local physical processes involved in permeation. If the diffusion coefficient is a continuous function of concentration, the steady state flux is given by Fick's law

$$J = -D(c)\frac{\mathrm{d}c}{\mathrm{d}x} \tag{1}$$

where J is the flux, with respect to the local mass average velocity, $D(c)$ is the local diffusion coefficient, c is the local concentration of permeant, and x is the distance across the membrane. If there are no reactions within the membrane and if the concentration of permeant within the membrane is low, as is usually the case, bulk flow is negligible and J is then also the flux with respect to stationary coordinates. The permeability coefficient is now defined by eq 2, and is seen to be a function of both upstream and downstream pressures

$$P = \frac{Jt}{\Delta p} = \frac{1}{(p_1 - p_2)}\int_{c_2}^{c_1} D\,\mathrm{d}c \tag{2}$$

where P is the permeability coefficient and p_1, p_2 are the upstream and downstream pressures on the membrane, respectively. Normally P is measured at several upstream pressures with a constant, often zero, downstream pressure p^*, and then P can be calculated for any pair of upstream and downstream pressures greater than p^* by the use of eq 3. The permeability coefficient

$$P(p_1, p_2) = \frac{P(p_1, p^*)[p_1 - p^*] - P(p_2, p^*)[p_2 - p^*]}{p_1 - p_2} \tag{3}$$

is thus easy to measure and expresses flux in the most natural physical variable, pressure. Equation 3, however, arises from the fact that the flux is continuously dependent on concentration within the membrane rather than from the definition of the permeability coefficient. Furthermore the natural physical variable within the membrane is concentration, and its local variation, together with the local diffusion coefficient, best describe the local flux. The permeability coefficient, being an over-all coefficient, cannot be used to describe local behavior, nor can it be used in unsteady-state situations. It would be convenient under certain situations to substitute for the permeability coefficient a function of the local concentration, as locally relevant as the diffusion coefficient, yet as convenient as the permeability coefficient.

Suppose the solubility is expressed as a function of pressure by eq 4 where S is continuous and single valued. Transforming eq 1 into the new variable p by

$$C = pS(p) \tag{4}$$

formal use of eq 4, we obtain an alternative formulation of Fick's law (eq 5). The function of pressure defined

$$J = -D(p)\frac{\partial}{\partial p}(pS(p))\frac{\mathrm{d}p}{\mathrm{d}x} \tag{5}$$

by eq 6 is similar to the diffusion coefficient but is

$$\mathrm{F}(p) \equiv D(p)\frac{\partial}{\partial p}(pS(p)) \tag{6}$$

expressed in a variable which is numerically equal to the upstream and downstream pressures at the edges of the membrane, while within the membrane it may be conveniently regarded as a transformed concentration rather than pressure. A local description of the flux, which applies whenever Fick's law is valid, may then be written as

$$J = -\mathrm{F}(p)\frac{\mathrm{d}p}{\mathrm{d}x} \tag{7}$$

For steady-state permeation between p_1 and p_2 the flux can be obtained from F by simply integrating eq 7 across the membrane.

$$-J(p_1, p_2) = \frac{1}{t}\int_{p_1}^{p_2}\mathrm{F}(p)\,\mathrm{d}p \tag{8}$$

Obviously this function is an alternative to the permeability coefficient and has the conceptual advantage of being a local rather than an over-all quantity. It can be calculated from measurements of steady-state flux with varying upstream pressure and constant downstream pressure, such as are made to calculate the permeability coefficient.

$$t\left(\frac{\partial J(p_1, p_2)}{\partial p_1}\right)_{p_2} = \mathrm{F}(p)|_{p=p_1} = D(p)\frac{\partial}{\partial p}(S(p)p)|_{p=p_1} \tag{9}$$

The function F is thus tabulated as a function of p_1 while the value of p_2 is unimportant as long as it is constant. If it is found that p_2 influences the calculated value of F, either Fick's law is invalid under the experimental conditions used, or else the flux varies throughout the membrane. The latter situation can arise under steady-state conditions if there are reactions taking place within the membrane. Under no other conditions would the value of p_2 influence F. The permeability function F is thus a clear representation of local transport conditions within the membrane. The efforts of some authors to express the permeability coefficient as an empirical function of a single pressure or pressure difference indicate a need for a more truly local function such as F.[1,2] The permeability function and permeability coefficient are identical when there is ideal behavior.

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Anomalous Light Scattering by Poly(4-vinylpyridine) in Nitromethane

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In the course of work with aggregates of chlorophyll derivatives with poly(4-vinylpyridine),[1] we attempted to measure the molecular weight and the radius of gyration of polymer samples in nitromethane by the light-scattering method. The attempt was frustrated by the existence of an anomaly in the dissymmetry of the scattered light which made impossible the determination of either property. The anomaly was that a greater amount of light was scattered in a backward direction than at

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the supplementary angle in the forward direction. The curves of constant concentration on the Zimm plot consequently had a negative slope, implying an apparent negative Z-average radius squared of gyration.

There are a number of reasons for believing that the anomaly is real, and not an artifact of the instrumentation or the procedure.

The anomaly was found with nitromethane as solvent, but not with ethanol, even though the same polymer sample was used and the same apparatus (a Brice–Phoenix light scattering photometer with a cylindrical cell supplied by the manufacturer). The normal-appearing Zimm plot for a polymer fraction in absolute ethanol is shown in Figure 1, and the abnormal Zimm plot for the same polymer in nitromethane is shown in Figure 2. Solutions of poly(4-vinylpyridine) in nitromethane exhibit some instability, perhaps due to oxidation or to photolysis of the solvent, and cannot be diluted and refiltered indefinitely. The solutions of each concentration shown in Figure 2 were prepared separately from dry polymer and distilled nitromethane. Refractive index increments $\Delta n/\Delta c$, determined for the three solutions separately, were 0.180, 0.159, and 0.152 ml/g at 0.60, 0.40, and 0.20 g/dl, respectively.

The four samples of polymers and polymer fractions examined in nitromethane gave Zimm plots with anomalies in the dissymmetry similar to that of Figure 2. Three of these, and several other polymer samples, gave normal appearing Zimm plots in ethanol, from which molecular weights, radii of gyration, and virial coefficients were calculated.

The anomalous dissymmetry did not reside in the instrument. The amount of light scattered from a nitromethane blank, like that from an ethanol blank, was small, and symmetrical about 90°. The fluorescence of a dilute solution of quinine, excited by 365-nm light, was perfectly symmetrical about 90°. A solution of Ludox showed a small dissymmetry, with greater scattering in the forward direction.

It was not possible to associate the anomaly with the presence of particles. Refiltration of a solution through an ultrafine filter had almost no effect on the intensity or the dissymmetry of the scattered light.

Scattering was usually excited with the 436-nm blue line of Hg. If the exciting light were partly absorbed, more light might escape the cell in the backward direction than in the forward. However, the solution was transparent to 436-nm light, and the amount of 405-nm light in the exciting beam was found to be inconsequential. Furthermore, the same anomaly was seen with the green Hg line (546 nm) as with the blue.

In the determination of the intrinsic viscosity of poly(2-vinylpyridine) in nitroalkanes, curves of reduced viscosity *vs.* concentration characteristic of polyelectrolytes have been reported.[2,3] We determined the intrinsic viscosity of many samples of poly(4-vinylpyridine) in nitromethane as well as in ethanol, and usually found the reduced viscosity curves to be normal for nonelectrolytes. Any viscometric evidence of partial ionization of the polymer could be eliminated by repurification of the nitromethane. The intrinsic viscosity of a polymer sample in nitromethane was about one-half the intrinsic viscosity in ethanol. As a further guard against ionization of the polymer, a drop of concentrated ammonia was added to each of the solutions for light scattering of Figures 1 and 2.[4,5]

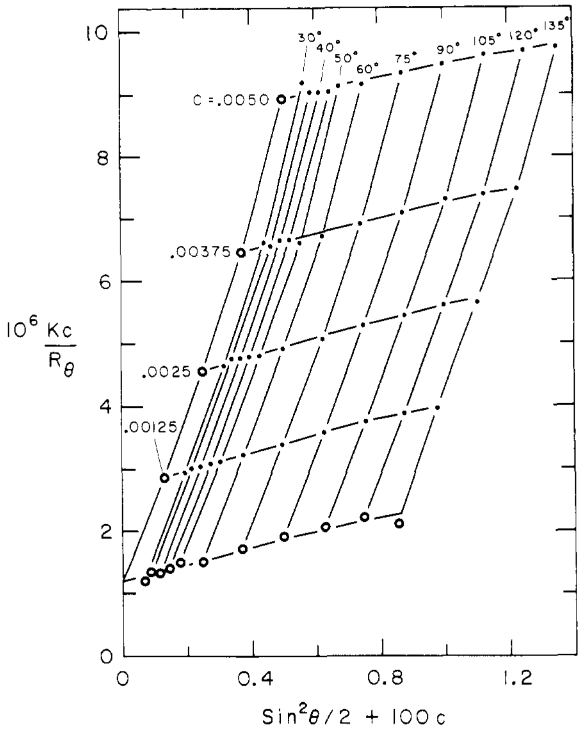

Figure 1. Zimm plot for a poly(4-vinylpyridine) fraction (M_w = 870,000) in absolute ethanol. Ammonia added to suppress ionization. Concentrations (c) in grams per milliliter.

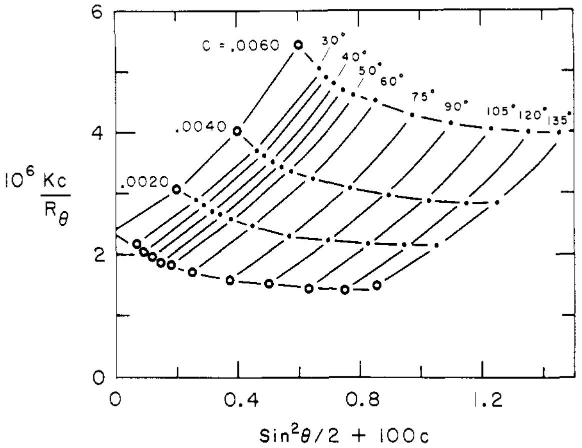

Figure 2. Zimm plot of poly(vinylpyridine) fraction of Figure 1 in nitromethane. Ammonia added to suppress ionization. Concentrations (c) in grams per milliliter.

There have been reports of negative limiting slopes of the constant concentration curves in Zimm plots for poly(vinylpyridines),[5,6] poly(acrylonitrile),[7] gelatin,[8] and

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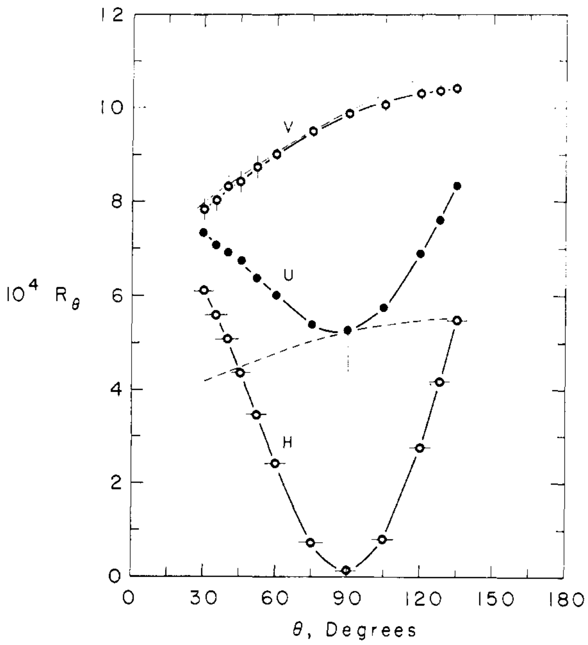

Figure 3. Angular dependence of reduced scattering ratios R_θ for poly(vinylpyridine), 0.479 g/dl in nitromethane, excited with unpolarized (*U*), vertically (*V*), and horizontally (*H*) polarized light. Upper and lower dashed curves are *H* and *U* corrected for geometrical dependence on angle, *viz.*, $[H - H(90°)]/\cos^2\theta$ and $U/(1 + \cos^2\theta)$.

a polyampholyte based on methacrylate.[9] Arichi[5] has shown a Zimm plot with anomalous dissymmetry very much like ours (Figure 2) for poly(2-vinylpyridine) in methanol. However, the anomaly was connected with an ionized form of the polymer, because it was suppressed by ammonia.

Ehrlich and Doty[9] tried to explain their results as the consequence of a particular kind of clustering which produced long-range interference effects. More recently Schurz, *et al.*,[7] Nakagaki,[10] and Utiyama and Kurata,[11] have shown that anomalies in the dissymmetry may be explained by optical anisotropy of the polymer segments. Utiyama and Kurata have interpreted some of Ehrlich and Doty's data with considerable success, and also their own data on atactic and isotactic polystyrene.[11,12] Although their theory in its present form can account for negative limiting slopes in the Zimm plots, it cannot account for more intense scattering in the backward direction than in the forward,[13] which is shown by some of the data of Ehrlich and Doty,[9] Arichi,[5] and us.

Schurz, *et al.*, found that their anomaly disappeared when the exciting light was vertically polarized.[7] To see if this were so in our system, and to estimate the amount of anisotropy by depolarization, we measured the intensity of scattering of vertically and horizontally polarized incident light, using a solution of the same polymer fraction as in Figure 1. A plot (Figure 3) of the reduced scattering ratios R_θ with vertically (*V*) and horizontally (*H*) polarized incident light against the angle of observation shows first that the depolarization (*i.e.*, the relative value of *H* at 90°) is quite small, and second, that regardless of the polarization, more light is scattered backward than forward. The angular dependences of V and of $[H - H(90°)]/\cos^2\theta$ are very similar.

The phenomenon therefore appears to be essentially different from Utiyama's,[12] for example, which can be explained as an effect of scattering segment anisotropy.[11]

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Newtonian Viscosity–Molecular Weight Relationship for Concentrated Solutions of Monodisperse Polystyrene

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In spite of its importance and the length of time that the problem has been of scientific and practical interest, there is still not complete agreement on the effect of molecular weight on the zero shear rate viscosity of concentrated polymer solutions and polymer melts. In most work on polymers with a moderately broad distribution of molecular weights, best correlations were found with weight average molecular weight.[1,2] In general, log–log plots of zero shear viscosity, η_0, *vs.* weight average molecular weight, which we will denote here simply as *M*, are approximated by two straight lines intersecting at a point M_c, the critical molecular weight for the inception of chain entanglement.

It has been shown[1] that for linear polymers

$$\eta_0 = \mathrm{F}(M)\mathrm{f}(\rho) \tag{1}$$

where F(*M*) is a function only of molecular weight and f(ρ) is a function only of the density ρ. For the case where $M \leq M_c$, F(*M*) is approximately proportional to *M*;[3,4] hence

$$\eta_0 = K_{T,M}M \tag{2}$$

for $M \leq M_c$, where $K_{T,M}$ is a coefficient depending on temperature and molecular weight *M*. The molecular weight dependency of $K_{T,M}$ enters through the dependence of ρ, and thus free volume, on chain ends. Clearly this dependence would be far greater in bulk polymer than in concentrated solutions. Consequently we could expect η_0 to be more nearly proportional to *M* in the latter.[5] For long-chain members

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