Molecular Diffusion in Polymer Solutions

JAMES S. VRENTAS
Department of Chemical Engineering
Illinois Institute of Technology
Chicago, Illinois 60616

and

J. LARRY DUDA
Department of Chemical Engineering
The Pennsylvania State University
University Park, Pennsylvania 16802

Methods for estimating mutual diffusion coefficients for polymer-solvent systems are reviewed. Procedures are recommended for the determination of the temperature, concentration, and molecular weight dependences of diffusivities both for dilute and concentrated solutions.

SCOPE

Information on diffusion coefficients in polymer solutions is required for the analysis of many important polymer processing steps. Only a small amount of diffusivity data applicable to the analysis of polymer processes is available in the literature. In addition, correlative and predictive methods developed for solutions of small molecules are generally not useful in determining estimates of diffusivities for polymer-solvent systems. In this paper, methods for predicting diffusion coefficients for polymer solutions are reviewed, and procedures are recommended for calculating the variation of mutual diffusion coefficients with temperature, concentration, and polymer molecular weight.

CONCLUSIONS AND SIGNIFICANCE

A method is recommended for anticipating anomalous diffusion phenomena and for determining when classical diffusion theory can be used to analyze diffusional processes involving macromolecules. It is proposed that the Kirkwood-Riseman theory and a modified form of this theory be used to estimate diffusivities for infinitely dilute polymer solutions. For dilute polymer solutions, an adaptation of the two-parameter and Pyun-Fixman theories can be utilized to predict diffusivities, and, for concentrated solutions, a method based on free volume theory is recommended. The comparisons between the predictions of the proposed methods and experimental data show many areas of agreement, and reliable and extensive diffusivity data are needed for a comprehensive evaluation of the proposed predictive schemes.

The growth of the polymer industry has been spectacular, and the volumetric production of polymers will soon exceed that of all metals. Initially, this growth was due mainly to the synthesis of new polymers. However, it appears that continued growth will be more directly associated with sophisticated engineering which will lead to improved processes and new applications (Markovitz, 1971, 1972). Diffusion coefficients for polymer solutions are required for the analysis of many polymer formation and fabrication processes. The importance of mass transfer is perhaps most prominent in the formation of polymers, where the rate of polymerization can be controlled or strongly influenced by the molecular diffusion of monomers, initiators, long chain free radicals, dead polymer chains, or low molecular weight condensation products. After formation of the polymer, volatile residues such as monomers, solvents, condensation by-products, and other impurities have to be removed before further processing. Consequently, a devolatilization process which involves molecular diffusion in concentrated polymer solutions often follows the polymerization reactor. The volatile residues are usually removed by vacuum or steam stripping of a polymer melt or of polymer particles. The optimum design of these devolatilizers has become a crucial problem in recent years as tighter health standards dictate the removal of volatile molecules which are potential carcinogens.

There are numerous other examples where mass transfer plays an important role in processes involving polymer-penetrant systems. The formation of cellular polymer foams, whether by foam extrusion or other techniques, is often influenced by the diffusion of blowing agents in polymer melts. The distribution of plasticizers, light

---

0001-1541-79-2167-0001-$02.55.

stabilizers, dyes, flame retardants, and other additives into polymers can also involve molecular diffusion in molten polymers. Finally, diffusion data are needed in evaluating the barrier properties of polymer films.

From the above discussion, it is evident that information on diffusion coefficients in solutions consisting of macromolecules and low molecular weight solvent molecules is required for the analysis of many important polymer processing steps. Unfortunately, obtaining such diffusivity data is often a formidable task for the process engineer. First of all, only a small amount of diffusivity data which is applicable to the analysis of polymer processes is available in the literature. Most diffusion studies with polymers have been conducted to investigate the motions of macromolecules, to elucidate polymer morphology, or to determine the barrier properties of polymer membranes. Furthermore, correlative and predictive methods which have been developed for diffusion in solutions of small molecules are not particularly helpful for determining estimates of diffusion coefficients in solutions where one of the species is a macromolecule. An additional complication is that diffusion phenomena in polymer-solvent systems can exhibit characteristics which are usually not observed in diffusion studies with solutions of small molecules. For example, diffusivities for polymer solutions are often very strong functions of temperature and concentration. It is not unusual to observe an increase in the diffusion coefficient by a factor of more than 1 000 when 10 wt% solvent is added to an amorphous polymer melt. Apparent activation energies of over 40 000 cal/g mole have been reported for some systems, and the apparent activation energy can be a strong function of temperature and concentration. Furthermore, many phenomena which can not be explained by classical diffusion theory, such as case II transport, solvent crazing, and thickness anomalies (Park, 1968; Hopfenberg and Stannett, 1973; Duda and Vrentas, 1970), have been observed under some conditions in polymer-solvent systems. These phenomena can not be described by the usual equations of the classical theory, and it is thus evident that not all mass transfer processes involving polymer solutions can be analyzed simply by knowing the mutual diffusion coefficient.

At present, there exists no general theory which is capable of describing the complete range of the complex diffusional behavior exhibited by polymer-solvent systems. Very little progress has been made in the formulation of theories which describe the anomalous mass transport behavior which has been frequently observed for polymer solutions. Furthermore, until recently, no comprehensive theory was available for the prediction of mutual diffusion coefficients for polymer-penetrant systems for use under conditions where the classical theory of diffusion is applicable. However, recent studies indicate that a framework for the prediction and correlation of diffusion coefficients in polymer solutions may be emerging. The purpose of this review is to discuss the methods presently available for the determination of polymer-solvent mutual diffusion coefficients which can be used to describe purely viscous diffusion phenomena for polymer solutions. A precise definition of a purely viscous diffusion process is given below. This review has two basic objectives. We first critically discuss the predictive methods which can be used to give reasonable estimates of diffusivities for polymer solutions. Emphasis will be placed on theories which predict the temperature, concentration, and molecular weight dependence of polymer-solvent diffusion coefficients from a limited amount of mass transfer, viscosity, and thermodynamic data. Second, we outline suggested predictive procedures for the utilization by polymer process engineers who need diffusivity data but do not have the time or expertise to ferret out the information which is pertinent to their needs.

This review will be limited to the prediction of mutual diffusion coefficients for binary solutions consisting of an amorphous, monodisperse, uncross-linked polymer and a low molecular weight penetrant. Many of the results will generally be valid only for linear, flexible chain polymers at molecular weights of ordinary interest. Diffusive transport in semicrystalline polymers is complicated by the geometrical difficulties inherent to transport in heterogeneous systems (Barrer, 1968), and diffusion in cross-linked systems is not necessarily adequately described by a purely viscous theory of diffusion (Fujita, 1968). Branched and ring polymers and stiff chains are not considered since they introduce complications into the statistical mechanics of polymer chains which are beyond the scope of this review (Yamakawa, 1971). Polymer-polymer diffusion theory does not appear to be sufficiently developed at the present time, so we do not include it. The exclusion of polydisperse polymers is not a severe limitation since, as will be shown below, diffusion coefficients for polymer solutions are independent of molecular weight over most of the concentration range.

Mutual diffusion coefficients can be determined using the techniques described below over the complete temperature, concentration, and molecular weight range of interest for a particular polymer-solvent system. However, these predicted diffusion coefficients will probably be of little use in describing diffusive transport at low temperatures and low solvent concentrations since, under such conditions, classical diffusive transport is not observed in the time scale of everyday experience, owing to the slow reorientation of polymer molecules. Roughly speaking, then, the diffusivities predicted using methods proposed here will not be applicable in the temperature-concentration region below the effective glass transition temperature of the particular polymer-solvent system under consideration. The pressure dependence of diffusivities for polymer solutions is not considered here, since this appears to be of secondary importance in polymer processing. Assink (1977) has considered some aspects of the effect of pressure in polymer diffusion.

This review consists of three major sections. The first section considers the general characteristics of diffusion in polymer solutions and presents a method for determining when classical diffusion theory is applicable. In the second section, statistical mechanical results are utilized to formulate a theory for diffusion in dilute polymer solutions. The third section is concerned with diffusion in concentrated polymer solutions; the suggested predictive method for this concentration region is based on free volume theory. Comparisons of the theoretical predictions with experimental data are made whenever possible. Most of these comparisons involve diffusion data for polystyrene solutions, since polystyrene is probably the most widely studied amorphous polymer.

ANTICIPATION OF ANOMALOUS DIFFUSION

A unique and troublesome feature of unsteady state diffusion in concentrated polymer solutions is that, in numerous instances, the mass transfer process can not be described by the classical theory of diffusion. This means, of course, that the usual purely viscous constitutive equation for the mass diffusion flux (often referred to as Fick's first law of diffusion) can not be utilized in the analysis of the diffusion process. Anomalous mass transfer behavior in polymers has usually been observed during a sorption experiment in which a slab or film of polymer is exposed to a solvent, and the weight pickup of the solvent is measured as a function of time. The deviation from the predictions of classical diffusion theory can be quite subtle, such as cases where the measured diffusion coefficient is observed to be a function of the thickness of the polymer sample (Odani, 1967). On the other hand, the departure can be quite dramatic, as, for example, in the study of Alfrey et al. (1966) where the weight pickup of the solvent was observed to be a linear function of time instead of the square root of time function consistent with classical diffusion theory. These phenomena and other examples of nonclassical diffusion, such as solvent crazing and swelling fracture, are usually referred to as anomalous or non-Fickian diffusional behavior. Reviews discussing such phenomena have been presented by Park (1968) and by Hopfenberg and Stannett (1973).

It appears that these anomalous mass transfer processes are associated with the sluggish relaxation of large polymer molecules. As the concentration field in a polymer solution changes with time, the system must adjust to new conformations consistent with new values of concentration at each point in the system. In classical diffusion theory, it is implicitly assumed that an equilibrium liquid structure consistent with the local concentration exists at all points in the diffusion field. This assumption is valid only if the local relaxation in the system is fast compared to the diffusion process, a situation which is sometimes not achieved for diffusion with polymer solutions. Consequently, a theory which includes the influence of the relaxation in the system on the diffusive transfer is required to describe some mass transfer processes involving macromolecules. It is beyond the scope of this review to discuss experimental evidence of non-Fickian diffusional behavior and possible theoretical interpretations, but it would be very helpful if some method were available for anticipating conditions under which anomalous effects can be expected during diffusion involving amorphous polymer-solvent systems. Such a method would indicate to the investigator whether classical diffusion theory can be used to analyze a particular mass transfer process. Only if the classical theory is applicable can the analyst use diffusivities predicted by the methods discussed below in conjunction with the species continuity equation and other pertinent equations of change.

Definition of the Deborah Number

Alfrey (1965) apparently was the first to systematically characterize anomalous mass transfer in polymer solutions by constructing temperature-penetrant concentration diagrams which qualitatively depicted the different types of diffusional transport in polymer-penetrant systems. This concept was extended by Hopfenberg and Frisch (1969) who constructed a more elaborate version of the temperature-concentration diagram. Duda and Vrentas (1970) later noted that the various regions on such diagrams could be distinguished by the ratio of two characteristic times, a characteristic relaxation time for the polymer-solvent system and a characteristic diffusion time.

The temperature-concentration diagram concept was put on a quantitative basis by Vrentas et al. (1975) who introduced a diffusion Deborah number defined by

$$(DEB)_D = \frac{\lambda_m}{\theta_D} \tag{1}$$

and discussed methods for the evaluation of λ_m and θ_D. This dimensionless group is analogous to the dimensionless group which has been used to study the flow behavior of viscoelastic fluids (Astarita and Marrucci, 1974). The characteristic time for the polymer-solvent system can be taken to be the mean relaxation time

$$\lambda_m = \frac{\int_0^\infty sG(s)ds}{\int_0^\infty G(s)ds} \tag{2}$$

whereas the definition of the characteristic diffusion time depends on the type of diffusion process under consideration. For unsteady, one-dimensional mass transfer in polymer films, the usual definition for the characteristic diffusion time is simply

$$\theta_D = \frac{L^2}{D^*} \tag{3}$$

A convenient and reasonable definition for D^* is given by the following expression (Vrentas et al., 1975):

$$D^* = x_2 D_1 + x_1 D_2 \tag{4}$$

The value of the Deborah number for a given set of conditions identifies the type of diffusional transport that can be expected. When the Deborah number is small (say less than 0.1), the local relaxation in the system is fast compared to the diffusion process. Conformational changes in the polymer take place essentially instantaneously, and both solvent and polymer behave like purely viscous fluids. Consequently, this low Deborah number or purely viscous diffusion process can be described by the usual equations of the classical theory. Mutual diffusion coefficients which are estimated using the methods of this review can thus be utilized for all diffusion processes with sufficiently low Deborah numbers.

In the other extreme, when the Deborah number is large (say greater than 10), there is essentially no time variation of the structure of the polymer during the diffusion process. Under these conditions, a solvent molecule migrates in a material which appears to have the properties of an elastic solid. This type of diffusional transport can be denoted as elastic diffusion. Meares (1954, 1957), Zhurkov and Ryskin (1954), and Kishimoto et al. (1960) obtained diffusion data for small amounts of penetrants in polymers below the glass transition temperature, and they concluded that the diffusion process could be described by the equations of the classical theory with a concentration independent diffusivity. The diffusion Deborah numbers for these experiments were presumably large, and we can thus conclude tentatively that diffusional transport for large Deborah numbers can be satisfactorily described by classical diffusion theory even though the system is obviously not a purely viscous fluid mixture. Theoretical justification for this is not considered here. Although the diffusion of trace amounts of penetrants below the glass temperature of the polymer is generally treated (Stannett, 1968) using Fick's first law even though it is an elastic diffusion process, it should be noted that mutual diffusion coefficients for such phenomena can not generally be predicted using the techniques presented in this review. The methods proposed here are valid for the prediction of the diffusivity for systems with equilibrium liquid structures. Materials below the glass transition temperature generally have nonequilibrium liquid configurations which, for elastic diffusion, remain invariant during the diffusion process. Furthermore, there do not exist unique values of the diffusivity for classical diffusion below the glass temperature, since the structure of a nonequilibrated liquid sample depends on the manner in which the sample is deformed and cooled as it is taken below the transition temperature. Some aspects of diffusion phenomena at low penetrant concentrations below the glass temperature are considered elsewhere (Vrentas and Duda, 1978).

For values of the Deborah number of the order of one (say from 0.1 to 10), the molecular relaxation and diffusive transport processes occur in comparable time scales. The rearrangement of polymer chains and the relative motion of solvent molecules take place simultaneously, and the instantaneous molecular configuration is generally different from the equilibrium liquid structure. This type of diffusional behavior, which can be denoted as viscoelastic diffusion, can be explained only by a theory significantly more complex than the purely viscous diffusion theory.

Construction of Deborah Number Diagrams

Before methods are discussed for constructing Deborah number diagrams which can be used to anticipate anomalous diffusion phenomena, it is useful to list some of the limitations of such diagrams. First, the Deborah number defined by Equation (1) is to be used only to describe polymer-solvent diffusion in the absence of externally induced flow so that all deformations are the result of concentration gradients. An extended definition of the Deborah number must be utilized if deformations in the system are a result of a combination of surface tractions, body forces, and concentration gradients. Second, for a precise analysis of a polymeric diffusion process, the Deborah number concept should be applied to each material particle in the system. Since it is not possible at the present time to consider the time variation of a diffusion Deborah number for each material particle in a polymer solution (Vrentas and Duda, 1977*c*), it is necessary to formulate a Deborah number which, in some average sense, describes the diffusion process for the entire collection of material particles. There are numerous examples in fluid mechanics and mass transfer where a single value of a dimensionless group is used to facilitate the analysis of a complex transport process.

A third difficulty is caused by the fact that λ_m is usually a strong function of the local state variables for a polymer-solvent mixture. Consequently, a single value of the Deborah number can be used to describe a particular diffusion process only if the spatial and time variations of the state variables are small. For an isothermal diffusion process with a monodisperse polymer, the pressure must be essentially uniform and independent of time, and the spatial and time variations of the solvent concentration about an average concentration must be small. For example, a single value of $(DEB)_D$ can be used to characterize the unsteady, isothermal diffusion of a solvent in a thin film only if the difference in the final and initial equilibrium concentrations is sufficiently small. The interpretation and utility of Deborah number diagrams for such sorption experiments (usually referred to as differential sorption experiments) is clear, and an example of this type of temperature-concentration diagram is given below. If large concentration changes occur during a sorption experiment, it is still possible to gain considerable insight into the nature of the diffusive transport by calculating Deborah numbers at the initial and final conditions of the diffusion process. Special types of Deborah number diagrams can be constructed for sorption experiments with large concentration changes (usually referred to as integral sorption experiments), and an example of this type of Deborah number diagram is also presented below. It should, of course, be evident that a different Deborah number diagram must be constructed for each diffusion process, since the definition of θ_D is generally not the same for different processes. Finally, we note that the definition for $(DEB)_D$ is obviously not unique. However, it is to be expected that all reasonable definitions for the Deborah number will lead to temperature-concentration diagrams which show that nonclassical diffusion behavior can be expected in approximately the same temperature and concentration regions.

A method for calculating the temperature, concentration, and molecular weight dependence of the Deborah number for the special case of sorption experiments has been presented by Vrentas et al. (1975) and by Vrentas and Duda (1977*c*). The sorption experiment involves unsteady, one-dimensional diffusion of a solvent from an effectively pure gas phase into a film of thickness L. The film is exposed to solvent vapor on one side only, and the initial solvent mass density is ρ_{10}. The unsteady diffusion process is initiated by introducing a step change in the gas phase pressure to a value which gives a solvent mass density ρ_{1E} when equilibrium has been reestablished between the penetrant vapor and the liquid film. If $\rho_{1E} - \rho_{10}$ is sufficiently small, then a single Deborah number, calculated at $(\rho_{1E} + \rho_{10})/2$, can be used to characterize this differential sorption process. If $\rho_{1E} - \rho_{10}$ is not small, then Deborah numbers calculated at the initial and final concentrations can be used to describe this integral sorption process.

It can be shown (Vrentas and Duda, 1977*c*) that the temperature, concentration, and molecular weight dependence of the Deborah number for a sorption experiment involving a film of thickness L is given by

$$(DEB)_D = \left[\frac{x_2 D_1(T, \omega_1)}{D_2(T, \omega_1)} + x_1 \right] \frac{D_2(T_o, \omega_{10}) \lambda_{mo}}{L^2} \tag{5}$$

Here, $D_1(T, \omega_1)$ and $D_2(T, \omega_1)$ are self-diffusion coefficients for the solvent and a polymer of a particular molecular weight at the temperature and concentration of interest (T, ω_1) and $D_2(T_o, \omega_{10})$ is the polymer self-diffusion coefficient at reference conditions (T_o, ω_{10}). The temperature and concentration variations of the self-diffusion coefficients can be determined using the free volume analysis presented later, and, consequently, the only additional data needed for Deborah number calculations are values of λ_{mo} at the molecular weights of interest. It is convenient to let $\omega_{10} = 0$ so that values of λ_{mo} can be calculated from Equation (2) by using modulus-time data for different molecular weight samples of pure polymer at a convenient reference temperature. Modulus-time data are available for many amorphous polymers; for example, Akovali (1967) has presented this type of data for a number of monodisperse polystyrene samples.

For differential sorption experiments, the diffusion process can be characterized by a single value of the Deborah number which immediately suggests the type of diffusional transport which can be expected for the particular temperature and concentration of interest. A Deborah number diagram for differential sorption experiments is presented in Figure 1 for the ethylbenzene-polystyrene system with $M_2 = 3 \times 10^5$ and $L = 10^{-3}$ cm. The elastic, viscous, and viscoelastic regions of diffusional transport, separated by lines of constant $(DEB)_D$, are included in this figure along with a curve which represents the effective glass transition temperature of the polymer-penetrant mixture as measured by experiments of conventional duration. For integral sorption experiments, special types of Deborah number diagrams can be constructed, and an example of such a diagram is presented in Figure 2 for the same system considered in Figure 1, with $L = 0.032$ cm. This figure describes the diffusional phenomena which are observed when a pure polymer is exposed to various final solvent concentrations at a given temperature. For each temperature, the initial value of the Deborah number is calculated from the properties of the pure polymer, and the final value of

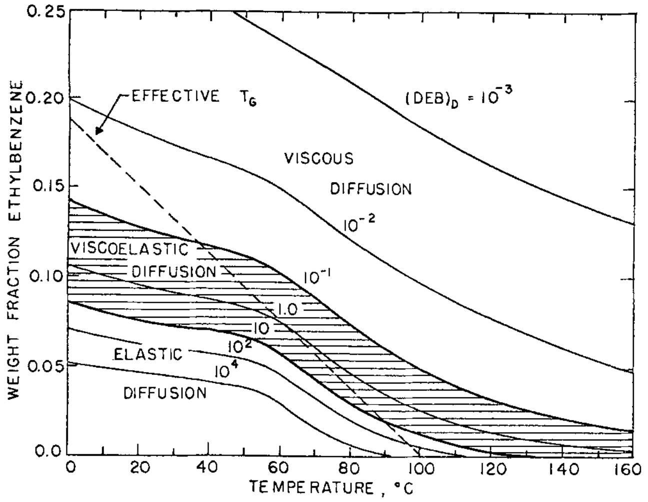

Fig. 1. Deborah number diagram for differential sorption experiment for ethylbenzene-polystyrene system with $M_2 = 3 \times 10^5$ and $L = 10^{-3}$ cm.

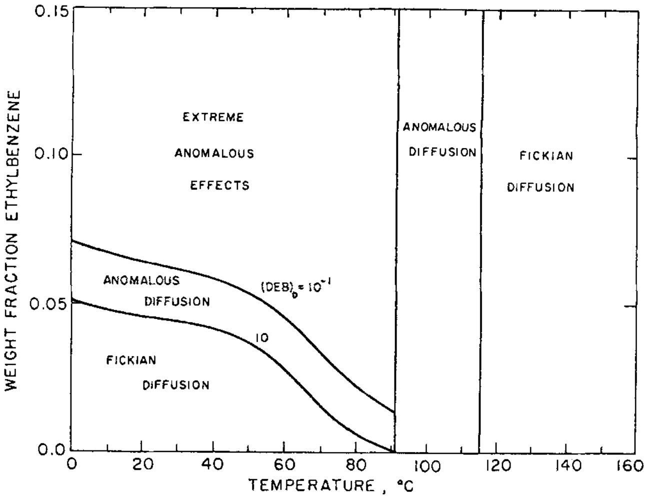

Fig. 2. Deborah number diagram for integral sorption experiment for ethylbenzene-polystyrene system with $M_2 = 3 \times 10^5$ and $L = 0.032$ cm.

$(DEB)_D$ can be varied by exposing the system to different solvent concentrations. Consequently, Figure 2 has been constructed by associating various phenomena with the final value of $(DEB)_D$ for the sorption experiment. It should be noted that extreme anomalous effects like case II transport, solvent crazing, and swelling fracture are not associated with particular regions of a Deborah number diagram but rather with the change in $(DEB)_D$ that occurs during the diffusion process. A more detailed discussion of this type of penetrant concentration-temperature diagram is given elsewhere (Vrentas et al., 1975).

The diffusion Deborah number should be calculated as the first step in the analysis of a mass transfer process involving macromolecules in order to determine if classical diffusion theory is applicable. This procedure should also be used in the design of experiments used to measure diffusion coefficients, since erroneous data may result if anomalous effects are not avoided. It would be useful if a particular polymeric diffusion process could be characterized without utilizing the rather involved procedure prescribed above. Unfortunately, no easy methods for the evaluation of $(DEB)_D$ appear to exist. However, if rough estimates of a characteristic diffusion coefficient and a characteristic relaxation time are available at the lowest temperature and solvent concentration levels in the system, then the maximum value of $(DEB)_D$ can be estimated using Equation (1). If this is sufficiently small (say less than 0.1), then classical theory is applicable. Finally, a rough rule of thumb is that purely viscous diffusion behavior can not generally be expected in the temperature-concentration region below the effective glass transition temperature of the polymer-solvent mixture. Some aspects of the effect of diluents on the glass transition temperature have been discussed by Boyer (1970).

DIFFUSION IN DILUTE SOLUTIONS

The characteristics of polymer solutions change significantly as the entire concentration range is traversed. At one extreme, we have infinitely dilute polymer solutions where the polymer molecules are widely dispersed in the solvent and there are no interactions between individual polymer chains. As the polymer concentration is increased, polymer molecules begin to interact hydrodynamically with each other, even though the domains of individual polymer molecules do not yet overlap. This concentration region can be referred to as the dilute solution region. As the polymer concentration is further increased, the domains of polymer molecules begin to overlap so that there is a considerable amount of polymer-polymer contact, and entanglements are formed between polymer molecules. Solutions with concentrations higher than the concentration at which overlap begins will be referred to as concentrated polymer solutions. An approximate calculation of this transition concentration is considered below.

Although a general theory which can describe molecular diffusion throughout the complete concentration range has not as yet been proposed, independent theories have been developed which are applicable to specific regions

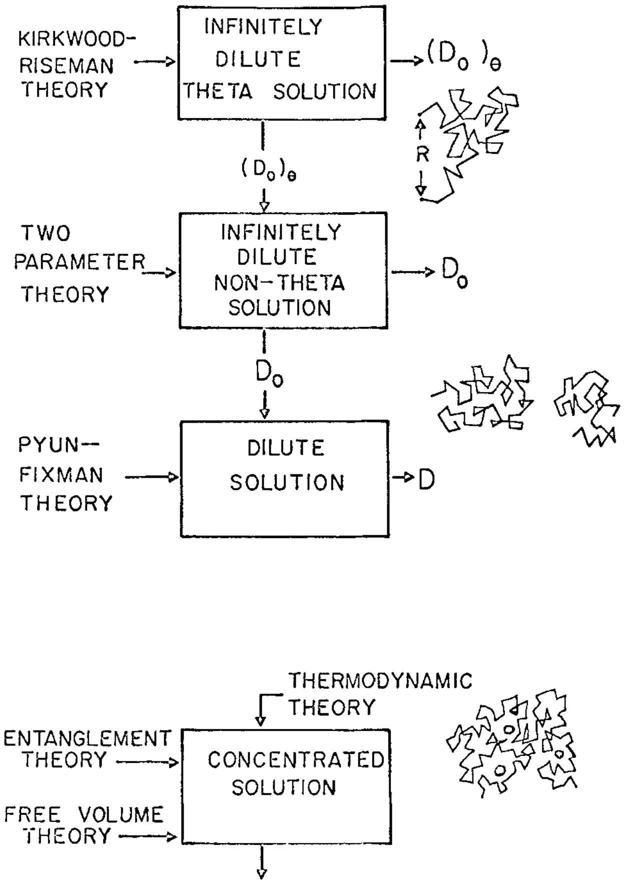

Fig. 3. Outline of diffusion theories for dilute and concentrated solutions.

of the concentration interval. In this section, we shall consider theories based on statistical mechanical concepts which are useful in the description of the diffusion process in the infinitely dilute and dilute regions. An outline of the various theories which will be considered in this review and schematic illustrations of the molecular state of the solution at different levels of concentration are presented in Figure 3.

The concentration dependence of the mutual diffusion coefficient for dilute polymer solutions can conveniently be expressed by a series expansion of the following form:

$$D = D_o[1 + k_D\rho_2 + \ldots] \tag{6}$$

It is evident that prediction of the diffusivity for dilute solutions reduces to the derivation of equations for the determination of D_o and k_D. The prediction of D_o involves consideration of intramolecular forces, whereas both intramolecular and intermolecular forces must be considered in the determination of k_D.

The evaluation of mutual diffusion coefficients for dilute polymer solutions is carried out by computing the frictional force that the solvent exerts on the individual polymer molecules. The solvent can be regarded as a continuous, viscous fluid, and the segments which constitute the polymer chain are regarded as the centers of resistance to flow. Since the frictional properties of polymer solutions are intimately related to the dimensions of the polymer chain, it is first necessary to consider some aspects of polymer chain configurations in solution. An excellent review of the application of statistical mechanics to the analysis of the equilibrium and nonequilibrium properties of polymer solutions has been given by Yamakawa (1971).

Average Dimensions of Polymer Chains

A linear polymer chain immersed in an infinite sea of solvent assumes a complex spatial configuration which is continuously changing owing to thermal fluctuations. It is convenient to characterize the molecular dimensions of this chain by appropriate averages of the possible configurations which can be realized by the polymer molecule. Two average molecular dimensions which are frequently utilized are the mean-square end-to-end distance, $<R^2>$, and the mean-square radius of gyration, $<S^2>$. These quantities can be computed once distribution functions for the chain are determined. The simplest case to treat statistically is the freely jointed linear chain in which the individual segments of the chain are linked together in a completely random fashion, similar to the steps of a three-dimensional random flight. For a chain of n segments each of length a, the mean square of the distance R between the ends of the chain is given by the equation

$$<R^2> = na^2 \tag{7}$$

which states that $<R^2>$ is proportional to the polymer molecular weight. It can also be shown that

$$<S^2> = \frac{1}{6}<R^2> = \frac{na^2}{6} \tag{8}$$

for the random flight chain.

Equation (7) seriously underestimates the average dimensions of real polymer chains because two classes of interferences have been neglected in the random flight model:

1. Short-range intramolecular interferences due to fixed bond angles and hinderances to rotation lead to values of $<R^2>$ which can be five to ten times greater than those predicted by Equation (7) (Billmeyer, 1971).
2. Long-range interferences occur because chains can not assume configurations in which two segments occupy the same space at the same time since they have finite volumes. This type of intramolecular interaction is usually referred to as the excluded volume effect, and the precise magnitude of this effect will depend on the nature of the solvent.

The effect of short-range interferences on average molecular size can be computed (Flory, 1969; Yamakawa, 1971), and it has been found that $<R^2>_o/M_2$ is again independent of polymer molecular weight for sufficiently long chains. Here, $<R^2>_o$ is the mean-square end-to-end distance of the unperturbed or ideal chain. The term unperturbed is taken here to refer to a polymer chain whose size is not affected by long-range interferences. The properties of an unperturbed chain can also be examined experimentally by a judicious choice of solvent and temperature. It is obvious that the exclusion of segments from space already occupied will increase $<R^2>$. On the other hand, in a poor solvent, polymer segments tend to associate with other polymer segments rather than with solvent molecules, and there is a contraction of the polymer chain dimension. Consequently, the temperature and solvent composition can be manipulated so that a balance can be achieved where there is no net excluded volume and the polymer chain attains its unperturbed dimension. When excluded volume effects are eliminated, the polymer is in a theta state, and the solvent is called a theta solvent. The existence of a theta state can be detected by several experimental procedures (Billmeyer, 1971), and the quantity $<R^2>_o$ can be measured using light scattering techniques. It is thus possible to characterize the theta or unperturbed state of a particular polymer by a single parameter A defined by

$$A = \left[\frac{<R^2>_o}{M_2}\right]^{1/2} \tag{9}$$

For a given polymer, A depends on the temperature and on the nature of the solvent, but solvent effects are usually insignificant, at least for nonpolar polymers (Kurata and Stockmayer, 1963; Berry and Casassa, 1970; Yamakawa, 1971). Values of A have been tabulated by Kurata and Stockmayer (1963) and by Kurata et al. (1975) for a large number of polymers.

The analysis of the excluded volume effect is considerably more complex than the determination of the effect of short-range interferences because long-range interferences can not be described by random flight statistics. The mean-square radius of gyration for a real linear macromolecule in an infinitely dilute solution is generally expressed as

$$<S^2> = \alpha_S^2<S^2>_o \tag{10}$$

The quantity α_s measures the extent to which the excluded volume effect perturbs the linear molecular dimension of a polymer chain from its unperturbed dimension. The expansion factor α_S can be determined from light scattering experiments, but information on α_S is not always available since this parameter depends on temperature, polymer molecular weight, and solvent characteristics. This situation is to be contrasted with that for the determination of dimensions of unperturbed chains where the parameter A, which usually has a modest temperature dependence, leads to the average dimension of a particular polymer chain for all solvents and any molecular weight. It is evident that development of a theory for chain dimensions is particularly useful under conditions where long-range interferences can not be neglected.

There is as yet no exact theory for the determination of α_S when the excluded volume effect is large. Exact perturbation series solutions have been developed for small excluded volumes, and approximate solutions have been obtained which are valid for large excluded volumes (Yamakawa, 1971). Both approaches illustrate the non-Markoff nature of the excluded volume effect, and, in both types of theories, the average molecular dimensions and other properties of dilute polymer solutions can be expressed in terms of two parameters. One of these parameters is A and the other, which is usually denoted as B, is a measure of the effective volume excluded to one segment by the presence of another. Clearly, $B = 0$ for a theta solvent, and, for a particular polymer, B generally depends on the temperature and on the nature of the solvent. The group of theories which express the properties of dilute polymer solutions in terms of A and B are called two-parameter theories, and the parameters A and B serve to represent short- and long-range interferences, respectively.

The two-parameter scheme requires that α_S be expressed by an equation of the following form:

$$\alpha_S = \alpha_S(A, B, M_2) \qquad (11)$$

Since we would like to be able to predict chain dimensions of polymers in good solvents, we are here interested in approximate expressions for α_S which are valid over a wide range of excluded volumes. Yamakawa (1971) has considered the available approximate expressions and compared their predictions with experiment. This comparison favors the Yamakawa-Tanaka (1967) expression for α_S, and we adopt it here since it appears to be consistent with experimental data:

$$\alpha_S^2 = 0.541 + 0.459(1 + 6.04z)^{0.46} \qquad (12)$$

$$z = \left(\frac{3}{2\pi}\right)^{3/2} \frac{M_2^{1/2}B}{A^3} \qquad (13)$$

Unfortunately, the evaluation of B for a particular polymer-solvent system is not an easy matter. Theoretical evaluation of B (Yamakawa and Fujii, 1973) leads to values which differ by one order of magnitude from experimental results. Berry (1966, 1967) has advocated a method for the experimental determination of B which utilizes an assumed temperature dependence for this parameter and which does not depend on results of the two-parameter theory. Yamakawa (1971, 1972) has criticized this approach, claiming that the validity of the assumed temperature dependence is questionable, except for temperatures near the theta temperature. Berry and Casassa (1970) have also warned that caution must be exercised in using this method. Hence, it appears that at the present time B is best determined from a combination of experiment and the equations of the two-parameter theory. The preferred method for calculation of B involves the utilization of light scattering measurements to determine α_S at several polymer molecular weights. The quantity z can then be determined for each value of M_2 from Equation (12), and, by Equation (13), B can be estimated from the slope of a z vs. $M_2^{1/2}$ plot. If light scattering data are not available, intrinsic viscosity data can be used to estimate B; Yamakawa (1971, 1972) discusses techniques for determining B from $[\eta]$ vs. M_2 data. Although there exist more intrinsic viscosity data than light scattering measurements, there seems to be no completely satisfactory two-parameter theory for intrinsic viscosity (Yamakawa, 1971), and light scattering data should be used when possible.

A quick and reasonable estimate of B can be deduced by utilizing intrinsic viscosity data expressed in terms of the Mark-Houwink-Sakurada (Kurata and Stockmayer, 1963) empirical relationship

$$[\eta] = K'M_2^{\nu} \qquad (14)$$

TABLE 1. B VALUES FOR POLYSTYRENE-SOLVENT SYSTEMS

Solvent	$B \times 10^{27}$ (cm^3)
Benzene	2.25
Ethyl benzene	1.53
Methyl ethyl ketone	0.266-0.377
Toluene	2.12
THF	2.92

which is valid over a given range of M_2. Values of K' and ν are available for particular molecular weight ranges for numerous polymer-solvent pairs (Kurata and Stockmayer, 1963; Kurata et al., 1975). From empirical results for the intrinsic viscosity (Yamakawa, 1971), it is easy to show that B can be estimated from

$$B = \frac{K'M_2^{\nu-1/2} - 1.05\,\Phi_o A^3}{0.287\,\Phi_o M_2^{1/2}} \qquad (15)$$

which can be used when $BM_2^{1/2}/A^3 \leqq 5.06$. Theoretical values of the viscosity constant Φ_o range from 2.66×10^{23} to 2.87×10^{23} molecules/g mole. Berry (1967) and Matsumoto et al. (1972) present data for homogeneous polymers which support the lower theoretical value, whereas Yamakawa (1971, 1972) claims that the best experimental value is 2.5×10^{23} molecules/g mole. Differences in the observed values of Φ_o may be due to sample polydispersity. Kurata et al. (1975) recommend that 2.7×10^{23} can be used for well-fractioned polymers and 2.5×10^{23} for ordinary fractionated polymers, and we utilize this recommendation in this review.

Representative values of B for several polystyrene-solvent pairs calculated using Equation (15) are presented in Table 1. These values were computed using appropriate K' and ν values listed in the table of Kurata et al. (1975) and reported by McDonnell and Jamieson (1977), and the calculation was performed at the average molecular weight of the indicated molecular weight interval. The values of B presented in Table 1 are in reasonably good agreement with values of this parameter derived from light scattering data. For example, for toluene at 25°C, Equation (15) gives 2.12×10^{-27} cm^3, whereas Yamakawa (1971) reports 2.19×10^{-27} cm^3 at 12°C.

Determination of D_o for Theta Solutions

Kirkwood and Riseman (1948) developed a theory for diffusive transport in infinitely dilute polymer solutions by considering the hydrodynamic friction between an unperturbed polymer chain and a solvent. This theory provides the best available method for predicting the mutual diffusion coefficient at infinite dilution under theta conditions for linear, flexible chain polymers. The Kirkwood-Riseman theory provides for a varying amount of hydrodynamic interaction between the segments of an isolated polymer chain which are taken to be point sources of friction. At one limit ($X = 0$), there are no interactions between the segments of the polymer molecule, and the velocity field of the solvent around a segment is not influenced by neighboring segments. This is referred to as the free draining limit. In the nonfree draining limit ($X = \infty$), there exists a very large hydrodynamic interaction between segments, and the polymer chain behaves hydrodynamically as a rigid molecule since penetration of the solvent is minimized. The general result of the Kirkwood-Riseman theory can be expressed as

$$D_o = \frac{kT}{n\zeta}\left(1 + \frac{8}{3}X\right) \qquad (16)$$

$$X = \frac{2^{1/2} n^{1/2} \zeta}{\eta_1 a (12\pi^3)^{1/2}} \tag{17}$$

where the draining parameter X provides the measure of hydrodynamic interaction between polymer chain segments.

The intrinsic viscosity data of Krigbaum and Flory (1953) show that there is no draining effect for flexible chain, linear polymers under theta conditions for molecular weights of ordinary interest. In addition, Yamakawa (1971) has presented evidence for the absence of a draining effect under nontheta conditions, and it is assumed here that the draining effect is negligible for flexible chains irrespective of the solvent. Thus, it appears that the Kirkwood-Riseman theory has practical significance for linear, flexible chain polymers only in the nonfree draining limit ($X = \infty$), and hence we write Equation (16) as

$$(D_o)_\theta = \frac{0.196\, kT}{\eta_1 A M_2^{1/2}} \tag{18}$$

Since data for A and solvent viscosity are usually available, determination of $(D_o)_\theta$ for most polymer-solvent pairs is relatively simple. Note that both η_1 and A contribute to the temperature dependence of $(D_o)_\theta$.

The Kirkwood-Riseman theory is based on an approximate model of polymer transport, and not all results of the theory conform to the expected behavior of polymer solutions. For example, Zwanzig et al. (1968) have shown that the Kirkwood-Riseman theory leads to negative translational diffusion coefficients at some values of the draining parameter. This result appears to cast doubt on the Kirkwood-Riseman approach of treating polymer segments as point sources of friction, and it may be necessary to consider segments of finite size to obtain consistent results. Consequently, because of the approximate nature of the model, some comparison of the predictions of Equation (18) with experiment should be carried out to verify the validity of the Kirkwood-Riseman theory in the nonfree draining limit. Vrentas and Duda (1976*a*) have carried out such a comparison and have concluded that the Kirkwood-Riseman result for $X = \infty$ accurately predicts polymer-solvent diffusion coefficients at infinite dilution under theta conditions. Figure 4 illustrates the comparison of predicted and experimental $(D_o)_\theta$ for monodisperse polymer samples. Although the agreement between theory and experiment is quite good, it should, of course, be remembered that Equation (18) is limited to theta solutions, and, thus, the Kirkwood-Riseman result, by itself, is of limited utility. However, in the next section, we show that the Kirkwood-Riseman theory can form the basis for the determination of D_o in good solvents.

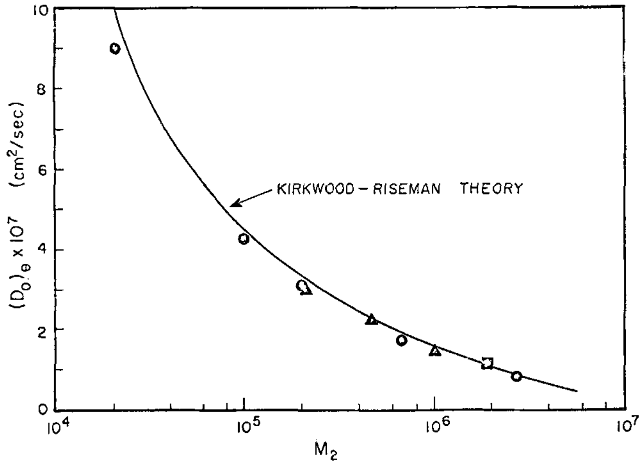

Fig. 4. Comparison of Kirkwood-Riseman theory with experiment for cyclohexane-polystyrene system: (●) data of King et al. (1973*a*) (▲) data of Cowie and Cussler (1967) (■) data of Jacob et al. (1962).

Determination of D_o for Nontheta Solutions

Many solvents encountered in actual practice are relatively good solvents, and the diffusion coefficient at infinite dilution for such systems will be less than $(D_o)_\theta$ since the polymer chains are expanded by excluded volume effects. The analysis of frictional behavior in mixtures of good solvents and polymers can be carried out by relating the intrinsic viscosity and the diffusion coefficient for a nontheta solution to the intrinsic viscosity and diffusivity for an unperturbed chain by using the expansion factors α_η and α_f:

$$[\eta] = [\eta]_\theta \alpha_\eta^3 \tag{19}$$

$$[\eta]_\theta = \Phi_o A^3 M_2^{1/2} \tag{20}$$

$$D_o = \frac{(D_o)_\theta}{\alpha_f} \tag{21}$$

These definitions simply focus the problem on the theoretical determination of the z dependence of α_η and α_f. We now show how these equations lead to two methods for determining D_o for a linear polymer diffusing in a nontheta solvent.

One method for determining D_o (Vrentas and Duda, 1976*a*) is based on utilizing Equation (21) and the observation that there is an insignificant difference between α_f and α_S. Kurata and Stockmayer (1963) compared both exact perturbation series results for α_f and α_S and approximate results for these quantities in the limit of very good solvents and concluded that the difference between α_f and α_S does not exceed 2%. We thus approximate Equation (21) by the result

$$D_o = \frac{(D_o)_\theta}{\alpha_S} \tag{22}$$

and, since $\alpha_S \geqq 1$ except for very poor solvents, we note that the Kirkwood-Riseman result provides an upper bound for diffusion coefficients in infinitely dilute polymer-solvent systems for all solvents of practical importance:

$$D_o \leqq (D_o)_\theta \tag{23}$$

If A and B are known for a particular polymer-solvent system, then an estimate of D_o at a given temperature and polymer molecular weight can be obtained from Equations (12), (13), (18), and (22). A comparison of the predictions of this method and experimental data is considered below.

Rudin and Johnston (1971) suggested a method for the estimation of D_o from intrinsic viscosity data. They did not apply appropriate results from the theory of polymer solutions, however, and we here present a modified version of their proposed method. Combination of Equations (14) and (19) to (21) yields the following form of a known result (McDonnell and Jamieson, 1977):

$$\frac{D_o}{(D_o)_\theta} = \frac{A\Phi_o^{1/3}}{K'^{1/3} M_2^{\nu/3-1/6}} \frac{\alpha_\eta}{\alpha_f} \tag{24}$$

Experimental evidence (Yamakawa, 1971) shows that a maximum error of about 7% in $D_o/(D_o)_\theta$ will result if α_η/α_f is set equal to one. Consequently, with this approximation, Equation (24) can be used to estimate D_o if the parameters in the empirical intrinsic viscosity expression [Equation (14)] are available. We note here that $\alpha_\eta \leqq \alpha_f$, and we would thus expect that the

TABLE 2. COMPARISON OF EQUATIONS (22) AND (24)

	$D_o/(D_o)_\theta$		
$M_2 \times 10^{-3}$	Data of Meyerhoff and Nachtigall (1962)	Equation (22)	Equation (24)
44	0.79	0.85	0.89
140	0.75	0.80	0.82
520	0.68	0.73	0.74
950	0.54	0.69	0.70
2 700	0.57	0.64	0.65

approximate version of Equation (24) will lead to high estimates for D_o.

In Table 2, we present a comparison of the predictions of Equations (22) and (24) with the diffusivity data of Meyerhoff and Nachtigall (1962) taken on a system of toluene and narrow molecular weight fractions of polystyrene. A value of $B = 2.19 \times 10^{-27}$ cm^3 was used in Equation (22). Both theories predict values of $D_o/(D_o)_\theta$ which are higher than the experimental results, but Equation (22) provides better estimates than Equation (24) for this particular instance. We believe that Equation (22) is generally superior to Equation (24) for the following reasons. First of all, the approximation $\alpha_f = \alpha_S$ used to derive Equation (22) is better than the assumption $\alpha_\eta = \alpha_f$ needed for the application of Equation (24). Second, diffusivities computed from Equation (24) will, of course, be strictly valid only over the same molecular weight range as the empirical intrinsic viscosity relationship. Finally, some of the same input data needed for Equation (22) must be utilized in calculating the concentration dependence of D, and hence Equation (22) fits better in an integrated scheme for the determination of D for dilute solutions. The only disadvantage in using Equation (22) is that the predictions of this equation are, of course, dependent on the accuracy of the approximate expression for α_S.

In Figure 5 we have presented a graph of the molecular weight dependence of $D_o/(D_o)_\theta$ at 25°C for polystyrene-solvent systems with $A = 0.670 \times 10^{-8}$ cm and B ranging from 0 to 10^{-26} cm^3. This figure depicts the manner in which D_o decreases with increasing molecular weight and increasing volume exclusion as predicted by Equation (22). Evaluation of the utility of these theoretical predictions is somewhat limited owing to the lack of reliable experimental data for monodisperse polymer-solvent systems at infinite dilution. Data for the solvents methyl ethyl ketone, toluene, and THF, taken primarily using narrow polystyrene fractions, are included in Figure 5. Lines drawn through the points representing the toluene data of Meyerhoff and Nachtigall (1962) and the methyl ethyl ketone data of King et al. (1973*b*) and of Tsvetkov and Klenin (1958) would be in reasonable agreement with the shapes of the theoretical curves. Furthermore, as is discussed in detail elsewhere (Vrentas and Duda, 1976*a*), the values of B which fit these diffusivity data are in reasonably good agreement with values of this parameter determined from unrelated experiments, especially when the slow change of $D_o/(D_o)_\theta$ with B for good solvents is considered. However, the methyl ethyl ketone data of Ford et al. (1970) and of McDonnell and Jamieson (1977) do not agree with the above data and also lead to much higher values of B. There is poor agreement between theory and experiment for the THF data of McDonnell and Jamieson (1977). More will be said later about discrepancies in dilute solution diffusivity data.

Determination of k_D

As the concentration of the polymer in dilute solution is increased, the individual polymer chains begin to interact hydrodynamically with each other (but do not overlap and entangle), and both increases and decreases of the mutual diffusion coefficient with concentration have been reported (Meyerhoff and Nachtigall, 1962; King et al., 1973*a*, *b*). The nature of the variation of D with concentration is dependent on the interaction between hydrodynamic, thermodynamic, and volumetric effects in the dilute polymer solution. Consequently, the starting point for the analysis of the concentration dependence for such systems is an equation which relates k_D to these competing influences:

$$k_D = 2A_2M_2 - k_S - b_1 - 2\hat{V}_{20} \qquad (25)$$

The thermodynamics of the solution is represented by A_2, the second virial coefficient for a dilute polymer solution; k_S is a coefficient in a series expansion for the concentration dependence of the friction coefficient

$$f_{12} = (f_{12})_o[1 + k_S\rho_2 + \ldots] \qquad (26)$$

and b_1 is defined by the following series expression:

$$\hat{V}_1 = \hat{V}_1{}^o[1 + b_1\rho_2 + \ldots] \qquad (27)$$

Equation (25) was derived by Vrentas and Duda (1976*c*), and it represents a generalization and modification of the results of previous investigators (Pyun and Fixman, 1964; Yamakawa, 1971) who either ignored the contributions of b_1 and $\hat{V}_{20}$ to k_D or included the $\hat{V}_{20}$ term incorrectly. The effects of b_1 and $\hat{V}_{20}$ on k_D will be of some importance when k_D is less than 20 cm^3/g (Vrentas and Duda, 1976*c*).

Since the quantities b_1 and $\hat{V}_{20}$ can be determined from straightforward density experiments or can certainly be adequately approximated, we focus our attention on the evaluation of A_2 and k_S for a particular polymer-solvent system. The second virial coefficient A_2 is zero for theta solutions, and experimental values of this quantity for nontheta polymer solutions have been compiled for a large number of polymer-solvent pairs by Klärner and Ende (1975). If data for A_2 are not available, then the results of the two-parameter theory

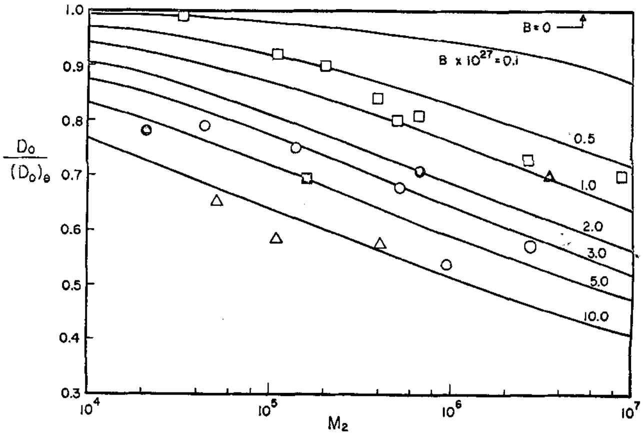

Fig. 5. Comparison of modified Kirkwood-Riseman theory with experimental data: (□) methyl ethyl ketone data of King et al. (1973*b*); (▲) methyl ethyl ketone data of Tsvetkov and Klenin (1958); (■) methyl ethyl ketone data of McDonnell and Jamieson (1977); (●) methyl ethyl ketone data of Ford et al. (1970); (○) toluene data of Meyerhoff and Nachtigall (1962); (△) THF data of McDonnell and Jamieson (1977).

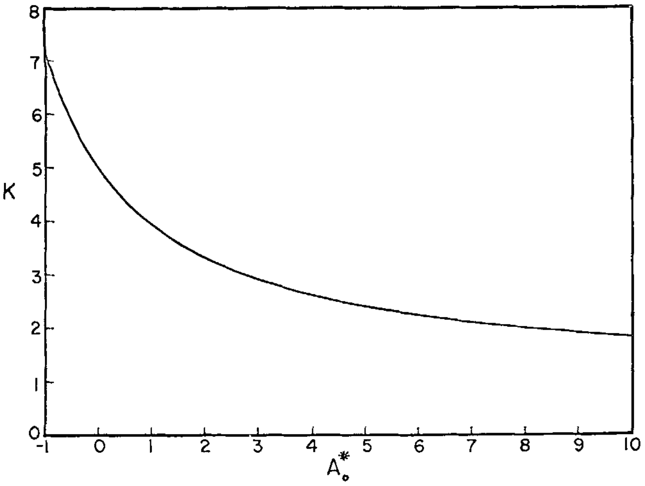

Fig. 6. Graph of K vs. A_0^*. K is defined by Equation (35).

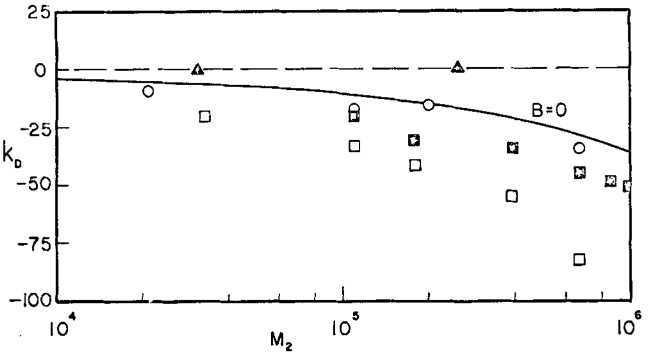

Fig. 7. Comparison of theoretical predictions for k_D(cm^3/g) with experimental data for theta solutions: (○) data of King et al. (1973*a*); (▲) data of Cantow (1959); (■) data of Frost and Caroline (1977); (□) data of Lacharojana and Caroline (1977).

of solutions can be used to estimate A_2 for solutions of linear, flexible chain polymers. Both perturbation series and approximate closed expressions have been derived for A_2 (Yamakawa, 1971). Since we are generally interested in a wide range of excluded volumes, we adopt here the approximate result of the Kurata-Yamakawa (Kurata et al., 1964; Yamakawa, 1968) theory for A_2 since it is consistent with the Yamakawa-Tanaka (1967) expression for α_S and since it appears to represent experimental data satisfactorily (Yamakawa, 1971):

$$A_2 = \frac{N_A B h_o(\bar{z})}{2} \tag{28}$$

$$\bar{z} = \frac{z}{\alpha_S{}^3} \tag{29}$$

$$h_o(\bar{z}) = \frac{0.547[1 - (1 + 3.903\,\bar{z})^{-0.4683}]}{\bar{z}} \tag{30}$$

Values of α_S are computed from Equations (12) and (13). These results should provide satisfactory estimates for A_2 when data are not available.

The analysis of frictional behavior in dilute polymer solutions is, of course, significantly more complicated than for infinitely dilute systems because both intermolecular and intramolecular forces must be considered. Yamakawa (1962), Pyun and Fixman (1964), and Imai (1969) have developed theories which lead to expressions for the coefficient k_S. Yamakawa's theory, which is based on a random coil model, involves some approximations which have been criticized by Pyun and Fixman. Both the theory of Yamakawa and that of Imai predict that $k_S = 0$ at the theta temperature. Since $A_2 = 0$ for theta solutions, Equation (25) yields

$$k_D = -b_1 - 2\hat{V}_{20} \tag{31}$$

for diffusion of unperturbed chains. This expression predicts a weak concentration dependence for polymer-solvent diffusion under theta conditions since k_D is usually about 2 cm^3/g. The theory derived by Pyun and Fixman for the concentration dependence of friction coefficients considers polymer molecules to be interpenetrable spheres of uniform segment density. Both hard and soft spheres were considered in their model which is obviously a less realistic portrayal of polymer solutions than the random coil models utilized by Yamakawa and Imai. The Pyun and Fixman theory predicts that k_S is not zero at the theta point and, in fact, increases as $M_2^{1/2}$. It follows that this theory predicts a substantial concentration dependence of the mutual diffusion coefficient in theta solutions at sufficiently high polymer molecular weights.

The data of King et al. (1973*a*), Lacharojana and Caroline (1977), and Frost and Caroline (1977) show a very significant concentration dependence for D for theta solutions, whereas the data of Cantow (1959) indicate that there is essentially no concentration dependence. It is not possible at this time to state a definitive conclusion as to the magnitude of k_S for theta solvent systems, but, in light of the extensive recent data, it appears to us quite probable that k_S is not zero. Hence, we recommend the utilization of the Pyun and Fixman

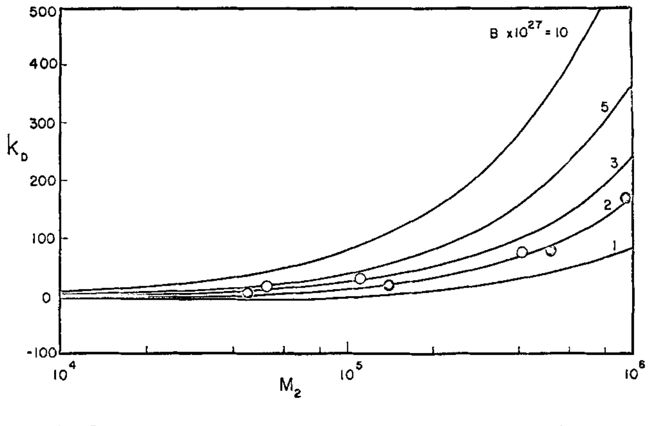

Fig. 8. Comparison of theoretical predictions for k_D(cm^3/g) with experimental data for good solvents: (●) toluene data of Meyerhoff and Nachtigall (1962); (○) THF data of McDonnell and Jamieson (1977).

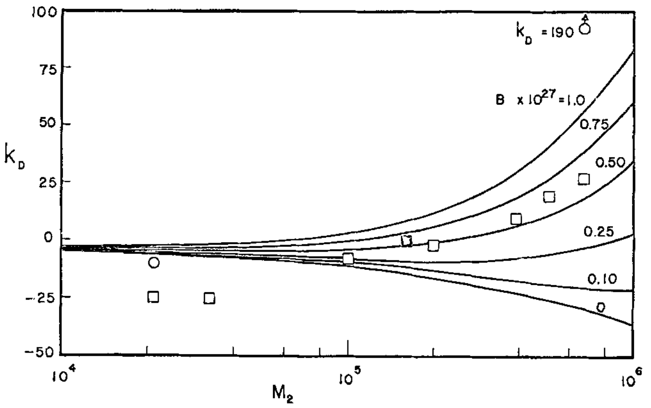

Fig. 9. Comparison of theoretical predictions for k_D(cm^3/g) with experimental data for methyl ethyl ketone: (□) data of King et al. (1973*b*); (■) data of McDonnell and Jamieson (1977); (○) data of Ford et al. (1970).

theory for k_S even though it is based on a less realistic model than the other two theories. Vrentas and Duda (1976*b*) have adapted the Pyun and Fixman model for use in the analysis of polymer-solvent diffusion by accounting for the fact that the spheres used in this theory are composed of both polymer and trapped solvent. The coefficient k_S can be evaluated from the following equations which represent an appropriate combination of the Pyun-Fixman and two-parameter theories:

$$k_S = [7.16 - K(A_o^*)]\frac{4\pi a_o^3 N_A}{3M_2} - \hat{V}_{20} - b_1 \quad (32)$$

$$a_o = \frac{6^{1/2}\pi^{1/2} A M_2^{1/2} \alpha_S}{16} \quad (33)$$

$$A_o^* = \frac{4\,096z}{72\pi\alpha_S^3} \quad (34)$$

$$K(A_o^*) = 24\int_o^1 \left\{ \frac{2\ln[1 + x + (2x + x^2)^{1/2}]}{(2x + x^2)^{1/2}} - 1 \right\} x^2 \times \exp[-A_o^*(1 - x)^2(2 + x)]dx \quad (35)$$

A graph of $K(A_o^*)$ vs. A_o^* is included in Figure 6 for convenience. It is evident from above that if A, B, $\hat{V}_{20}$, and b_1 are known for a particular polymer-solvent system, then Equations (12), (13), (25), (28) to (30), and (32) to (35) can be used to estimate k_D for a given temperature and polymer molecular weight.

It should be noted here that the friction coefficient which is used in a relationship with the mutual diffusion coefficient must be introduced using a frame indifferent constitutive equation. A valid friction coefficient can be defined by an equation of the form (Vrentas and Duda, 1976*b*)

$$\text{Force on a polymer molecule} = f_{12}(u_2 - u_1) \quad (36)$$

where u_1 and u_2 are the velocity of solvent and polymer, respectively, with respect to a convenient reference frame. Yamakawa (1962) evaluated the concentration dependence of the friction coefficient defined by Equation (36), and his original result should be used directly in the determination of k_D. In a later publication, Yamakawa (1971) derived a modified expression for k_S based on another friction coefficient which was defined as the ratio of the external force on a polymer molecule to its average translational velocity. This second friction coefficient is introduced using a constitutive equation which is not frame indifferent, and hence it is not a valid material property. A number of investigators (King et al., 1973*a*, *b*; Lacharojana and Caroline, 1977; Frost and Caroline, 1977; McDonnell and Jamieson, 1977) have used the second definition of the friction coefficient rather than Equation (36) to evaluate k_D. We believe this is an incorrect application of the theory of Yamakawa to diffusive motions in polymer solutions.

Theoretical results for the variation of k_D with molecular weight are presented in Figures 7 to 9 along with data taken primarily using polystyrene samples with narrow molecular weight distributions. For these calculations, we have set $A = 0.670 \times 10^{-8}$ cm, $b_1 = 0$, and $\hat{V}_{20} = 0.9$ cm^3/g, and B ranges from 0 to 10^{-26} cm^3. Consequently, these figures describe concentration effects in dilute polystyrene-solvent systems at approximately 25°C. These figures indicate that D will always decrease with concentration for theta solutions ($B = 0$), and this decrease can be quite significant as the molecular weight increases. For good solvents (say, $B > 1$), D increases with concentration for molecular weights of ordinary interest. For mediocre solvents (say, $0 < B < 1$), D decreases with concentration at low molecular weights and increases with concentration at high molecular weights.

In Figure 7, the theory is compared with four sets of diffusivity data taken under theta conditions. The agreement between the theoretical curve for $B = 0$ and the cyclohexane-polystyrene data of King et al. (1973*a*) is quite good, but the data of Cantow (1959), Lacharojana and Caroline (1977), and Frost and Caroline (1977) show appreciable deviations from the theory. Furthermore, the first set of data is effectively in agreement with the theoretical prediction that k_D varies as $M_2^{1/2}$ for theta solvents, whereas the other three data sets are not. Lacharojana and Caroline and Frost and Caroline used mixed solvent systems, and it is possible that muticomponent diffusion phenomena may have affected these data.

Five sets of diffusivity data taken on nontheta solvents are compared with the predictions of the theory in Figures 8 and 9. The toluene data of Meyerhoff and Nachtigall (1962) are satisfactorily represented by a curve with a value of B of about 2×10^{-27} cm^3 which is in excellent agreement with the value 2.19×10^{-27} cm^3 derived by Yamakawa (1971) from light scattering data. The polystyrene-THF data of McDonnell and Jamieson (1977) are described by a curve with B somewhere between 2.5 and 3.0×10^{-27} cm^3. This is in good agreement with the value of $B = 2.92 \times 10^{-27}$ cm^3 derived from intrinsic viscosity data and listed in Table 1. Only the three highest molecular weights reported by these investigators are presented in Figure 8, since they implied in their paper that the data for the lower molecular weights were questionable. The methyl ethyl ketone data of McDonnell and Jamieson and the data of King et al. (1973*b*) for this solvent above a molecular weight of 2×10^5 are reasonably well represented by a value of B slightly greater than 0.5×10^{-27} cm^3. This value falls between the value of $B = 0.76 \times 10^{-27}$ cm^3 reported by Berry and Casassa (1970) and the values derived from intrinsic viscosity data and presented in Table 1. The three data points of King et al. (1973*b*) for molecular weights below 2×10^5 disagree with the theory and with the data of Ford et al. (1970) which also are not in accord with theoretical predictions.

The agreement of the estimates of the proposed predictive methods with much of the experimental data is encouraging, and the observed discrepancies are not necessarily due to weaknesses in the theory. It is evident from the above comparisons that significantly different values of D_o and k_D have been reported for the same polystyrene-solvent systems. Furthermore, some of the experimental results (McDonnell and Jamieson, 1977; Lacharojana and Caroline, 1977) are in qualitative disagreement with the expected behavior of polymer solutions. There is a lack of reliable diffusivity data for monodisperse polymer-solvent systems owing to the difficulty in conducting diffusion experiments. Laser light scattering methods have increased the speed with which diffusion data can be obtained, but there are instances of considerable disagreement between reported diffusivity data acquired using this method. A complete evaluation of the theories presented above must wait until consistent data are available.

Summary of Suggested Predictive Method

The suggested predictive procedure for estimating D for dilute polymer solutions is summarized in Figure 10. The predicted diffusivities should be applicable for concentrations ranging from a trace amount of polymer to the concentration at which the domains of polymer molecules just overlap. Berry and Fox (1968) derived an approximate expression for this transition volume fraction

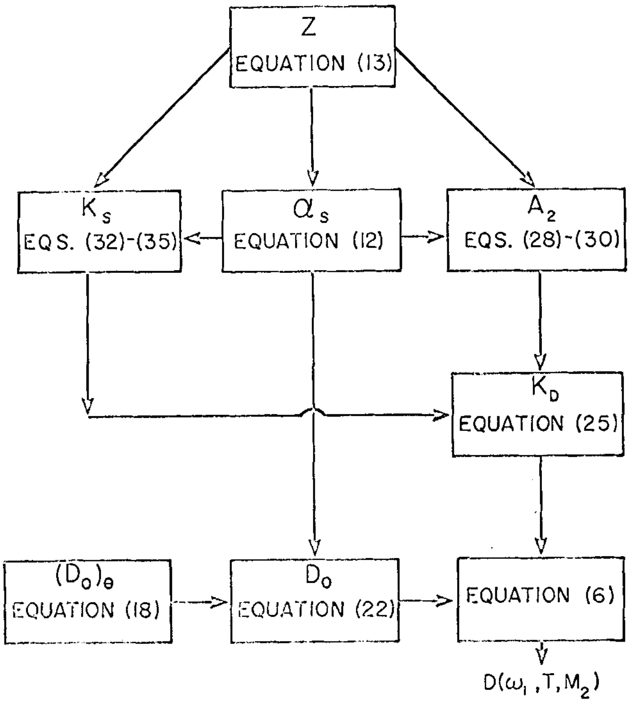

Fig. 10. Summary of predictive scheme for infinitely dilute and dilute solutions.

by considering a close packed arrangement of polymer spheres. Their result for the transition volume fraction ϕ_2^* can be written as

$$\phi_2^* = \frac{(4.3 \times 10^{-24})\hat{V}_2^0}{M_2^{1/2}A^3} \qquad (37a)$$

This can be converted to mass fraction for a particular polymer-solvent system. For example, for the ethylbenzene-polystyrene system, the approximate critical mass fraction of polymer can be computed from the following result:

$$\omega_2^* = \frac{4}{1 + 0.2M_2^{1/2}} \qquad (37b)$$

By the suggested procedure, the binary mutual diffusion coefficient at a given temperature and polymer molecular weight can be estimated for linear polymer-solvent systems for concentrations less than the transition concentration if the properties η_1, A, B, b_1, and $\hat{V}_{20}$ are known. The solvent viscosity η_1 and the density related properties b_1 and $\hat{V}_{20}$ are often available, can be easily measured, or can be adequately estimated in most cases. The parameter A has been measured for many polymers and has been conveniently tabulated (Kurata and Stockmayer, 1963; Kurata et al., 1975). The parameter B can be estimated from light scattering or intrinsic viscosity data, as discussed above.

DIFFUSION IN CONCENTRATED SOLUTIONS

As the concentration of polymer molecules in the solution is increased, a particular polymer chain begins to overlap the domains occupied by other molecules, and, at even higher concentrations, a significant number of entanglements occur among the interpenetrating polymer chains. The analysis of transport in concentrated solutions is considerably more complex than in dilute solutions because of the strong interactions between polymer chains. Some effort has been expended to investigate the properties of concentrated solutions using a statistical mechanical basis (Fixman, 1961, 1965; Fixman and Peterson, 1964; Williams, 1966). However, it appears that concentrated polymer solutions are too complicated to treat rigorously using molecular mechanics because of the numerous degrees of freedom and the complex intramolecular and intermolecular interactions. Consequently, theories for the description of transport processes in concentrated polymer solutions are approximate and heuristic in nature. In this section, we will show how one such theory can be utilized to predict diffusion coefficients for concentrated solutions as a function of temperature, concentration, and polymer molecular weight using a limited number of experimental measurements.

Before discussing the recommended predictive method, which is based on a free volume theory of transport, we consider other theories for diffusional transport in concentrated polymer solutions. All of these theories consider the limiting case of diffusion of a trace of solvent in the polymer, and, thus, these developments do not provide a comprehensive picture of transport in polymer-solvent systems. Barrer (1957) formulated a zone theory of diffusional transport by postulating that the activation energy for diffusion is distributed through the degrees of freedom in the system. The diffusion coefficient was related to the thermal vibration frequency, the jump distance, and the total energy of the activated zones. Barrer did not relate this total energy to molecular structure, but Brandt (1959) formulated a molecular model for the estimation of this quantity. Brandt used his model to predict activation energies for the diffusion process, but the theoretical values were 25 to 70% of the experimental value. Furthermore, the theory does not predict D, since the thermal vibration frequency and jump distance are generally not known.

DiBenedetto (1963) formulated a molecular model for the prediction of the activation energy of diffusion, and DiBenedetto and Paul (1964) developed a volume fluctuation theory for this quantity. Each theory involves one unknown parameter (the number of segments involved in a diffusional jump), and each theory predicts only the activation energy, not D. Van Krevelen (1972) developed an empirical method for predicting the diffusivity of simple gases in rubbery polymers by using the Arrhenius expression for the temperature dependence of the diffusivity:

$$D = \overline{D}_0 \exp\left[-\frac{E_D}{RT}\right] \qquad (38)$$

The two parameters $\overline{D}_0$ and E_D can be evaluated from a correlation developed by Van Krevelen if the molecular diameter of the gas and the glass transition temperature of the polymer are known. Although this correlation is useful in predicting diffusion coefficients for polymer-gas systems, there appears to be no simple extension of the method to mixtures of polymers and organic solvents in the infinitely dilute limit. Stannett (1968) has discussed various aspects of the diffusion of simple gases in polymers and has compiled diffusivity data for gas-polymer systems.

It appears that the free volume theory of diffusion is the only theory which has been developed sufficiently at the present time to describe the complex diffusional transport in concentrated polymer solutions. In this section, we first consider the utilization of free volume theory in the derivation of expressions for self-diffusion coefficients in polymer-solvent systems. The relationship between the mutual diffusion coefficient and the self-diffusion coefficients is discussed, and methods of obtaining the necessary thermodynamic parameters are considered. A procedure for determining the constants of free volume theory from experimental data is presented. Finally, the predictions of the theory are compared with the observed general behavior of diffusion coefficients in polymer-solvent systems and with actual experimental diffusivity data. It is seen that diffusivities for polymer-solvent systems are often strong functions of temperature, concentration, and the characteristics of the solvent. In contrast with dilute systems, however, diffusion coefficients for concentrated solutions are weakly dependent on polymer molecular weight in the molecular weight range of usual interest.

For dilute solutions, the polymer chain dimension is generally different than the unperturbed dimension. However, it is generally accepted that polymer molecules assume their unperturbed dimensions as the polymer concentration increases, since a polymer segment is unable to distinguish between segments from its own chain and those from other chains. Fixman and Peterson (1964) have shown theoretically that the expansion factor for a polymer chain does indeed decrease toward unity as the polymer concentration increases. It is reasonable to assume that negligible polymer chain expansion persists for volume fractions greater than ϕ_2^*, and unperturbed dimensions should be used to characterize the size of a polymer molecule for concentrated solutions.

Free Volume Theory for Self-Diffusion Coefficients

There has been a long history of theoretical and experimental papers which are concerned with the development of the free volume concept in the description of transport in liquid systems. The original work is probably that of Batschinski (1913) who postulated that the viscosity of a liquid was inversely proportional to the amount of free space in the system. Much later, Doolittle (1951, 1952) and Doolittle and Doolittle (1957) utilized an empirical exponential representation for the dependence of viscosity on free volume to describe the temperature variation of viscosity for low molecular weight liquids. Bueche (1953) derived an expression for the polymer segmental mobility by considering volume fluctuations, and Meares (1958) utilized this theory to interpret allyl chloride-polyvinyl acetate diffusivity data. Fujita et al. (1960) formulated a free volume description of diffusion in concentrated polymer solutions by utilizing a Doolittle type of expression for the diffusion coefficient.

Cohen and Turnbull (1959) and Turnbull and Cohen (1961, 1970) considered molecular transport in a liquid of hard spheres and derived an expression relating the self-diffusion coefficient to the free volume in the system. Their model assumes that molecular transport occurs by the movement of molecules into voids formed by redistribution of the free volume in the material. The Cohen-Turnbull result can be regarded as giving a theoretical basis for free volume equations of the Doolittle type, since Cohen and Turnbull argued that their hard sphere theory should apply to real liquids. Bueche (1962*a*) derived a modified form of the Doolittle equation but concluded that the new equation and the Doolittle equation predicted essentially identical behavior in the temperature range of interest. Macedo and Litovitz (1965) derived a generalized version of the Cohen-Turnbull result for molecular transport by considering attractive forces as well as the availability of free space. Chung (1966) put the Macedo-Litovitz expression on a firmer theoretical basis by deriving it from statistical mechanical arguments. Naghizadeh (1964) obtained another extended version of the Cohen-Turnbull result by including a redistribution energy for the voids in the system, as contrasted to the random distribution of voids assumed by Cohen and Turnbull. Finally, Fujita (1961) utilized the Cohen-Turnbull equation as a starting point for a free volume interpretation of polymer-solvent diffusion. The theory in this Fujita paper, which was summarized by Fujita (1968) later, has served as the basis for the analyses of diffusion in polymer-solvent systems for the past 15 yr. Berry and Fox (1968), Kumins and Kwei (1968), Haward (1970), and Machin and Rogers (1972) have presented surveys on various aspects of free volume theories for molecular transport.

Although the Fujita version of the free volume theory of transport has provided a useful basis for describing the temperature and concentration dependence of diffusion coefficients for polymer-solvent systems, there are shortcomings in the Fujita theory (Fujita, 1961; Vrentas and Duda, 1977*a*). First of all, it has been shown by Vrentas and Duda (1977*a*) that Fujita introduced four assumptions (three of them implicitly) in adapting the Cohen-Turnbull theory to binary diffusion in polymer-solvent systems. It is evident that these assumptions limit the results of Fujita to sufficiently low solvent concentrations, and, indeed, Fujita (1961) states that his theory should be valid only for solvent volume fractions less than 0.15. Furthermore, one of the assumptions restricts Fujita's theory to solvents with a molecular weight approximately equal to the molecular weight of a jumping unit of the polymer chain. More will be said later about the implications of this assumption. In the modified free volume theory proposed by Vrentas and Duda (1977*a*, *b*) and considered below, none of these assumptions is introduced in the original equations of the theory. A second shortcoming of the Fujita theory is that it has been set up as a correlative rather than a predictive theory, in the sense that diffusivity vs. volume fraction data are needed at each temperature to evaluate $\beta(T)$, a quantity which represents the effectiveness of the diluent in increasing the free volume of the system. It is, in principle, possible to convert the Fujita scheme to more of a predictive basis so that the diffusion coefficient at a particular temperature and concentration can be estimated from a limited amount of diffusion and viscosity data. However, diffusivity data both at infinite solvent dilution and at higher solvent concentrations would be needed to evaluate the parameters of the Fujita theory in its present form. For the modified version of the free volume theory, viscosity data and as few as two values of the diffusion coefficient at infinite solvent dilution are needed to calculate the constants of the theory.

Before we discuss the modified version of the free volume theory of Fujita, we briefly attempt to put free volume theories of molecular transport in perspective. It should be obvious that any free volume theory is a crude model for molecular motion rather than a rigorous molecular theory of liquids. Since the theory does not include detailed information on intermolecular potentials, it is unrealistic to expect that expressions for viscosities and self-diffusion coefficients can be derived in terms of molecular parameters. Furthermore, the free volume of the system available for molecular transport is a quantity which cannot be determined by methods which are independent of viscosity and self-diffusion measurements. Consequently, it is not possible to obtain an estimate of the viscosity of a pure material at a given temperature if transport data for the system are not available. However, it is reasonable to expect that a limited number of transport measurements can be used to predict viscosities and self-diffusion coefficients at other temperatures and concentrations. Thus, for binary systems, free volume theory can be a useful method for predicting the transport properties of a mixture from those of effectively pure components, since unknown molecular mechanisms are conveniently hidden inside parameters which are determined from transport data. An alternative theory of molecular transport has been derived by Adam and Gibbs (1965). This theory offers additional insight into molecular motion, but it suffers many of the same shortcomings as free volume theory (Berry and Fox, 1968).

The migration of solvent molecules or polymer chains in concentrated solutions is impeded by the presence of neighboring molecules. Under such conditions, a molecule migrates by jumping into a void or hole which forms because the free volume in the system is being continuously redistributed by thermal fluctuations. In the case of relatively small solvent molecules, the jumping unit is the entire molecule, and, for a flexible chain linear polymer, the jumping unit is some small part of the entire chain. It is assumed that this jumping unit can move into a void without affecting neighboring jumping units of the polymer chain.

Two requirements must be fulfilled before a molecule or jumping unit can migrate in solution: a hole or free volume space of sufficient size must appear adjacent to the molecule, and the molecule must have enough energy to move or jump into this void. Thus, the probability of a jump occurring is the product of the probability that a fluctuation in local density will produce a hole of sufficient size and the probability that the jumping unit will acquire, from the distribution of thermal energy, sufficient energy to overcome attractive forces in order to jump into the void. From the results of Cohen and Turnbull (1959), Macedo and Litovitz (1965), and Chung (1966), the self-diffusion coefficient for a one-component simple liquid system is given by

$$D_1 = \overline{D}_{o1} \exp\left[- \frac{\gamma \overline{V}_1{}^*}{\overline{V}_{FH}} \right] \exp\left[- \frac{E^*}{kT} \right] \quad (39)$$

The overlap factor γ (which should be between one half and one) is introduced because the same free volume is available to more than one molecule. The quantity E^* is the critical energy a molecule must obtain to overcome attractive forces which hold it to its neighbors; this quantity will necessarily depend on the details of intermolecular interaction and, thus, on molecular structure. In the derivation of the above expression, it has been assumed that a jump occurs only when a volume greater than the critical hole free volume $\overline{V}_1{}^*$ is available. Also, it has been assumed that the free volume available for molecular transport can be redistributed with no change in energy. Bueche (1962*a*) and Naghizadeh (1964) have derived different versions of Equation (39), but Berry and Fox (1968) have pointed out that there should be no significant differences between either of these results and Equation (39) for the temperature intervals usually considered.

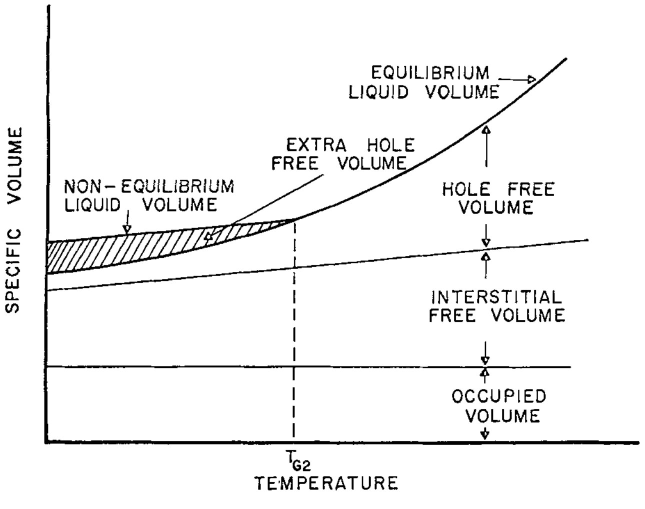

Fig. 11. Illustration of the division of the specific volume of an amorphous polymer.

For concentrated polymer solutions at temperatures of ordinary interest, the specific hole free volume of the system will usually be relatively small, since the temperature of the diffusion process is generally not significantly above the glass transition temperature of the mixture (which is a low free volume state). Consequently, the probability of obtaining a hole of sufficient size is significantly less than that for acquiring the necessary energy, and the self-diffusion process is dominated by free volume effects. Hence, for temperature ranges usually encountered in polymer-solvent diffusion, it is possible to absorb the energy term in the expression for the self-diffusion coefficient into the preexponential factor. For example, for a one-component simple liquid system, Equation (39) can be written as

$$D_1 = D_{o1} \exp\left[- \frac{\gamma \overline{V}_1{}^*}{\overline{V}_{FH}} \right] \quad (40)$$

where it is assumed that the quantity D_{o1} is far less temperature dependent than the exponential and, hence, can be treated as a constant.

Bueche (1962*b*) extended the above result to the self-diffusion of polymer molecules by introducing the concept of a jumping unit of the polymer chain. Vrentas and Duda (1977*a*) generalized these one-component results to a binary mixture of polymer and solvent by assuming that the nature of the molecular species in a binary system does not influence the distribution of hole free volume. They showed that the self-diffusion coefficients for a polymer-solvent system can be expressed as

$$D_1 = D_{o1} \exp\left[- \frac{\gamma(\omega_1 \hat{V}_1{}^* + \omega_2 \xi \hat{V}_2{}^*)}{\hat{V}_{FH}} \right] \quad (41)$$

$$D_2 = \frac{A_o}{\dfrac{N^*}{N} M_2} \exp\left[- \frac{\gamma(\omega_1 \hat{V}_1{}^* + \omega_2 \xi \hat{V}_2{}^*)}{\hat{V}_{FH} \xi} \right] \quad (42)$$

The parameter ξ is defined by the equation $\xi = \hat{V}_1{}^* M_1 / \hat{V}_2{}^* M_j$. The linear polymer is composed of N freely orienting segments, and N^* is the effective number of segments per chain; N^* is larger than N because of the existence of entanglements between chains in concentrated solutions. Finally, it is assumed that the temperature dependences of A_o and D_{o1} can be ignored. It should be noted that precise definitions of self-diffusion coefficients and mutual diffusion coefficients have been presented by Bearman (1961). Mutual diffusion coefficients are used to describe diffusion in solutions under the influence of concentration gradients, whereas a self-diffusion coefficient is an indication of the rate at which a concentration gradient of a labeled species is dissipated in an otherwise uniform solution.

In the present free volume formulation, the specific volume of the liquid $\hat{V}$ is considered to be composed of three components, as depicted in Figure 11. The occupied volume is the close packed volume of the liquid, and it is conveniently defined as the volume of the equilibrium liquid at 0°K. This quantity can be estimated by a variety of methods discussed by Haward (1970). The remainder of $\hat{V}$ is taken to be free volume. As a first approximation, it can be assumed that this free volume can be divided into two types. We postulate that part of the free volume is distributed uniformly among the molecules of a given species since the energy for redistribution is large. Kaelble (1969) has called this type of free volume the interstitial free volume. The remaining free volume is associated with the discontinuous distribution of holes in the liquid, and it is assumed that no energy change is required for redistribution of this portion of the free volume. It is evident that it is this type of free volume, usually denoted as the hole free volume, which is available for molecular transport and which forms the basis for the free volume theory for self-diffusion coefficients, as is evidenced by its inclusion in Equations (39) to (42). There appears to be no direct way of predicting what fraction of the free volume can be redistributed and can thus assist in the molecular jumping processes which characterize flow and diffusion phenomena. Consequently, the amount of available hole free volume must be identified by appropriate interpretation of viscosity or self-diffusion experiments.

As a first approximation, it is reasonable to equate the critical amount of local hole free volume per gram to the specific occupied volume of the liquid:

$$\hat{V}_1^* = \hat{V}_1^o(0) \tag{43}$$

$$\hat{V}_2^* = \hat{V}_2^o(0) \tag{44}$$

Furthermore, if it is assumed that there is additivity of the volumes formed from the sum of the specific occupied volume and the specific interstitial free volume, it follows that (Vrentas and Duda, 1977*a*)

$$\hat{V}_{FH} = \hat{V} - \omega_1[\hat{V}_1^o(0) + \hat{V}_{FI1}(T_{G1})] \exp\left[\int_{T_{G1}}^{T} \alpha_{c1} dT\right] - \omega_2[\hat{V}_2^o(0) + \hat{V}_{FI2}(T_{G2})] \exp\left[\int_{T_{G2}}^{T} \alpha_{c2} dT\right] \tag{45}$$

It is evident that $\hat{V}_{FH}$ has been expressed in terms of four free volume parameters which must be evaluated from transport experiments, as is discussed below.

Diffusion coefficients for purely viscous diffusion must be calculated using $\hat{V}$ data for equilibrium liquid structures. In actual practice, when a system is cooled below its glass transition temperature, the liquid assumes a nonequilibrium liquid configuration. As is evident from Figure 11, this leads to excess hole free volume which enhances the transport in such systems. Some aspects of the free volume theory of transport for nonequilibrium liquid structures are considered elsewhere (Vrentas and Duda, 1978).

Determination of Mutual Diffusion Coefficients

At this point in the development, it has not been necessary to introduce any of the four assumptions which, according to Vrentas and Duda (1977*a*), Fujita (1961) utilized in formulating his theory. However, as will be evident from the discussion below, an additional assumption must now be applied in order to derive an expression which relates the binary mutual diffusion coefficient D to the self-diffusion coefficients of the solvent and the polymer, D_1 and D_2. The connection between D and the self-diffusion coefficients is made via the friction coefficients for the system ζ_{11}, ζ_{12}, and ζ_{22} (Bearman, 1961):

$$D = \frac{M_2\rho_1\hat{V}_2}{N_A^2\zeta_{12}}\left(\frac{\partial\mu_1}{\partial\rho_1}\right)_{T,p} \tag{46}$$

$$D_1 = \frac{RT}{N_A^2\left(\dfrac{\rho_1\zeta_{11}}{M_1} + \dfrac{\rho_2\zeta_{12}}{M_2}\right)} \tag{47}$$

$$D_2 = \frac{RT}{N_A^2\left(\dfrac{\rho_2\zeta_{22}}{M_2} + \dfrac{\rho_1\zeta_{12}}{M_1}\right)} \tag{48}$$

In order to derive an equation which relates D to D_1 and D_2 and contains none of the friction coefficients, it is necessary to express the friction coefficient ζ_{12} solely in terms of D_1 and D_2. However, since Equations (47) and (48) constitute a set of two equations which must be solved for three friction coefficients, an additional relation is needed if ζ_{11}, ζ_{12}, and ζ_{22} are to be eliminated from the final result for D.

At the present time, there appears to be no appropriate theory which can be readily evaluated to yield an expression relating ζ_{11}, ζ_{12}, and ζ_{22} for polymer-solvent systems. In addition, there are insufficient experimental data for D, D_1, and D_2 which can be used to suggest the form of an expression which relates the friction coefficients for a polymer-diluent mixture. Loflin and McLaughlin (1969) summarize approximate theories for relating D to D_1 and D_2 and also discuss the statistical mechanical result of Rice and Allnatt (1961). A frequently used expression for relating the friction coefficients is the geometric mean approximation

$$\zeta_{12} = (\zeta_{11}\zeta_{22})^{1/2} \tag{49}$$

which leads to the simple result

$$D = \frac{(D_1x_2 + D_2x_1)}{RT}\left(\frac{\partial\mu_1}{\partial \ln x_1}\right)_{T,p} \tag{50}$$

However, both Loflin and McLaughlin and McCall and Douglass (1967) have compared the predictions of Equation (50) with experimental data for simple liquid systems and have concluded that, in general, this equation is in qualitative, but not quantitative, agreement with experiment. A similar conclusion was reached by these investigators for other expressions which estimate the concentration dependence of D using D_1 and D_2.

Since little progress has been made in relating D to D_1 and D_2 for simple liquid mixtures, it might appear that similar difficulty can be expected for polymer-solvent systems. However, $D_1 >> D_2$ for mixtures of a polymer and a simple liquid, and it is possible that this inequality may lead to a simplification in the analysis. From Equations (46) and (47), it can easily be shown that (Vrentas and Duda, 1977*a*)

$$D = \frac{\rho_2\hat{V}_2\rho_1}{RT}\left[\frac{D_1}{1 - \dfrac{D_1}{D_1^*}}\right]\left(\frac{\partial\mu_1}{\partial\rho_1}\right)_{T,p} \tag{51}$$

where

$$D_1^* = \frac{RTM_1}{\rho_1\zeta_{11}N_A^2} \tag{52}$$

Since D_1/D_1^* ranges from zero at $\omega_1 = 0$ to one at $\omega_1 = 1$, it is evident that the reduced form of Equation (51)

$$D = \frac{D_1\rho_2\hat{V}_2\rho_1}{RT}\left(\frac{\partial\mu_1}{\partial\rho_1}\right)_{T,p} = \frac{D_1x_2}{RT}\left(\frac{\partial\mu_1}{\partial \ln x_1}\right)_{T,p} \tag{53a}$$

will yield a good approximation for D in some concentration interval near $\omega_1 = 0$, where D_1/D_1^* is sufficiently small. If D_1/D_1^* is small over the major part of the concentration range, then D can be predicted from Equation (53a) using only free volume and thermodynamic considerations. For example, if the friction coefficients obey Equation (49), then calculations show (Vrentas and Duda, 1977b) that Equation (53a) estimates D with less than 10% error for approximately 85% of the concentration interval. This is one example where the large difference in D_1 and D_2 forces D_1/D_1^* to be small except near $\omega_1 = 1$.

We believe the present evidence is in favor of tentatively recommending utilization of Equation (53a) for the determination of D in polymer-solvent systems. Hence, the equations of free volume theory used in conjunction with thermodynamic data suffice for the evaluation of D. This type of assumption was implicitly introduced by Fujita (1961), and this is the only assumption of the four alluded to earlier which is incorporated here in the modified version of the theory. We further note that Equations (50) and (53a) will generally yield equivalent results over the major part of the concentration interval since the contribution of $D_2 x_1$ will be negligible at most concentrations because $D_1 >> D_2$. If data for D_1 and D vs. concentration were available for a typical polymer-solvent system, the validity of Equation (53a) could be ascertained. Finally, we note the following equality for D_1 and D:

$$\lim_{\rho_1 \to 0} D_1 = \lim_{\rho_1 \to 0} D \qquad (53b)$$

Thermodynamic Data

The temperature, concentration, and molecular weight dependence of D can be determined from Equations (41), (43) to (45), and (53a) if the following information is available:

1. $\hat{V}$, the specific volume of the mixture, and μ_1, the chemical potential per mole of the solvent in the binary system.
2. D_{01}, γ, ξ, $\hat{V}_{FI1}(T_{G1})$, and $\hat{V}_{FI2}(T_{G2})$.
3. $\hat{V}_1^\circ(0)$ and $\hat{V}_2^\circ(0)$.
4. $\alpha_{c1}(T)$ and $\alpha_{c2}(T)$.

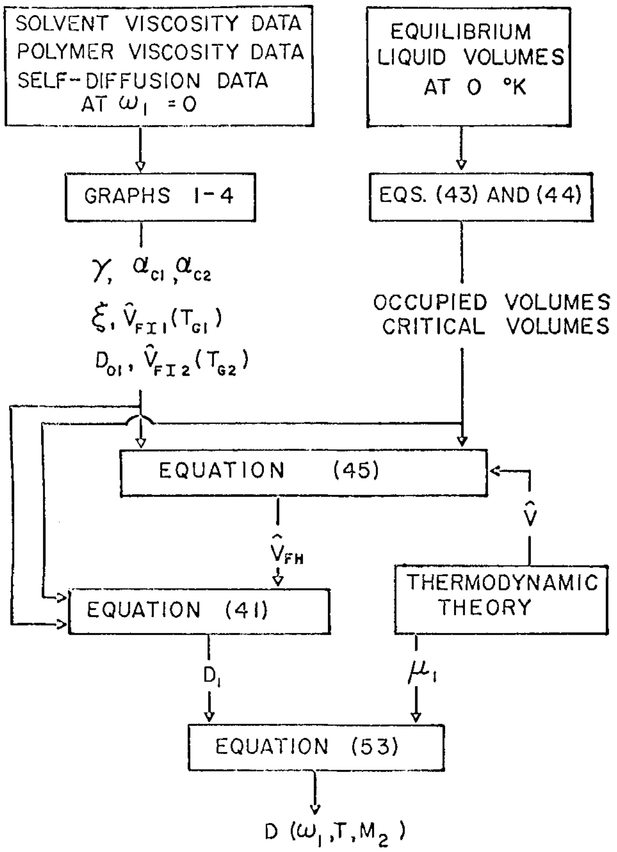

Fig. 12. Summary of predictive scheme for concentrated solutions.

Procedures for estimating equilibrium liquid volumes at 0°K for both polymers and simple liquids have been discussed by Haward (1970), and adequate estimates to $\hat{V}_1^\circ(0)$ and $\hat{V}_2^\circ(0)$ can usually be obtained. As a first approximation, it is reasonable to neglect the temperature dependence of α_{c1} and α_{c2}. Consequently, the theory has seven constants [D_{01}, γ, ξ, $\hat{V}_{FI1}(T_{G1})$, $\hat{V}_{FI2}(T_{G2})$, α_{c1}, and α_{c2}] which must be evaluated using viscosity and self-diffusion data. This is discussed in the next section. The additional information needed to carry out the calculation of D is the thermodynamic data, $\hat{V}$ and μ_1.

Density and chemical potential data are available for many polymer-solvent systems, since these data can be collected using conventional experiments. However, in most cases, only a limited amount of data is available, and a theory is required to correlate these data and predict the concentration and temperature variations of $\hat{V}$ and μ_1 over the complete range of interest. A variety of theories has been proposed for the prediction of the thermodynamic properties of the liquid state (Bondi, 1968; Flory, 1970; Bonner, 1975), but it is fair to conclude that no completely satisfactory theory is available at the present time. However, it is reasonable to expect that adequate estimates of $\hat{V}$ and μ_1 can be obtained from a number of the existing theories. It is beyond the scope of this review to evaluate the available theories and recommend a thermodynamic theory for utilization in the diffusivity calculations. Vrentas and Duda (1977b) used the Flory (1970) theory in the estimation of diffusion coefficients for the ethylbenzene-polystyrene system. This theory requires only a limited amount of mixture data in addition to extensive pure component data. Details of the application of the Flory theory in the estimation of the mutual diffusion coefficient are given elsewhere (Vrentas and Duda, 1977b).

One of the major deficiencies of the Flory theory is the variation of the characteristic parameters of the theory with temperature, but this leads to little difficulty for the present purpose since the properties of a mixture at a given temperature can be determined using the characteristic parameters appropriate to that temperature. The Flory theory may also be inappropriate for predicting properties of gas-liquid systems, since it fails at low densities. In such instances, other liquid models, such as the Ising fluid (Lacombe and Sanchez, 1976), may be more useful.

Since D_2 does not appear in the proposed approximate expression for D, there is no need to consider the variation of the effective entanglements in the system with temperature, concentration, and polymer molecular weight. The number of effective entanglements can be computed, if necessary, using the theory of Bueche (1962b), and details of this calculation are considered elsewhere (Vrentas and Duda, 1977b).

Evaluation of Constants of Free Volume Theory

It does not appear that the parameters of the free volume formulation can be determined directly from measurements which do not involve molecular transport. It is, however, possible to devise a procedure for evaluating these constants using pure component viscosity data and a small amount of self-diffusion data for a system consisting of a trace of solvent in the polymer. In light of Equation (53*b*), this latter set of data is also mutual diffusion data. The procedure for calculating the seven free volume parameters [D_{01}, γ, ξ, $\hat{V}_{FH1}(T_{G1})$, $\hat{V}_{FH2}(T_{G2})$, α_{c1}, and α_{c2}] from experimental measurements is outlined in Figure 12 and is discussed in detail elsewhere (Vrentas and Duda, 1977*b*). An important addition in this review is the introduction of a second method for the evaluation of D_{01}.

The determination of the free volume parameters is facilitated if the equations used to analyze the transport data are simplified by using an appropriate average value for each thermal expansion coefficient. The suggested procedure can be summarized as follows.

1. Choose a convenient reference temperature T_1 and construct a graph (graph 1) of $(T - T_1)/\ln[\eta_1(T_1)/\eta_1(T)]$ vs. $T - T_{G1}$ using viscosity data for the solvent. The slope S_1 and the intercept I_1 of this straight line plot are related to free volume parameters by the following equations:

$$S_1\gamma\hat{V}_1^* = \hat{V}_1^0(T_{G1})[T_1 - T_{G1}][\alpha_1 - \alpha_{c1}(1 - f_{H1}^G)] + \hat{V}_1^0(T_{G1})f_{H1}^G \quad (54)$$

$$I_1\alpha_1 - I_1\alpha_{c1}(1 - f_{H1}^G) - S_1 f_{H1}^G = 0 \quad (55)$$

The quantity f_{H1}^G, which is the fractional hole free volume of the solvent at its glass transition temperature, can be expressed in terms of $\hat{V}_{FH1}(T_{G1})$ using the result

$$\hat{V}_{FH1}(T_{G1}) = \hat{V}_1^0(T_{G1})[1 - f_{H1}^G] - \hat{V}_1^0(0) \quad (56)$$

and α_1 is an appropriate average value for the solvent thermal expansion coefficient over the temperature interval of interest. In the construction of graph 1, it is assumed that free volume theory adequately portrays the temperature dependence of η_1 at temperatures which are usually significantly above T_{G1}. Vrentas and Duda (1977*b*) concluded that ethylbenzene viscosity data could be described by a free volume equation in the range 160° to 400°K, which extends nearly 300°C above the estimated glass transition temperature of this solvent. However, Barlow et al. (1966) and Berry and Fox (1968) concluded that the temperature dependence of the viscosity of a simple liquid could not always be described over a wide temperature range by free volume theory. Each solvent must, of course, be treated individually, and low temperature viscosity data are critical in the determination of meaningful free volume constants. Finally, we note that estimation of T_{G1} is not always a simple matter.

2. Construct a graph (graph 2) of $(T - T_1)/\ln[\eta_2(T_1)/\eta_2(T)]$ vs. $T - T_{G2}$ using viscosity data for the polymer molecular weight of interest. The slope S_2 and the intercept I_2 of this straight line plot are related to the free volume parameters in the following manner:

$$S_2\gamma\hat{V}_2^* = \hat{V}_2^0(T_{G2})[T_1 - T_{G2}][\alpha_2 - \alpha_{c2}(1 - f_{H2}^G)] + \hat{V}_2^0(T_{G2})f_{H2}^G \quad (57)$$

$$I_2\alpha_2 - I_2\alpha_{c2}(1 - f_{H2}^G) - S_2 f_{H2}^G = 0 \quad (58)$$

The reference temperature T_1 for the polymer is, of course, generally different from that of the solvent, α_2 is again an average thermal expansion coefficient, and f_{H2}^G is defined by an equation similar to Equation (56).

3. Use mutual diffusion data in the limit of zero solvent concentration to construct a graph (graph 3) of $\ln D(\omega_1 = 0)$ vs. $1/(I_2/S_2 + T - T_{G2})$. The slope S_3 and intercept I_3 of this straight line plot are related to free volume parameters by

$$I_3 = \ln D_{01} \quad (59)$$

$$S_3 = -\frac{\xi}{S_2}\left[\frac{I_2}{S_2} + T_1 - T_{G2}\right] \quad (60)$$

4. As an alternative method for the calculation of D_{01}, convert the data for solvent viscosity to self-diffusion vs. temperature data using the following expression proposed by Dullien (1972):

$$\frac{\eta_1\tilde{V}_1 D_1(\omega_1 = 1)}{RT} = 0.124 \times 10^{-16}V_c^{2/3} \quad (61)$$

Construct a graph (graph 4) of $\ln D_1(\omega_1 = 1)$ vs. $1/(I_1/S_1 + T - T_{G1})$. The intercept I_4 is related to a free volume constant by the result

$$I_4 = \ln D_{01} \quad (62)$$

Obviously, either Equation (59) or Equation (62) can be used to evaluate D_{01}. The disadvantage in using Equation (59) is that it is based on mutual diffusion data (or, equivalently, self-diffusion data) for $\omega_1 = 0$, and there is some error in determining $D(\omega_1 = 0)$ from experimental data owing to the strong concentration dependence of D near $\omega_1 = 0$. On the other hand, Equation (62) follows from the application of free volume theory in a temperature region where its validity may be in question. Both equations are used below to predict diffusivities for the ethylbenzene-polystyrene system. Comparisons with experimental data indicate that, at least for this case, Equation (62) gives the better result.

Equations (54), (55), (57), (58), (60), and either Equation (59) or Equation (62) constitute a set of six equations for seven unknowns: α_{c1}, α_{c2}, f_{H1}^G [or $\hat{V}_{FH1}(T_{G1})$], f_{H2}^G [or $\hat{V}_{FH2}(T_{G2})$], γ, ξ, and D_{01}. The number of equations is one less than the number of unknowns because the first five of these constants appear as part of four groups, and only these four groups, rather than unique values of the five parameters, can be determined. As has been explained in detail elsewhere (Vrentas and Duda, 1977*b*), it can be shown that the individual values of the five parameters are, in general, not critical in the determination of D_1 as long as Equations (54), (55), (57), and (58) are satisfied. It is thus sufficient for most purposes to assign γ a value between one half and one and calculate α_{c1}, α_{c2}, f_{H1}^G, and f_{H2}^G using these four equations.

If Equation (62) is used to calculate D_{01}, then, in some instances, no mutual diffusion data will be needed to determine the free volume parameters. For two solvents diffusing in the same polymer, it is evident from the definition of ξ that the following relationship should hold:

$$\frac{\xi\ (\text{solvent 1})}{\xi\ (\text{solvent 2})} = \frac{\text{Molar Volume at } 0°\text{K (solvent 1)}}{\text{Molar Volume at } 0°\text{K (solvent 2)}} \quad (63)$$

Vrentas and Duda (1977*d*) examined the effect of solvent size on diffusion in polystyrene and concluded that the data satisfactorily follow Equation (63). Consequently, in principle, if mutual diffusion data are available for

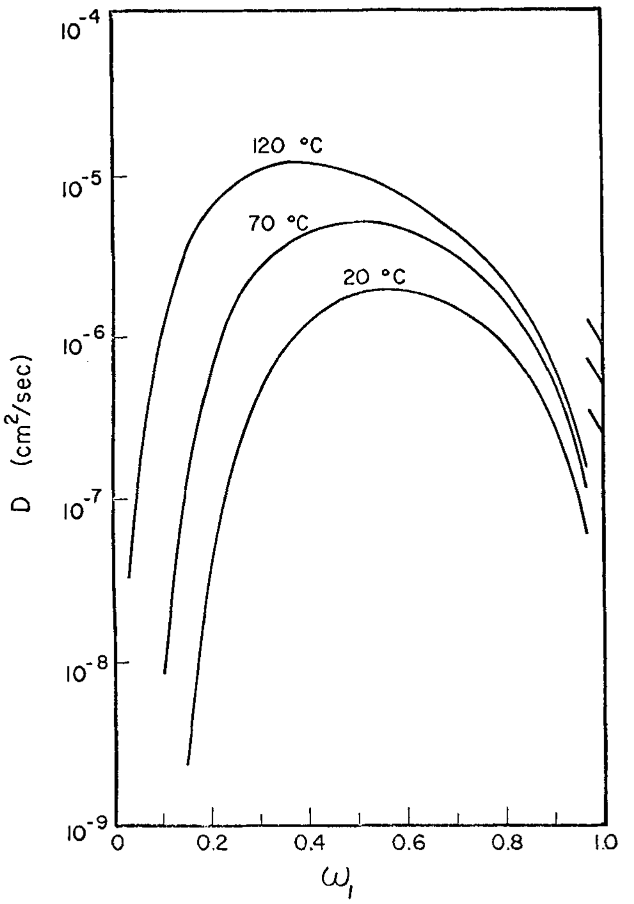

Fig. 13. Theoretical prediction of temperature and concentration dependence of D for ethylbenzene-polystyrene system with $M_2 = 3 \times 10^5$. The two sets of curves represent predictions of dilute solution and free volume theories.

a single solvent in a particular polymer, then ξ for any other solvent can be determined from Equation (63), and no mutual diffusion data would be needed for the second solvent. Equation (63) and, indeed, the entire development presented above are based on the assumption that the entire solvent molecule undergoes a jump in the transport process. This assumption is valid for sufficiently simple or spherically shaped molecules, but it is reasonable to expect that long, flexible, solvent molecules may have jumping units which constitute only a portion of the solvent molecule. Modification of the theory for solvents of this type is presently under consideration.

Predictions of the Free Volume Theory

Since estimates of the variation of D with temperature, concentration, and polymer molecular weight can be obtained for concentrated polymer solutions using the procedure outlined in Figure 12, it is useful to compare the predictions of the theory with the type of behavior usually observed for polymer-solvent systems. Also, a comparison between theory and experiment is carried out for the ethylbenzene-polystyrene system. Some of the pertinent predictions of the theory can be summarized as follows.

1. Figure 13 illustrates the strong temperature and concentration dependences of D for the ethylbenzene-polystyrene system, particularly at low temperatures and low solvent concentrations. This figure was constructed by combining predictions from free volume theory with those from dilute solution theory. Values of D_0 and k_D were determined using the value of B listed in Table 1 and ignoring the temperature variations of A and B.

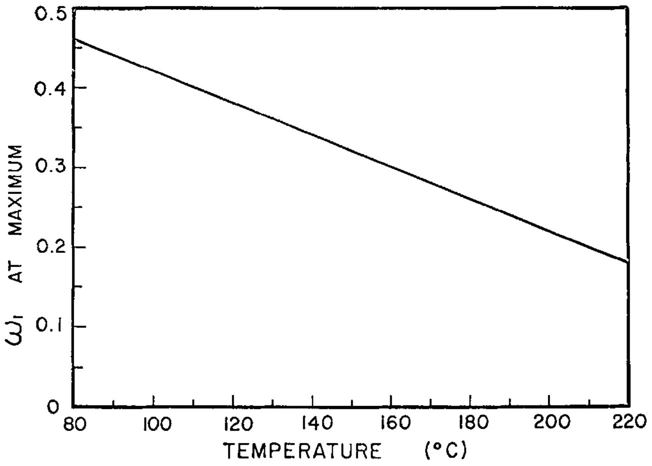

Fig. 14. Theoretical calculation of the temperature dependence of the maximum in D vs. ω_1 curve for ethylbenzene-polystyrene system with $M_2 = 3 \times 10^5$.

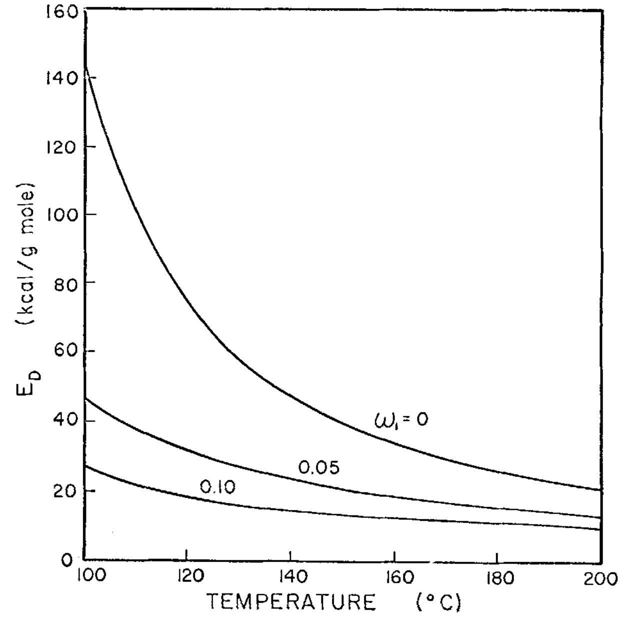

Fig. 15. Theoretical prediction of the temperature and concentration dependence of the diffusion activation energy for ethylbenzene-polystyrene system with $M_2 = 3 \times 10^5$.

It is clear from this figure that the predictions of the two regions do not meet at the transition concentration. Either the theoretical predictions in one or both regions are somewhat in error or there exists an intermediate region which can not be described by either theory. In the latter case, there would be a curve which presumably would smoothly join the two regions. Unfortunately, very few data exist near the transition concentration, and it is not possible to say whether there is a flattening of the diffusivity-concentration curve past the dilute region. At present, it is possible to construct an empirical interpolation between the predictions of the dilute and concentrated regions.

It is also evident from this figure that D assumes a maximum value in the concentration interval, and this maximum shifts to smaller solvent concentrations as the temperature increases. The temperature dependence of the maximum in the D vs. ω_1 curve is depicted in Figure 14 for the ethylbenzene-polystyrene system. The strong temperature and concentration dependences are well known (Fujita et al., 1960; Fujita, 1961, 1968), and the appearance of a maximum has been observed experi-

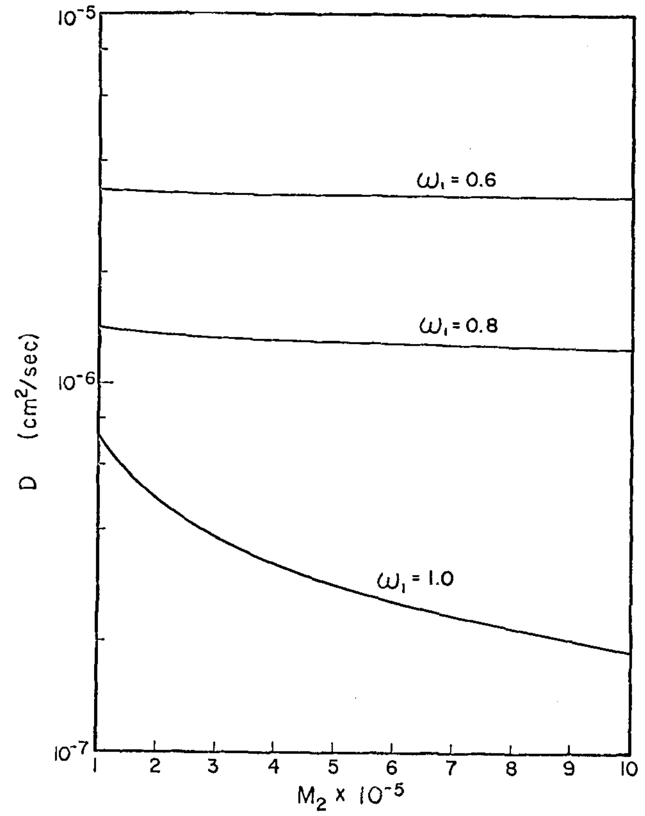

Fig. 16. Theoretical calculation of the variation of D with polymer molecular weight for ethylbenzene-polystyrene system at 50°C.

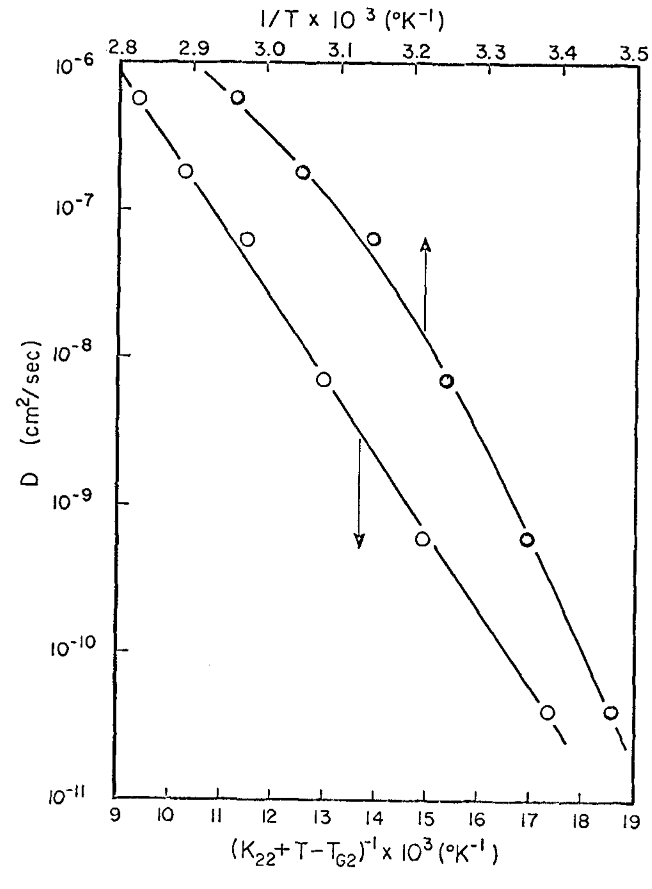

Fig. 17. Temperature dependence of D at zero solvent concentration for ethyl acetate-polymethyl acrylate system (Fujita, 1968). The data are satisfactorily described by free volume theory but not by an equation of the Arrhenius type.

mentally for polystyrene-solvent systems by Chalykh and Vasenin (1966) and by Rehage et al. (1970). In both of these investigations, it was also observed that the maximum in the diffusivity-concentration curve shifts to lower diluent mass fractions with increasing temperature.

2. Figure 15 illustrates the temperature and concentration dependences of the effective activation energy for diffusion in an ethylbenzene-polystyrene mixture. This activation energy is defined by the expression

$$E_D = RT^2\left(\frac{\partial \ln D}{\partial T}\right)_{p,\omega_1} \tag{64}$$

In the limit of zero solvent mass fraction, the activation energy assumes very high values and decreases significantly as the temperature is increased. The activation energy decreases with increasing solvent concentration at a particular temperature, and the change of activation energy with temperature becomes relatively small at the higher solvent mass fractions. Again, these predictions of the theory are in accord with what is observed experimentally (Rehage et al., 1970).

3. The variation of D with polymer molecular weight is illustrated in Figure 16 for the ethylbenzene-polystyrene system at 50°C. The mutual diffusion coefficient exhibits a negligible dependence on the molecular weight of the polymer, except near $\omega_1 = 1$, where there is an appreciable molecular weight dependence as required by dilute solution diffusion theory.

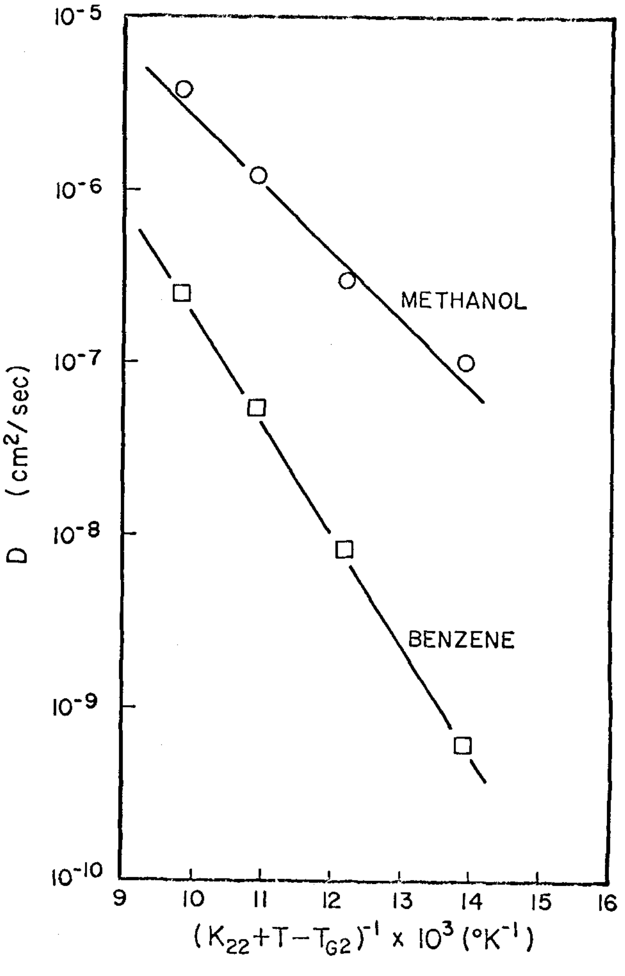

Fig. 18. Temperature dependence of D at zero solvent concentration for methanol and benzene diffusing in polymethyl acrylate (Fujita, 1968). The data are satisfactorily described by free volume theory.

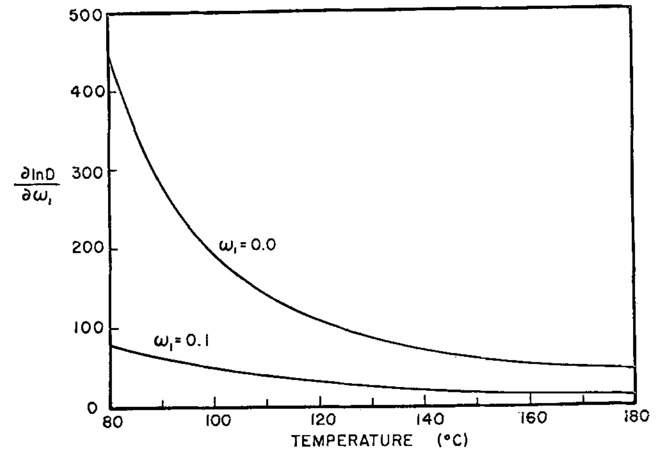

Fig. 19. Theoretical calculation of the concentration and temperature variations of the concentration dependence of D for ethylbenzene-polystyrene system with $M_2 = 3 \times 10^5$.

4. The temperature dependences of the mutual diffusion coefficients for three solvents in polymethyl acrylate (Fujita, 1968) at zero solvent concentration are considered in Figures 17 and 18. From Figure 17 and from other data (Lundberg et al., 1963; Vrentas and Duda, 1977*d*), it is evident that the temperature dependence of $D(\omega_1 = 0)$ for a polymer-solvent system can not generally be described by an equation of the Arrhenius type, particularly at temperatures relatively close to the glass transition temperature of the polymer. However, the new version of free volume theory predicts that plots of $\ln D(\omega_1 = 0)$ vs. $1/(K_{22} + T - T_{G2})$ should lead to straight lines (Vrentas and Duda, 1977*d*). Here, $K_{22} = I_2/S_2$ is a fundamental free volume parameter. It is evident from Figures 17 and 18 that the data are well represented by the straight line relationship predicted by free volume theory. The same conclusion was reached by Vrentas and Duda (1977*d*) for diffusivity data for a number of polystyrene-solvent systems.

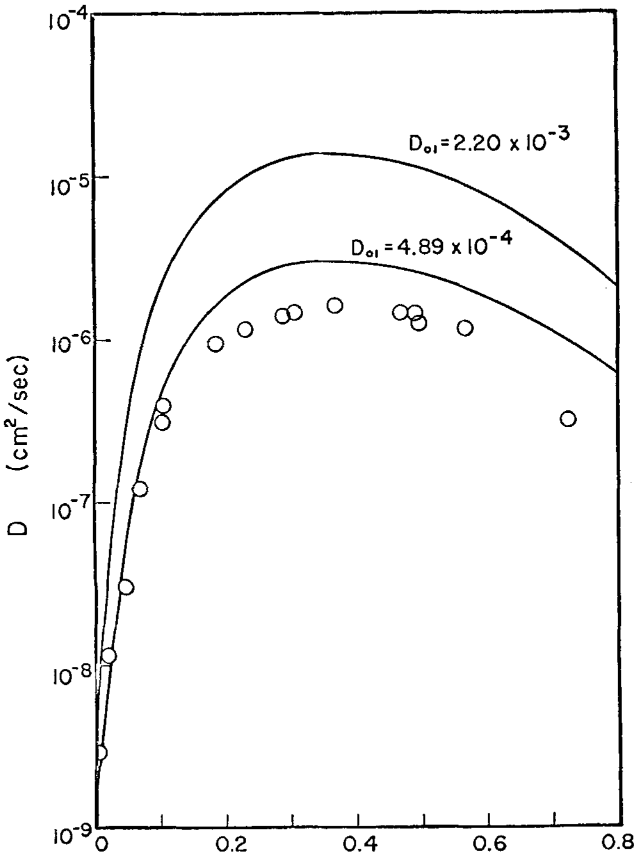

Fig. 20. Comparison of data with theory for ethylbenzene-polystyrene system at 130°C. For lower theoretical curve, D_{01} was calculated using Equation (62) and, for upper theoretical curve, D_{01} was calculated using Equation (59).

5. Meares (1954, 1957) measured diffusion coefficients for seven gases in polyvinyl acetate just above the glass transition temperature of the polymer and concluded that plots of the logarithm of $D(\omega_1 = 0)$ vs. $1/T$ were linear so that the activation energy for diffusion of each of the gases is independent of temperature. However, it can be easily shown that free volume theory does not predict an Arrhenius relationship for the temperature dependence of the diffusion coefficient at zero mass fraction of solvent, particularly at temperatures relatively close to the glass temperature of the polymer. Vrentas and Duda (1976*d*) have pointed out that the data of Meares are not necessarily inconsistent with the new version of free volume theory by showing that Arrenhius type of behavior is approached for sufficiently small temperature intervals, for small solvents, and for temperature intervals sufficiently far above the glass temperature of the polymer.

6. Fujita (1961) has noted that experimental data show that the concentration dependence of D at a given temperature generally decreases with increasing concentration near $\omega_1 = 0$. Furthermore, at the same value of concentration, the variation of experimentally determined diffusion coefficients with concentration decreases with increasing temperature. This behavior is predicted by the present version of free volume theory, as is shown in Figure 19, using calculations for the ethylbenzene-polystyrene system.

7. Fujita (1961) has also noted the difference which exists between the diffusional behavior of organic solvents and of water in amorphous polymers. The mutual diffusion coefficient for an organic solvent exhibits a strong dependence on concentration near $\omega_1 = 0$ just above the polymer glass temperature (Fujita, 1961), whereas diffusivities for water-polymer systems show little or no concentration dependence (Kishimoto et al., 1960; Fujita, 1961). Fujita further noted that this behavior could not be explained by his version of the free volume theory. Vrentas and Duda (1976*d*) have shown, however, that the new version of free volume theory predicts that the concentration dependence of D near $\omega_1 = 0$ is dependent on the ratio M_1/M_j; small values of this ratio mean a small variation of D with concentration near $\omega_1 = 0$. For organic solvents, it is reasonable to expect that the molecular weight of the solvent is relatively close to that of the polymeric jumping unit, since the polymer is often formed from a monomer which itself is an organic solvent. On the other hand, for small molecules of low molecular weight, M_1 will be significantly less than M_j. Thus, the modified free volume theory predicts a strong concentration dependence of D for organic solvents and a weak dependence for small penetrants like water, and this is just what has been observed. The theory of Fujita does not describe the behavior of low molecular weight penetrants because this theory incorporates the assumption $M_1 = M_j$.

8. In Figure 20, the predictions of the theory are compared with experimental data for the ethylbenzene-polystyrene system at 130°C (Duda et al., 1978). The prediction using a value of D_{01} calculated from Equation (62) is better than the theoretical curve based on a value of D_{01} computed using Equation (59). The agreement is very encouraging, although the theory is not

completely satisfactory. It should be noted that these predictions cover a concentration range where the diffusion coefficient changes by nearly three orders of magnitude, and the theory uses only limited diffusivity data at infinite solvent dilution. Furthermore, the estimation of mutual diffusion coefficients is particularly difficult because it is necessary to utilize a theory of molecular transport in liquids in conjunction with a thermodynamic theory for the liquid state. Some effort should be expended in separating the errors introduced by the free volume and thermodynamic theories. Finally, we note that there appears to be no other available theory which can even qualitatively predict the experimentally observed diffusion behavior for polymer-solvent systems over large concentration intervals.

CONCLUDING REMARKS

In this review, methods have been recommended for estimating the concentration, temperature, and molecular weight dependence of diffusion coefficients in amorphous polymer-solvent systems. Owing to the complexity of molecular transport in such systems, these methods are necessarily based on approximate theories of molecular diffusion. Consequently, more reliable diffusivity data are needed so that the predictive methods discussed here can be evaluated and improvements can be made where necessary. The recommended predictive methods must be considered as tentative until comprehensive comparisons with data are carried out.

ACKNOWLEDGMENT

This work was supported by the National Science Foundation Grant ENG 74-23095.

NOTATION

a = bond or segment length in polymer chain
a_o = radius of sphere composed of polymer and trapped solvent, defined by Equation (33)
A = parameter of two-parameter theory defined by Equation (9)
A_o = preexponential factor in Equation (42)
A_o^* = parameter defined by Equation (34)
A_2 = second virial coefficient for dilute polymer solution
b_1 = coefficient in series given by Equation (27)
B = parameter of two-parameter theory
D = binary mutual diffusion coefficient
D_I = self-diffusion coefficient of component I
D^* = diffusion coefficient for process defined by Equation (4)
D_o = mutual diffusion coefficient at zero polymer concentration
$(D_o)_\theta$ = mutual diffusion coefficient at infinite polymer dilution for a theta solution
D_1^* = quantity defined by Equation (52)
$\overline{D}_o$ = preexponential factor for Equation (38)
$\overline{D}_{o1}$ = preexponential factor for Equation (39)
D_{o1} = preexponential factor for Equation (40)
$(DEB)_D$ = diffusion Deborah number defined by Equation (1)
E_D = activation energy for diffusion
E^* = critical energy per molecule needed to overcome attractive forces
f_{12} = friction coefficient of polymer molecule defined by Equation (36)
$(f_{12})_o$ = friction coefficient at zero polymer concentration
f_{HI}^{G} = fractional hole free volume of component I at its glass transition temperature
G = shear relaxation modulus
$h_o(\bar{z})$ = quantity defined by Equation (30)
I_I = intercept for graph I
k = gas constant per molecule
k_D = coefficient in series given by Equation (6)
k_S = coefficient in series given by Equation (26)
K = quantity defined by Equation (35)
K' = intrinsic viscosity parameter defined by Equation (14)
K_{22} = fundamental free volume parameter
L = thickness of polymer film
M_1 = molecular weight of solvent
M_2 = molecular weight of polymer
M_j = molecular weight of polymer jumping unit
n = number of bonds or segments in chain
N = number of freely orienting segments in polymer chain
N^* = effective number of segments in polymer chain
N_A = Avogadro's number
p = pressure
R = gas constant per mole
$<R^2>$ = mean-square end-to-end distance of polymer chain
$<R^2>_o$ = mean-square end-to-end distance of unperturbed chain
$<S^2>$ = mean-square radius of gyration
$<S^2>_o$ = mean-square radius of gyration of unperturbed chain
S_I = slope for graph I
T = temperature
T_1 = reference temperature for viscosity data
T_o = reference temperature for mean relaxation time
T_{GI} = glass transition temperature of component I
u_I = velocity of component I with respect to a convenient reference frame
$\hat{V}$ = specific volume of mixture
$\hat{V}_I$ = partial specific volume of component I
$\hat{V}_I^o$ = specific volume of pure component I
$\hat{V}_I^o(0)$ = specific volume of pure component I at 0°K
$\hat{V}_I^o(T_{GI})$ = specific volume of pure component I at its glass transition temperature
$\hat{V}_2^o$ = specific volume of pure polymer
$\hat{V}_{20}$ = partial specific volume of polymer at zero polymer concentration
$\overline{V_I^*}$ = critical hole free volume of component I per molecule
$\hat{V}_I^*$ = specific critical hole free volume of component I required for a jump
$\overline{V}_{FH}$ = average hole free volume per molecule
$\hat{V}_{FH}$ = average hole free volume per gram of mixture
$\hat{V}_{FII}(T_{GI})$ = specific interstitial free volume of component I at T_{GI}
$\tilde{V}_1$ = molar volume of solvent
V_c = molar volume of solvent at its critical temperature
x_I = mole fraction of component I
X = quantity defined by Equation (17)
z = quantity defined by Equation (13)
$\bar{z}$ = quantity defined by Equation (29)

Greek Letters

α_I = thermal expansion coefficient for component I
α_{CI} = thermal expansion coefficient for component I for the sum of the specific occupied volume and the specific interstitial free volume

α_f = expansion factor defined by Equation (21)
α_η = expansion factor defined by Equation (19)
α_S = linear expansion factor for polymer chain defined by Equation (10)
γ = overlap factor for free volume
ζ = translational friction coefficient of chain segment
ζ_{IJ} = friction coefficient
η_I = viscosity of component I
$[\eta]$ = intrinsic viscosity
$[\eta]_\theta$ = intrinsic viscosity for theta solution
θ_D = characteristic diffusion time
λ_m = characteristic time of fluid
λ_{mo} = mean relaxation time at reference conditions
μ_1 = chemical potential of solvent per mole
ν = intrinsic viscosity parameter defined by Equation (14)
ξ = $\hat{V}_1{}^*M_1/\hat{V}_2{}^*M_j$
ρ_I = mass density of component I
$\phi_2{}^*$ = transition volume fraction of polymer
Φ_o = constant of intrinsic viscosity theory
ω_I = mass fraction of component I
ω_{10} = reference mass fraction for mean relaxation time
$\omega_2{}^*$ = transition mass fraction of polymer

Subscripts

1 = solvent
2 = polymer

LITERATURE CITED

Adam, G., and J. H. Gibbs, "On the Temperature Dependence of Cooperative Relaxation Properties in Glass-Forming Liquids," *J. Chem. Phys.*, 43, 139 (1965).

Akovali, G., "Viscoelastic Properties of Polystyrene," *J. Polymer Sci. A-2*, 5, 875 (1967).

Alfrey, T., "Glassy Polymer Diffusion," *Chem. Eng. News*, 43, No. 41, 64 (1965).

———, E. F. Gurnee, and W. G. Lloyd, "Diffusion in Glassy Polymers," *J. Polymer Sci.*, C12, 249 (1966).

Assink, R. A., "The Concentration and Pressure Dependence of the Diffusion of Dichlorodifluoromethane in Poly(dimethyl Siloxane)," *J. Polymer Sci., Polymer Phys. Ed.*, 15, 227 (1977).

Astarita, G., and G. Marrucci, *Principles of Non-Newtonian Fluid Mechanics*, McGraw-Hill, London, England (1974).

Barlow, A. J., J. Lamb, and A. J. Matheson, "Viscous Behavior of Supercooled Liquids," *Proc. Royal Soc.*, A292, 322 (1966).

Barrer, R. M., "Some Properties of Diffusion Coefficients in Polymers," *J. Phys. Chem.*, 61, 178 (1957).

———, "Diffusion and Permeation in Heterogeneous Media," in *Diffusion in Polymers*, J. Crank and G. S. Park, ed., Academic Press, New York (1968).

Batschinski, A. J., "Investigations of the Internal Friction of Fluids," *Z. phys. Chem.*, 84, 643 (1913).

Bearman, R. J., "On the Molecular Basis of Some Current Theories of Diffusion," *J. Phys. Chem.*, 65, 1961 (1961).

Berry, G. C., "Thermodynamic and Conformational Properties of Polystyrene. I. Light-Scattering Studies on Dilute Solutions of Linear Polystyrenes," *J. Chem. Phys.*, 44, 4550 (1966).

———, "Thermodynamic and Conformational Properties of Polystyrene. II. Intrinsic Viscosity Studies on Dilute Solutions of Linear Polystyrenes," *ibid.*, 46, 1338 (1967).

———, and E. F. Casassa, "Thermodynamic and Hydrodynamic Behavior of Dilute Polymer Solutions," *Macromol. Rev.*, 4, 1 (1970).

Berry, G. C., and T. G. Fox, "The Viscosity of Polymers and Their Concentrated Solutions," *Adv. Polymer Sci.*, 5, 261 (1968).

Billmeyer, F. W., *Textbook of Polymer Science*, 2 ed., Wiley, New York (1971).

Bondi, A., *Physical Properties of Molecular Crystals, Liquids, and Glasses*, Wiley, New York (1968).

Bonner, D. C., "Vapor-Liquid Equilibria in Concentrated Polymer Solutions," *J. Macromol. Sci., Revs. Macromol. Chem.*, C13, 263 (1975).

Boyer, R. F., "Physical Properties of Styrene Polymers-Glass Transition," in *Encyclopedia of Polymer Science and Technology*, Vol. 13, pp. 309-326, Wiley, New York (1970).

Brandt, W. W., "Model Calculation of the Temperature Dependence of Small Molecule Diffusion in High Polymers," *J. Phys. Chem.*, 63, 1080 (1959).

Bueche, F., "Segmental Mobility of Polymers Near Their Glass Temperature," *J. Chem. Phys.*, 21, 1850 (1953).

———, "Rate and Pressure Effects in Polymers and Other Glass-Forming Substances," *ibid.*, 36, 2940 (1962*a*).

———, *Physical Properties of Polymers*, Interscience, New York (1962*b*).

Cantow, H. J., "Determination of the Molecular-Weight Distribution in the Ultracentrifuge at θ—Temperature," *Makromol. Chem.*, 30, 169 (1959).

Chalykh, A. Y., and R. M. Vasenin, "Diffusion in Polymer-Solvent Systems," *Polymer Science USSR*, 8, 2107 (1966).

Chung, H. S., "On the Macedo-Litovitz Hybrid Equation for Liquid Viscosity," *J. Chem. Phys.*, 44, 1362 (1966).

Cohen, M. H., and D. Turnbull, "Molecular Transport in Liquids and Glasses," *ibid.*, 31, 1164 (1959).

Cowie, J. M. G., and E. L. Cussler, "Frictional Behavior of Polystyrene," *ibid.*, 46, 4886 (1967).

DiBenedetto, A. T., "Molecular Properties of Amorphous High Polymers. II. An Interpretation of Gaseous Diffusion Through Polymers," *J. Polymer Sci.*, A1, 3477 (1963).

———, and D. R. Paul, "An Interpretation of Gaseous Diffusion Through Polymers Using Fluctuation Theory," *ibid.*, A2, 1001 (1964).

Doolittle, A. K., "Studies in Newtonian Flow. II. The Dependence of the Viscosity of Liquids on Free-Space," *J. Appl. Phys.*, 22, 1471 (1951).

———, "Studies in Newtonian Flow. III. The Dependence of the Viscosity of Liquids on Molecular Weight and Free Space (In Homologous Series)," *ibid.*, 23, 236 (1952).

———, and D. B. Doolittle, "Studies in Newtonian Flow. V. Further Verification of the Free-Space Viscosity Equation," *ibid.*, 28, 901 (1957).

Duda, J. L., and J. S. Vrentas, "Physical Properties of Styrene Polymers—Diffusion," in *Encyclopedia of Polymer Science and Technology*, Vol. 13, pp. 326-342, Wiley, New York (1970).

Duda, J. L., Y. C. Ni, and J. S. Vrentas, "Diffusion of Ethylbenzene in Molten Polystyrene," *J. Appl. Polymer Sci.*, 22, 689 (1978).

Dullien, F. A. L., "Predictive Equations for Self-Diffusion in Liquids: a Different Approach," *AIChE J.*, 18, 62 (1972).

Fixman, M., "General Theory of Polymer Solutions," *J. Chem. Phys.*, 35, 889 (1961).

———, "Dynamics of Polymer Chains," *ibid.*, 42, 3831 (1965).

———, and J. M. Peterson, "Dimensions of Polymer Molecules in Concentrated Solutions," *J. Am. Chem. Soc.*, 86, 3524 (1964).

Flory, P. J., *Statistical Mechanics of Chain Molecules*, Wiley, New York (1969).

———, "Thermodynamics of Polymer Solutions," *Disc. Faraday Soc.*, 49, 7 (1970).

Ford, N. C., F. E. Karasz, and J. E. M. Owen, "Rayleigh Scattering from Polystyrene Solutions," *ibid.*, 228 (1970).

Frost, R. A., and D. Caroline, "Diffusion of Polystyrene in a Theta Mixed Solvent (Benzene-2-Propanol) by Photon-Correlation Spectroscopy," *Macromolecules*, 10, 616 (1977).

Fujita, H., "Diffusion in Polymer-Diluent Systems," *Fortschr. Hochpolym.-Forsch.*, 3, 1 (1961).

———, "Organic Vapors Above the Glass Transition Temperature," in *Diffusion in Polymers*, J. Crank and G. S. Park, ed., Academic Press, New York (1968).

———, A. Kishimoto, and K. Matsumoto, "Concentration and Temperature Dependence of Diffusion Coefficients for Systems Polymethyl Acrylate and n-Alkyl Acetates," *Trans. Faraday Soc.*, 56, 424 (1960).

Haward, R. N., "Occupied Volume of Liquids and Polymers," *J. Macromol. Sci., Revs. Macromol. Chem.*, C4, 191 (1970).

Hopfenberg, H. B., and H. L. Frisch, "Transport of Organic Micromolecules in Amorphous Polymers," *J. Polymer Sci.*, B7, 405 (1969).

Hopfenberg, H. B., and V. Stannett, "The Diffusion and

Sorption of Gases and Vapours in Glassy Polymers," in *The Physics of Glassy Polymers*, R. N. Haward, ed., Wiley, New York (1973).

Imai, S., "Concentration Dependency of the Sedimentation Constant," *J. Chem. Phys.*, **50**, 2116 (1969).

Jacob, M., R. Varoqui, S. Klenine, and M. Daune, "Measurements of Translational Diffusion and Sedimentation of Macromolecules in θ Solvent. Concentration and Velocity Effects," *J. Chim. Phys.*, **59**, 865 (1962).

Kaelble, D. H., "Free Volume and Polymer Rheology," in *Rheology*, F. R. Eirich, ed., Vol. 5, Academic Press, New York (1969).

King, T. A., A. Knox, W. I. Lee, and J. D. G. McAdam, "Polymer Translational Diffusion: 1. Dilute Theta Solutions, Polystyrene in Cyclohexane," *Polymer*, **14**, 151 (1973*a*).

King, T. A., A. Knox, and J. D. G. McAdam, "Polymer Translational Diffusion: 2. Non-theta Solutions, Polystyrene in Butan-2-one," *ibid.*, 293 (1973*b*).

Kirkwood, J. G., and J. Riseman, "The Intrinsic Viscosities and Diffusion Constants of Flexible Macromolecules in Solution," *J. Chem. Phys.*, **16**, 565 (1948).

Kishimoto, A., E. Maekawa, and H. Fujita, "Diffusion Coefficients for Amorphous Polymer and Water Systems," *Bull. Chem. Soc. Japan*, **33**, 988 (1960).

Klärner, P. E. O., and H. A. Ende, "Sedimentation Coefficients, Diffusion Coefficients, Partial Specific Volumes, Frictional Ratios and Second Virial Coefficients of Polymers in Solution," in *Polymer Handbook*, 2 ed., J. Brandrup and E. H. Immergut, ed., Wiley, New York (1975).

Krigbaum, W. R., and P. J. Flory, "Molecular Weight Dependence of the Intrinsic Viscosity of Polymer Solutions. II," *J. Polymer Sci.*, **11**, 37 (1953).

Kumins, C. A., and T. K. Kwei, "Free Volume and Other Theories," in *Diffusion in Polymers*, J. Crank and G. S. Park, ed., Academic Press, New York (1968).

Kurata, M., and W. H. Stockmayer, "Intrinsic Viscosities and Unperturbed Dimensions of Long Chain Molecules," *Fortschr. Hochpolym.-Forsch.*, **3**, 196 (1963).

Kurata, M., M. Fukatsu, H. Sotobayashi, and H. Yamakawa, "Second Virial Coefficient of Linear Polymer Molecules," *J. Chem. Phys.*, **41**, 139 (1964).

Kurata, M., Y. Tsunashima, M. Iwama, and K. Kamada, "Viscosity-Molecular Weight Relationships and Unperturbed Dimensions of Linear Chain Molecules," in *Polymer Handbook*, 2 ed., J. Brandrup and E. H. Immergut, ed., Wiley, New York (1975).

Lacharojana, S., and D. Caroline, "Diffusion of Polystyrene in Binary Solvents Near the Theta State," *Macromolecules*, **10**, 365 (1977).

Lacombe, R. H., and I. C. Sanchez, "Statistical Thermodynamics of Fluid Mixtures," *J. Phys. Chem.*, **80**, 2568 (1976).

Loflin, T., and E. McLaughlin, "Diffusion in Binary Liquid Mixtures," *ibid.*, **73**, 186 (1969).

Lundberg, J. L., M. B. Wilk, and M. J. Huyett, "Sorption Studies Using Automation and Computation," *Ind. Eng. Chem. Fundamentals*, **2**, 37 (1963).

Macedo, P. B., and T. A. Litovitz, "On the Relative Roles of Free Volume and Activation Energy in the Viscosity of Liquids," *J. Chem. Phys.*, **42**, 245 (1965).

Machin, D., and C. E. Rogers, "Free Volume Theories for Penetrant Diffusion in Polymers," *Die Makromolekulare Chemie*, **155**, 269 (1972).

Markovitz, H., ed., *Polymers in the Engineering Curriculum*, Carnegie Press, Pittsburgh, Pa. (1971).

Markovitz, H., ed., *Report of Workshop on Polymeric Materials*, University Park (1972).

Matsumoto, T., N. Nishioka, and H. Fujita, "Excluded-Volume Effects in Dilute Polymer Solutions. IV. Polyisobutylene," *J. Polymer Sci. A-2*, **10**, 23 (1972).

McCall, D. W., and D. C. Douglass, "Diffusion in Binary Solutions," *J. Phys. Chem.*, **71**, 987 (1967).

McDonnell, M. E., and A. M. Jamieson, "Quasielastic Light-Scattering Measurements of Diffusion Coefficients in Polystyrene Solutions," *J. Macromol. Sci., Phys.*, **B13**, 67 (1977).

Meares, P., "The Diffusion of Gases Through Polyvinyl Acetate," *J. Am. Chem. Soc.*, **76**, 3415 (1954).

———, "The Diffusion of Gases in Polyvinyl Acetate in Relation to the Second-Order Transition," *Trans. Faraday Soc.*, **53**, 101 (1957).

———, "Diffusion of Alkyl Chloride in Polyvinyl Acetate. Part I. The Steady State of Permeation," *J. Polymer Sci.*, **27**, 391 (1958).

Meyerhoff, G., and K. Nachtigall, "Diffusion, Thermodiffusion, and Thermal Diffusion of Polystyrene in Solution," *J. Polymer Sci.*, **57**, 227 (1962).

Naghizadeh, J., "Diffusion and Glass Transition in Simple Liquids," *J. Appl. Phys.*, **35**, 1162 (1964).

Odani, H., "Diffusion in Glassy Polymers. IV. Diffusion of Methyl Ethyl Ketone in Atactic Polystyrene Above the Critical Concentration," *J. Polymer Sci. A-2*, **5**, 1189 (1967).

Park, G. S., "The Glassy State and Slow Process Anomalies," in *Diffusion in Polymers*, J. Crank and G. S. Park, ed., Academic Press, New York (1968).

Pyun, C. W., and M. Fixman, "Frictional Coefficient of Polymer Molecules in Solution," *J. Chem. Phys.*, **41**, 937 (1964).

Rehage, G., O. Ernst, and J. Fuhrmann, "Fickian and Non-Fickian Diffusion in High Polymer Systems," *Disc. Faraday Soc.*, **49**, 208 (1970).

Rice, S. A., and A. R. Allnatt, "Approximate Theory of Transport in Simple Dense Fluid Mixtures," *J. Chem. Phys.*, **34**, 409 (1961).

Rudin, A., and H. K. Johnston, "Diffusion Coefficients and Intrinsic Viscosities of Polymers," *J. Polymer Sci.*, **B9**, 55 (1971).

Stannett, V., "Simple Gases," in *Diffusion in Polymers*, J. Crank and G. S. Park, ed., Academic Press, New York (1968).

Tsvetkov, V. N., and S. I. Klenin, "A Study of Diffusion in Polymer Solutions by the Use of the Polarization Interferometer," *J. Polymer Sci.*, **30**, 187 (1958).

Turnbull, D., and M. H. Cohen, "Free-Volume Model of the Amorphous Phase: Glass Transition," *J. Chem. Phys.*, **34**, 120 (1961).

————————, "On the Free-Volume Model of the Liquid-Glass Transition," *ibid.*, **52**, 3038 (1970).

Van Krevelen, D. W., *Properties of Polymers*, Elsevier, Amsterdam (1972).

Vrentas, J. S., C. M. Jarzebski, and J. L. Duda, "A Deborah Number for Diffusion in Polymer-Solvent Systems," *AIChE J.*, **21**, 894 (1975).

Vrentas, J. S., and J. L. Duda, "Diffusion in Infinitely Dilute Polystyrene Solutions," *J. Appl. Polymer Sci.*, **20**, 1125 (1976*a*).

————————, "Diffusion in Dilute Polystyrene Solutions," *J. Polymer Sci., Polymer Phys. Ed.*, **14**, 101 (1976*b*).

————————, "On Relationships Between Diffusion and Friction Coefficients," *J. Appl. Polymer Sci.*, **20**, 2569 (1976*c*).

————————, "Diffusion of Small Molecules in Amorphous Polymers," *Macromolecules*, **9**, 785 (1976*d*).

————————, "Diffusion in Polymer-Solvent Systems. I. Reexamination of the Free-Volume Theory," *J. Polymer Sci., Polymer Phys. Ed.*, **15**, 403 (1977*a*).

————————, "Diffusion in Polymer-Solvent Systems. II. A Predictive Theory for the Dependence of Diffusion Coefficients on Temperature, Concentration, and Molecular Weight," *ibid.*, 417 (1977*b*).

————————, "Diffusion in Polymer-Solvent Systems. III. Construction of Deborah Number Diagrams," *ibid.*, 441 (1977*c*).

————————, "Solvent and Temperature Effects on Diffusion in Polymer-Solvent Systems," *J. Appl. Polymer Sci.*, **21**, 1715 (1977*d*).

————————, "A Free-Volume Interpretation of the Influence of the Glass Transition on Diffusion in Amorphous Polymers," *ibid.*, **22**, 2325 (1978).

Williams, M. C., "Stresses in Concentrated Polymer Solutions: Part I. Shear Dependence of Viscosity," *AIChE J.*, **12**, 1064 (1966).

Yamakawa, H., "Concentration Dependence of the Frictional Coefficient of Polymers in Solution," *J. Chem. Phys.*, **36**, 2995 (1962).

———, and G. Tanaka, "Excluded-Volume Effects in Linear Polymer Chains: A Hierarchy of Differential Equations," *ibid.*, **47**, 3991 (1967).

Yamakawa, H., "Correlations Between the Excluded Volumes and the Second Virial Coefficients of Linear Polymer Chains," *ibid.*, 48, 2103 (1968).

———, *Modern Theory of Polymer Solutions*, Harper and Row, New York (1971).

———, "Excluded Volume Effects and Binary Cluster Integrals in Dilute Polymer Solutions," *Pure Appl. Chem.*, 31, 179 (1972).

———, and M. Fujii, "Binary Cluster Integrals in the Theory of Dilute Polymer Solutions," *J. Chem. Phys.*, 58, 1523 (1973).

Zhurkov, S. N., and G. Ya. Ryskin, "Diffusion in Polymers," *J. Tech. Phys. (USSR)*, 24, 797 (1954).

Zwanzig, R., J. Kiefer, and G. H. Weiss, "On the Validity of the Kirkwood-Riseman Theory," *Proc. Natl. Acad. Sci. U.S.*, 60, 381 (1968).

THE AUTHORS

James Vrentas received his B.S. from the University of Illinois and his M.Ch.E. and Ph.D. from the University of Delaware. He worked for the Dow Chemical Company from 1963-1972 and in 1972 joined the faculty of the Illinois Institute of Technology. His research interests include diffusion, fluid mechanics, transport phenomena, and applied mathematics.

Larry Duda received his B.S. from Case Institute of Technology and his M Ch.E. and Ph.D. from the University of Delaware. He worked for the Dow Chemical Company from 1963-1971 and in 1971 joined the faculty of the Pennsylvania State University. His research interests include diffusion, fluid mechanics, transport phenomena, and enhanced oil recovery.

Manuscript received March 31, 1978; revision received September 22, and accepted October 5, 1978.

Experimental Evaluation of Analytical and Smith Predictors for Distillation Column Control

C. B. G. MEYER
R. K. WOOD
and
D. E. SEBORG
Department of Chemical Engineering
University of Alberta
Edmonton, Alberta, Canada T6G 2G6

Two time delay compensation techniques, the Smith predictor and the analytical predictor, are used for bottom composition control of a pilot scale methanol-water distillation column. The closed-loop performance of the two predictor schemes is compared to that for a proportional-integral controller in experimental and simulation studies. The predictors resulted in improved control for both set point and feed flow disturbances.

SCOPE

Significant time delays can occur in processes due to the presence of recycle loops, distance-velocity lags in fluid flow, and the dead time inherent in many composition analyses. The detrimental effects of time delays on closed-loop stability and control system performance are widely recognized. Thus, there is considerable motivation for the development of time delay compensation techniques that provide improved control of systems with significant time delays.

This investigation provides an experimental evaluation of two time delay compensation techniques, the Smith predictor (Smith, 1957, 1959) and the analytical predictor (Moore, 1969; Moore et al., 1970). Both techniques employ a simple dynamic model to predict future outputs based on current information. These time delay compensation techniques and a conventional proportional-integral (PI) controller are used to control the bottom composition of a pilot scale, methanol-water, distillation column. The same techniques have been evaluated for top composition control in a related study (Meyer et al., 1977).

This investigation and the related study (Meyer et al., 1977) provide the first experimental applications of time delay compensation techniques to distillation column control that have been reported in the open literature.

CONCLUSIONS AND SIGNIFICANCE

In general, the analytical and Smith predictor control schemes performed better than a PI controller in controlling the bottom composition of the pilot scale column. The simulation study demonstrated that both time delay compensation techniques can provide significant improvements in regulatory and servo control. Use of the analytical predictor resulted in shorter settling times and lower integral absolute error (IAE) values than the Smith predictor, which, in turn, outperformed the PI controller. The experimental results tended to support the conclusions from the simulation study, but the degree of improvement that

C. B. G. Meyer is with Gulf Oil Canada Ltd., Toronto, Ontario. D. E. Seborg is with the Department of Chemical and Nuclear Engineering, University of California, Santa Barbara, California 93106.

0001-1541-79-1719-0024-$01.05.