to define χ

$$\ln a_2 = \ln \phi_2 + \phi_1 + \chi\phi_1^2 \tag{4}$$

where ϕ_2 is the volume fraction of solvent and ϕ_1 is the volume fraction of polymer in the solution. Equation 4 can be converted to the equilibrium ratio by dividing a_2 by the weight fraction

$$w_2 = \frac{\phi_2}{\phi_1/r + \phi_2} \tag{5}$$

where r is the ratio of the specific volume of the polymer to that of the solvent, v_1/v_2, at the column operating temperature. The resulting equation

$$\ln K = \ln [\phi_1/r + \phi_2] + \phi_1 + \chi\phi_1^2 \tag{6}$$

has proven to be extremely useful in correlating K *vs.* ϕ_1 provided χ is known. In the limit of pure polymer ($\phi_2 = 0$), eq 6 reduces to

$$\ln K = -\ln r + 1 + \chi \tag{7}$$

Note that for athermal solutions ($\chi = 0$) K will reduce to the natural logarithm base of 2.72 at $\phi_2 = 0$ only if $r = 1$, the special case derived by Littlewood.[11] Although Littlewood assumes that the solute and solvent molecules are of different size, nothing is stated about their specific volumes.

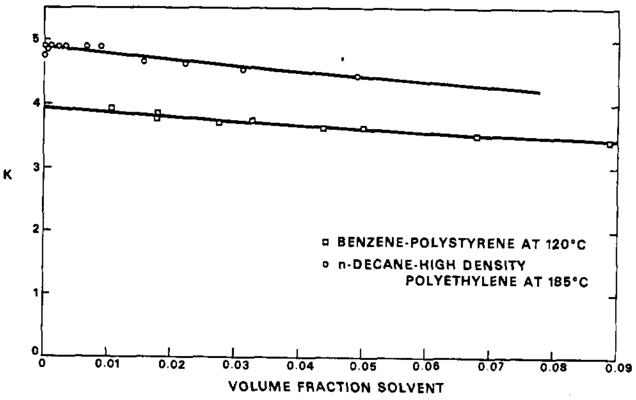

Figure 1. Vapor–polymer equilibrium ratios as a function of composition.

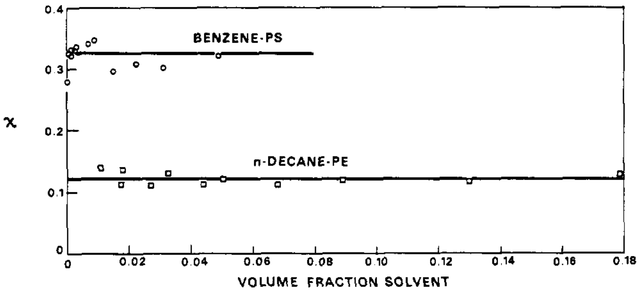

Figure 2. Interaction parameters as a function of composition.

The gc data were used to compute K as a function of composition (using eq 2) for two amorphous polymer systems: benzene in polystyrene at 120°, with a maximum of 0.49 mol fraction of benzene in the carrier gas, and *n*-decane in high-density polyethylene at 185°, with a maximum of 0.47 mol fraction of decane in the carrier gas. The K values computed from the experimental data are shown as points on Figure 1. Note that although the carrier plateau concentration is 50%, the solvent volume fraction is only 0.05 for benzene. This gas composition is close to the operating limit of the present apparatus.

The value of χ was calculated for each composition point in the present study by rearranging eq 6 to solve for χ.

$$\chi = \left[\ln\left[\frac{K}{\phi_1/r + \phi_2}\right] - \phi_1\right]\phi_1^{-2} \tag{8}$$

Equation 8 is a counterpart to eq 12 of Patterson, *et al.*,[2] with one important difference: it is not limited to infinite dilution. The χ values computed from the experimental data are shown for both polymer systems in Figure 2. The decane–polyethylene system has no trend in χ values, with an average of 0.12. Although the data precision is ±0.02, the accuracy is limited to ±0.05 by the procedures used. Patterson, *et al.*,[2] report a χ of 0.18 ± 0.05 for *n*-decane in linear polyethylene, which is an average value over the temperature range 145–190°, and limited to infinite dilution. Since the χ calculation includes the subtraction of two terms of the order of unity, the discrepancy between their value and ours may not be significant. Furthermore, some variation of χ is likely with temperature.

The χ value for the benzene–polystyrene system is well represented by a constant, 0.325. The first eight data points indicate an increase in χ from 0.28 to 0.35 as the first 1% of

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benzene is added. We are hesitant to attach significance to this, because it is barely greater than the experimental precision. However, other investigators have noticed a similar phenomenon at infinite dilution using gc[12] or at very low solvent fraction using a McBain balance.[13] The value of 0.325 is consistent with what is normal for a nonpolar system at these conditions.

Finally, the parameters following for each system were used in eq 6 to compute the K curves shown in Figure 1: benzene–polystyrene, $r = 0.768$, $\chi = 0.325$; n-decane–high-density polyethylene, $r = 0.785$, $\chi = 0.12$. The utility of correlating these amorphous systems by eq 6 is apparent.

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Molecular Weight Distribution of Synthetic Stereoregular Polysaccharides. I. Method of Sedimentation Velocity

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ABSTRACT: The applicability of the sedimentation velocity method for the determination of molecular weight distributions of synthetic, stereoregular tribenzyl glucans was investigated. Moderate to severe dependencies on pressure and concentrations, accompanied by diffusion, were observed with two polymers of low to medium polydispersity. The corrections for these effects were applied in a sequential manner, treating each effect independently from others. Polydispersities obtained from the corrected sedimentation coefficient distributions compared favorably with polydispersities obtained by independent methods.

The synthesis of stereoregular linear α-1,6-linked polysaccharides is under detailed investigation at this laboratory.[1–10] These studies have created a need for a relatively rapid and reliable method for the characterization of molecular weight distributions of the polymers. The requirements of the method include applicability to both the water-soluble parent polysaccharides and their derivatives soluble only in organic solvents, to molecular weight distributions of both narrow as well as moderate polydispersity, and to solutions not at their Θ temperature. Of a number of possible experimental techniques available for this purpose, the method of sedimentation velocity was investigated first. The latter technique has been used in the characterization of a number of synthetic polymers with apparent success, especially with polymers of narrow polydispersity and under Θ conditions.[11–16] In addition, the theory of sedimentation velocity is well understood.[17]

In the following, we report on the application of the sedimentation velocity method to two different high molecular weight tribenzyl derivatives of α-1,6-glucan, one of relatively narrow and the other of moderate polydispersity.

Theory

A system which is heterogeneous with respect to mass yields under the conditions of a sedimentation transport experiment a distribution of sedimentation coefficients. The sedimentation coefficient, S, which is defined

$$S = (\mathrm{d}r/\mathrm{d}t)(1/\omega^2 r) \tag{1}$$

is related to the mass of the molecule, m, by

$$S = m(1 - \bar{v}\rho)/f \tag{2}$$

where r is the distance from the center of revolution to a specified point in the ultracentrifuge cell, t is the time from the start of sedimentation, ω is the angular velocity of revolution, $\bar{v}$ is the partial specific volume of the molecule, f is its frictional coefficient, and ρ is the density of the solvent.

In general, for a polydisperse material, we can write that the fraction of material with sedimentation coefficient between S and $S + \mathrm{d}S$ is $g(S)\mathrm{d}S$. If for the present we neglect the effects of concentration, diffusion, and pressure, it is easily shown that the distribution of material with different S in a sector-shaped ultracentrifuge cell is given by

$$g(S) = \frac{1}{c_0}\frac{\mathrm{d}c_0}{\mathrm{d}S} = \frac{1}{c_0}\left(\frac{\mathrm{d}c}{\mathrm{d}r}\right)\left(\frac{r}{r_0}\right)^2 r\omega^2 t \tag{3}$$

where c is concentration, c_0 is the initial concentration, and r_0 is the position of the meniscus.[18] When Schlieren optics are

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