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A Study of Sedimentation Equilibrium and Viscosity of the System Polystyrene and Cyclohexane near the Flory Temperature

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The sedimentation–diffusion equilibrium method has been used to some extent to study thermodynamic interactions in non-ideal solutions. However, previous theoretical treatments of the problem by Schulz and by Wales, Williams and associates have been approximate to the extent that there was neglected the dependence on molecular weight of the pair thermodynamic interaction parameters which appear in the first term of the virial expansion for the logarithm of the activity coefficient of each solute in a polydisperse system. An attempt now has been made by Fujita to include this effect into the theory. It appears that for polydisperse systems the intercept and limiting tangent of a plot, $1/M_{app}$ *versus* C_0, permit calculation of M_w, and the second virial coefficient A_2', as obtained from light scattering experiments. A purpose of this report is to make use of this new theoretical information to determine the temperature variation of this second virial coefficient for the system polystyrene–cyclohexane in the region of the Flory-temperature. In addition, theoretical work by Kurata, *et al.*, has made it possible to predict the temperature dependence of the second virial coefficient of a given solution in such a temperature range from measurements of the intrinsic viscosity at corresponding temperatures. For the polymer–solvent system selected, osmotic pressure, light scattering and viscosity data are available; thus we have been enabled to study further the usefulness of the sedimentation–diffusion equilibrium experiment in the evaluation of polymer–solvent interaction.

Introduction

The use of the sedimentation–diffusion equilibrium experiment for the study of thermodynamic interactions in solutions of macromolecules is gradually becoming established. From the modest beginnings of Schulz[2] and of Wales and Williams and their associates[3,4] there now have been made available more direct and more exact thermodynamic analyses of the experiment.[5-8] Nonetheless these treatments of the problem were approximate or otherwise incomplete to the extent that a way was not found to take even into limited account the dependence on molecular weights of the pair thermodynamic interaction parameters which appear in the first term of the virial expansion for the logarithm of the activity coefficient of each solute in a polydisperse system. Real progress in this direction now has been made by one of us,[9] it having been shown that for polydisperse systems the intercept and the initial tangent of a plot for $1/M_{app}$ *versus* C_0 allow calculation of the weight-average molecular weight M_w, and the second virial coefficient A_2', equivalent to the one obtained from light scattering experiments. Here M_{app} is the apparent molecular weight which may be determined for each initial concentration C_0 from plots of the concentration gradient against cell distance at sedimentation equilibrium. The quantity A_2' will be termed the light scattering second virial coefficient for our purpose. We seek to use this theoretical information for the determination of the temperature dependence of the light scattering second virial coefficient for a polystyrene sample in cyclohexane near the Flory temperature.[10] Here by the Flory temperature is meant a temperature at which the solution becomes thermodynamically ideal; it is sometimes called the *theta* temperature and designated by the symbol Θ.

In recent years a number of statistical mechanical theories of dilute solutions of flexible chain polymers have been developed. Of these the recent theory of Kurata and his colleagues[11,12] seems to have the most satisfactory physical and mathematical foundations. It is essentially a theory which describes the behavior, configurational, thermodynamical and frictional, at temperatures close to the Flory point. Many interesting correlations of these properties are indicated in their theory. Thus it is possible to predict the temperature dependence of the second virial coefficient of a given solution near the Flory temperature from measurements either of the mean square radius of gyration $<s^2>$ of the polymer molecule or of the intrinsic viscosity $[\eta]$ in the corresponding temperature region. Although these quantitative correlations have enjoyed fairly satisfactory confirmation[12] with existing light scattering and osmotic pressure data, further data which may be used to test the theory are apparently to be desired. In the present paper, such a test is provided by using data from sedimentation equilibrium and viscosity measurements for a high molecular weight polystyrene in cyclohexane.

The system polystyrene and cyclohexane was chosen because (1) the Flory temperature of this system is so close to room temperature that there is no great difficulty in maintaining temperature control during the sedimentation equilibrium experiments, and (2) detailed data from osmotic pressure, light scattering, viscosity and others are available in the literature for this system. Comparison of our data with those of previous studies will provide an opportunity to examine critically the potentiality of the sedimentation equilibrium method

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(2) G. V. Schulz, *Z. physik. Chem.*, **A193**, 168 (1944).

(3) M. Wales, M. Bender, J. W. Williams and R. H. Ewart, *J. Chem. Phys.*, **14**, 353 (1946).

(4) M. Wales, *J. Phys. Colloid Chem.*, **52**, 235 (1948); **55**, 282 (1951).

(5) M. Wales, F. T. Adler and K. E. Van Holde, *ibid.*, **55**, 145 (1951).

(6) R. J. Goldberg, *ibid.*, **57**, 194 (1953).

(7) L. Mandelkern, L. C. Williams and S. G. Weissberg, *ibid.*, **61**, 271 (1957).

(8) J. W. Williams, K. E. Van Holde, R. L. Baldwin and H. Fujita, *Chem. Revs.*, **58**, 716 (1958).

(9) H. Fujita, *J. Phys. Chem.*, **63**, 1326 (1959).

(10) P. J. Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, New York, 1953.

(11) M. Kurata, H. Yamakawa and E. Teramoto, *J. Chem. Phys.*, **28**, 785 (1958).

(12) M. Kurata and H. Yamakawa, *ibid.*, **29**, 311 (1958).

for the study of thermodynamic interactions in non-ideal polymer solutions.

Experimental

Materials.—The polystyrene used in the present study was a fractionated sample.[13] As will be shown below, its weight-average molecular weight M_w and its z-weight average molecular weight, M_z, both determined from sedimentation equilibrium data at the Flory temperature, are 7.84 × 10^5 and 10.6 × 10^5, respectively. Therefore the ratio of M_z to M_w is about 1.35. Assuming a Schulz form for the molecular weight distribution, a value 1.54 is obtained for the ratio M_w/M_n, where M_n is the number-average molecular weight. These figures for the molecular weight ratios suggest that the material had been fairly sharply fractionated. This sample was used for all experiments without further purification and fractionation.

Reagent grade cyclohexane was distilled before being used in the preparation of the solutions.

Sedimentation Equilibrium.—A Svedberg equilibrium ultracentrifuge was used for these experiments. Three different concentrations of polymer were studied at the same time, using a rotor for four cells, with the fourth cell acting as a balancing weight and providing an index for the optical measurements. A Lamm scale optical system was used to measure concentration gradient distributions along the cell columns at sedimentation equilibria. Reference experiments with pure solvent were made at each speed of rotation used. Averages of four photographs, taken on consecutive days after sedimentation equilibrium had been reached, were calculated; scale line displacements were measured with a Gaertner microcomparator which has an accuracy of about ±1 μ. Equilibrium was attained in approximately eight to ten days at each speed of rotation used. Experiments were performed at four temperatures, 31.6, 34.2, 40.0 and 47.0°, encompassing the Flory temperature.[14] Temperatures were kept constant to within ±0.015° during each experiment. Only two results were obtained from the experiment at 47.0°, because one of the cells leaked, preventing any accurate calculation of the apparent molecular weight for this concentration. For each initial concentration C_0 at a given temperature the apparent molecular weight[4] M_{app} was calculated by numerical integration (Simpson's $^1/_3$ rule was used) of a smooth curve drawn through plots of concentration gradient dC/dr against cell distance r. Since only very dilute solutions were involved, densities of the solvent corrected for temperature, rather than those of the solutions, were used in molecular weight calculations. The partial specific volume of polystyrene was taken to be 0.950 ml./g. This value was calculated for 34.0° from the specific volume *versus* temperature relation obtained by Fox and Flory[15] for bulk polystyrene, under the assumption that in this poor solvent the partial specific volume of the polymer molecule is approximately equal to its specific volume in its undiluted state.[10] No literature value for the partial specific volume of polystyrene in cyclohexane is available so far as we are aware. A slight temperature dependence of the specific volume of bulk polystyrene in the range studied was here neglected.

From measurements using a double prism differential refractometer, values for dn/dC ranging from 1.73 × 10^{-3} dl./g. at 31° to 1.75 × 10^{-3} dl./g. at 47° were obtained for a monochromatic light of the wave length 5460 Å. Here dn/dC is the specific refractive index increment (expressed in 100 ml./g.). These values of dn/dC were sometimes used to check the concentrations of test solutions refractometrically.

Viscosity.—Viscosity measurements were made at four temperatures in the region of the Flory temperature, using a Ubbelohde viscometer (suspended meniscus) which has a flow time for water of 265.7 sec. at 25°. Kinetic energy corrections were found to be negligible in all cases. It was assumed that rate of shear corrections would be negligible in this poor solvent. For each measurement the temperature was kept constant to within ±0.01°.

Results

Sedimentation Equilibrium.—In Fig. 1, values of $1/M_{app}$ for the four temperatures studied are plotted against initial concentration C_0 (g./100 ml.). It is seen that the data for the temperature 34.2° fall on a horizontal line, indicating that all pair interaction parameters vanish at this temperature. Thus the temperature 34.2° (307.4°K.) may be identified as the Flory temperature Θ for the system polystyrene–cyclohexane. Previous determinations for Θ of polystyrene in cyclohexane show slight but probably significant variations around the value 307°K.[14] Our Θ value agrees with the datum reported from precipitation measurements by Krigbaum.[16] From the $1/M_{app}$ value at the Flory temperature the weight-average molecular weight M_w of the system can be unambiguously determined,[2,9] giving M_w = 7.84 × 10^5 for the present case. Higher average molecular weights of the system also may be calculated from sedimentation equilibrium data at the Flory temperature.[5] As noted above, an average value of 10.6 (±0.4) × 10^5 was deduced for the z-average molecular weight M_z of the present sample. Due to the difficulty of measuring accurately the concentration gradients near the ends of the cell no reliable values could be computed for M_{z+1} and higher-average molecular weights from our data.

As shown in the previous paper,[9] the curves for $1/M_{app}$ *versus* C_0 at different temperatures should converge to the same point as C_0 tends to zero. In accordance with this requirement a smooth curve was drawn through experimental points for each temperature in the fashion as shown in Fig. 1. The limiting tangents, denoted by B', of these curves at $C_0 = 0$ are related to the light scattering second virial coefficients A_2' for respective temperatures by the equation

$$A_2' = (B'/2)[1 + (\lambda^2 M_z^2/12)]^{-1} \qquad (1)$$

where λ is

$$\lambda = (1 - \rho\bar{v})\omega^2(b^2 - a^2)/2RT \qquad (2)$$

Here ρ is the density of the solvent, $\bar{v}$ is the partial specific volume of the polymer (assumed to be independent of molecular weight), ω is the angular speed of rotation, a and b are the radial distances measured from the axis of the rotor to the meniscus and the bottom of the cell, respectively, R is the gas constant, and T is the absolute temperature of the system. The A_2' is the coefficient appearing in the virial expansion of the excess turbidity τ of the solution over that of the solvent, *i.e.*

$$HC_0/\tau = 1/M_w + 2A_2'C_0 + O(C_0^2) \qquad (3)$$

where H is the familiar constant in the theory of light scattering.[10] In order for equation 1 to be valid, it is necessary[9] that the sedimentation experiments at each temperature be performed under such

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[13] It was provided by Professor J. D. Ferry of this Department; it originated in the Dow Chemical Company, Midland, Michigan.

[14] Reported values of Θ for the system polystyrene and cyclohexane are somewhat scattered around 34°, depending on the types of measurements and probably on the samples used. The accurate precipitation temperature measurements by Shultz and Flory (This Journal, **74**, 4760 (1952)) yielded Θ = 307.2°K.

[15] T. G. Fox and P. J. Flory, *J. Appl. Phys.*, **21**, 581 (1950).

[16] W. R. Krigbaum, This Journal, **76**, 3758 (1954).

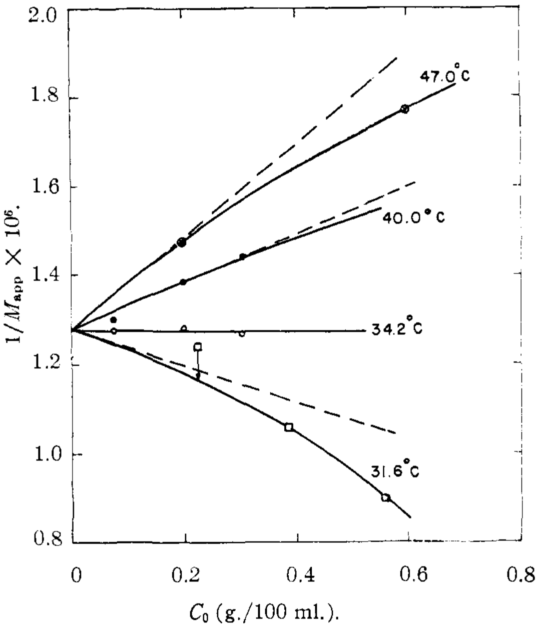

Fig. 1.—Plots for $1/M_{app}$ *versus* C_0 at various temperatures. M_{app} is the apparent molecular weight and C_0 is the initial concentration of a given solution.

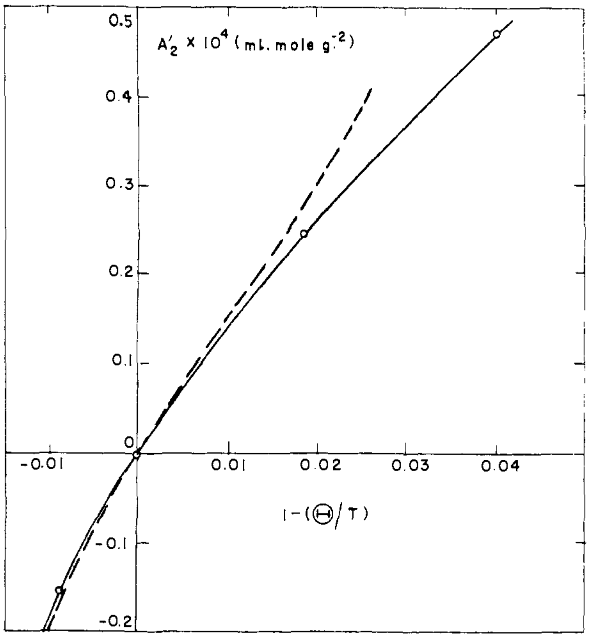

Fig. 2.—Light scattering second virial coefficients A_2' plotted against $1 - (\Theta/T)$: solid line, experimental; dashed line, calculated from viscosity data.

conditions that the values of λ for different concentrations are not only almost independent of C_0 but also so small as to satisfy the condition $\lambda^2 M_z^2/12 << 1$. All data reported in this paper were obtained from experiments so designed that these requirements were fully satisfied. As discussed previously,[9] equation 1 is not an exact relation, but the error involved therein is practically negligible subject to these conditions. In Table I are recorded values of A_2' calculated from values of B' (obtained from Fig. 1) and of λ. Figure 2 shows these values of A_2' plotted against $1 - (\Theta/T)$; here the value 307.4°K. was taken for Θ. The smooth curve in Fig. 2 was drawn to facilitate the theoretical analysis which will be presented below.

TABLE I

LIGHT SCATTERING SECOND VIRIAL COEFFICIENT A_2' DETERMINED FROM SEDIMENTATION EQUILIBRIUM

Temp. (°K.)	$B'/2$ (ml. mole g.$^{-2}$)	λ (Mole g.$^{-1}$)	A_2' (ml. mole g.$^{-2}$)
304.8	-0.166×10^{-4}	0.79×10^{-6}	-0.157×10^{-4}
307.4	.00	1.18×10^{-6}	.00
313.2	$.273 \times 10^{-4}$	1.21×10^{-6}	$.245 \times 10^{-4}$
320.2	$.525 \times 10^{-4}$	1.11×10^{-6}	$.471 \times 10^{-4}$

Intrinsic Viscosity.—Figure 3 gives results of viscosity measurements performed at four temperatures in the vicinity of the Flory temperature. Straight lines are drawn through experimental points for the several temperatures. Values of the intrinsic viscosity $[\eta]$ determined from the intercepts of these lines at $C_0 = 0$ are listed in Table II, where the values of the Huggins slope constant k' for respective temperatures are also indicated. It is of interest to note that near the Flory temperature the values of k' are not only considerably higher than the normal value 0.30 to 0.35 reported for many neutral linear polymers in good solvents but they are also markedly dependent on temperature. The ratios $[\eta]/[\eta]_\Theta$ for the four temperatures are plotted against $1 - (\Theta/T)$ in Fig. 4; here $[\eta]_\Theta$ denotes the intrinsic viscosity at the Flory temperature. The dashed line in the figure shows the tangent at $1 - (\Theta/T) = 0$ of the smooth curve drawn through the plotted points.

TABLE II

INTRINSIC VISCOSITIES $[\eta]$ AS A FUNCTION OF TEMPERATURE

Temp. (°K.)	$[\eta]$ (dl. g.$^{-1}$)	k'(Huggins const.)
305.2	0.643	0.67
307.4	.684	.63
311.2	.752	.545
315.2	.816	.495

Discussion

Kurata and his colleagues[11,12] have recently developed a statistical mechanical theory of dilute polymer solutions, again by taking the "excluded volume effect" into account. This effect arises from the fact that in real polymer solutions different chain segments, belonging either to the same molecule or to different molecules, cannot occupy the same volume element. In other words, this is the consequence of the fact that each chain segment has a finite volume. Flory and his colleagues[10] refer to this effect as the long range interference of polymer segments. Short range interferences refer to the bond angle restriction and the potential barrier between consecutive monomer units in a polymer chain; these cause restricted rotation of each monomer–monomer link relative to the neighboring ones.

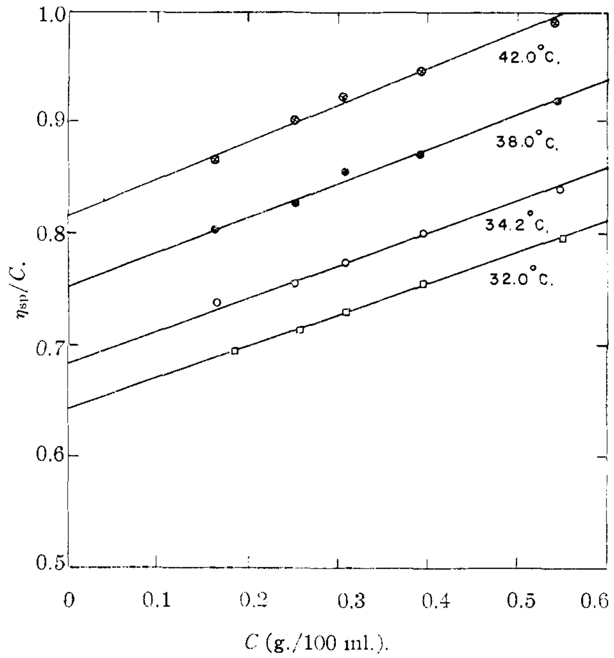

Fig. 3.—Plots for reduced viscosity η_{sp}/C *versus* concentration C at various temperatures.

The theory of Kurata, *et al.*, is applicable only to the temperature region near the Flory temperature of a given system, because all excluded volume effects are represented in the form of series which presumably converge only in such a temperature region. However, this is not a limitation in the present research where all experiments were performed under conditions which meet this theoretical requirement. It should be noted that even though the temperature range is limited in the theoretical analyses of Kurata, *et al.*, the physical and mathematical approaches used in them are superior in many respects to the similar (and earlier) theories which were developed by Zimm, Flory, Krigbaum and others.[17-19] In fact, as pointed out by Kurata and Yamakawa[12] and by Krigbaum and Carpenter,[20] there are some serious defects in Flory's uniform expansion model for a polymer molecule with the excluded volume effect.[10] In the use of the theory of Kurata, *et al.*, however, there is the fundamental difficulty that their equation for the second virial coefficient is applicable only for monodisperse fractions. The light scattering and osmotic second virial coefficients are generally different numerically for polydisperse systems.[6] The difference depends on the molecular weight distribution in the sample as well as the molecular weight dependence of the pair thermodynamic interaction parameters for each solute. Since the polydispersity of the present polystyrene sample is rather small, we assume here that no serious error will be introduced if we apply, as it stands, the equation for the second virial coefficient A_2 by Kurata, *et al.*,[12] to our

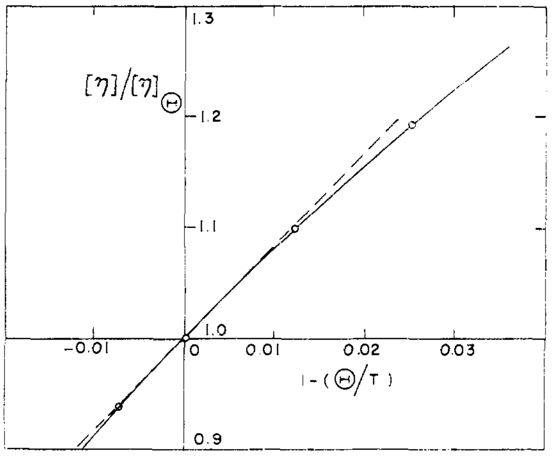

Fig. 4.—Viscosity ratios, $[\eta]/[\eta]_{\Theta}$, plotted against $1 - (\Theta/T)$.

light scattering second virial coefficients A_2'. The only modification we make here is to replace M, the molecular weight for the monodisperse polymer appearing in their equation, by the weight-average molecular weight M_w.

The expression for A_2' then reads[12]

$$A_2' = (2\pi/3)N_A b_0^3[1 - (\Theta/T)](1 - 2.865z + 18.51z^2 - \ldots) \quad (4)$$

where N_A is the Avogadro number (6.02×10^{23}) and z is a parameter defined by

$$z = (6/\pi)^{3/2}(b_0/a_0)^3[1 - (\Theta/T)](M_w)^{1/2} \quad (5)$$

In these equations a_0 and b_0 are constants defined by

$$a_0 = a/(M_0)^{1/2},\ b_0 = b/(M_0)^{1/3} \quad (6)$$

where a, b and M_0 are, respectively, the length, the diameter and the molar weight of a chain segment of the pearl-necklace model for a flexible linear polymer molecule. In the treatment of Kurata, *et al.*, it is assumed that each chain segment can rotate freely. Therefore it is reasonable to consider that such a chain segment is equivalent to the statistical segment defined by Kuhn's condition[21] (see also equation E29 in reference 12). Using this condition the value of M_0 for a given polymer can be calculated uniquely when the value of a_0 is known by experiment. Thus

$$M_0 = (a_0 m_0/l)^2 \quad (7)$$

where l and m_0 are, respectively, the monomer-monomer distance and the molar weight of the monomer for a given polymer; for polystyrene l = 3.08 Å. and m_0 = 104.

In equation 4 the terms containing z represent the excluded volume effect upon A_2'. The terms, $-2.865z$ and $18.51z^2$, are called the double contact term and the triple contact term, respectively. For a given polymer species the convergence of the z-series in equation 4 depends on the magnitudes of $1 - (\Theta/T)$ and M_w; to a first approximation a_0, b_0 and

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(17) B. H. Zimm, *J. Chem. Phys.*, **14**, 164 (1946).

(18) A. Ishihara and R. Koyama, *ibid.*, **25**, 712 (1956).

(19) P. J. Flory and W. R. Krigbaum, *ibid.*, **18**, 1086 (1950); T. A. Orofino and P. J. Flory, *ibid.*, **26**, 1067 (1957).

(20) W. R. Krigbaum and D. K. Carpenter, *J. Phys. Chem.*, **59**, 1166 (1955).

(21) W. Kuhn, *Kolloid-Z.*, **76**, 258 (1936); **87**, 3 (1939).

M_0 would be constants independent of temperature and molecular weight. Although the correct condition for the convergence of this series has to be awaited until higher contact terms are available, it appears that the range of applicability of equation 4 in its present form is limited only to values of z close to zero, *i.e.*, the Flory temperature of the system. This is because the coefficient for the triple contact term is considerably larger than that for the double contact term.

The theory of Kurata and Yamakawa[12] yields for $[\eta]$ an equation of the form

$$[\eta] = [\eta]_{\Theta}[1 + p(X)z - \ldots] \qquad (8)$$

where $p(X)$ is a function of the drainage parameter X defined by

$$X = (3/2\pi)^{1/2}[b_0/a_0(M_0)^{1/3}](M_w)^{1/2} \qquad (9)$$

Here, X represents the extent to which the polymer molecule allows permeation of solvent through it; thus $X = 0$ corresponds to the free-draining molecule, and $X = \infty$ represents the impermeable molecule. In the z-series, equation 8, no terms higher than the first power of z have yet been obtained. For $[\eta]_{\Theta}$ the equation by Kurata and Yamakawa corrected for polydispersity of the system reads

$$[\eta]_{\Theta} = (1/q_w)(N_A/100)(\pi/6)^{3/2}[XF_0(X)]a_0^3(M_w)^{1/2} \qquad (10)$$

where q_w is

$$q_w = (h + 1)^{1/2}\Gamma(h + 1)/\Gamma(h + 1.5) \qquad (11)$$

and Γ is the gamma function. The quantity h is a parameter appearing when we represent the molecular weight distribution $f(M)$ by the Schulz form

$$f(M) = (y^{h+1}/h!)M^h \exp(-yM) \qquad (12)$$

where y is

$$y = (h + 1)/M_w = (h + 2)/M_z \qquad (13)$$

Thus the value of q_w may be calculated if the value of M_z/M_w is determined experimentally; for the present polystyrene sample the ratio M_z/M_w is 1.35 and therefore the value of q_w is found to be 1.04. Numerical values of the functions $p(X)$ and $XF_0(X)$ ranging from zero to infinity are given in Table I and Table II of reference 12. The intrinsic viscosities, $[\eta]$ and $[\eta]_{\Theta}$, in the above equations are expressed in deciliters of solution per gram of solute, in conformity with the units used in Fig. 3 and Table II.

We now apply the various equations given above to our sedimentation equilibrium and viscosity data. To start with, we combine equations 4 and 5 to give

$$A_2'/[1 - (\Theta/T)] = P_0 + P_1[1 - (\Theta/T)] + \text{higher terms} \qquad (14)$$

where

$$P_0 = (2\pi/3)N_A b_0^3 \qquad (15)$$

$$P_1 = -2.865(2\pi/3)(6/\pi)^{1/2}b_0^6/a_0^3 N_A(M_w)^{1/2} \qquad (16)$$

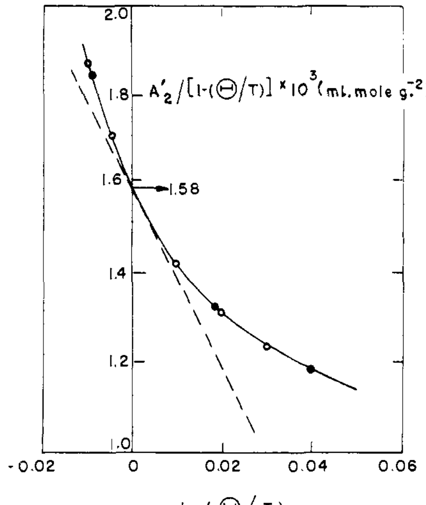

Fig. 5.—Plots for $A_2'/[1 - (\Theta/T)]$ *versus* $1 - (\Theta/T)$. Solid circles represent values calculated from directly measured A_2', and open circles are values obtained from the smooth solid curve in Fig. 2.

Equation 14 indicates that the intercept P_0 and the tangent P_1 of a plot for $A_2'/[1 - (\Theta/T)]$ *versus* $1 - (\Theta/T)$ at $1 - (\Theta/T) = 0$ may be used to evaluate the constants a_0 and b_0, provided the value of M_w is known. Figure 5 shows this plot, the location of the points having been calculated from the A_2' curve given in Fig. 2. From this curve the values of 1.58×10^{-3} (ml. mole/g.^{2}) and -2.00×10^{-2} (ml. mole/g.^{2}) may be determined for P_0 and P_1, respectively. The quantities P_0 and P_1 actually represent the tangent and curvature for the A_2' *versus* $1 - (\Theta/T)$ curve at the origin. Such quantities, especially the curvature, depend to a considerable extent on how we draw a smooth curve through the experimentally determined A_2' values. Furthermore, the values of A_2' themselves are calculated from the initial tangents of the smooth curves which are drawn through experimental plots of $1/M_{app}$ *versus* C_0. Thus the values derived for P_0 and P_1 are admittedly not very accurate in general. This is apparently the case also with the values of a_0 and b_0 derived therefrom by using equations 15 and 16. In particular, the accuracy of the value for a_0 so obtained may be quite limited. Substitution of $P_0 = 1.58 \times 10^{-3}$ and $P_1 = -2.00 \times 10^{-2}$ into equations 15 and 16 and solution for a_0 and b_0 yields

$$a_0 = 7.02_0 \times 10^{-9},\ b_0 = 1.07_8 \times 10^{-9} \qquad (17)$$

These data may be compared with corresponding values which were obtained by Kurata and Yamakawa[12] from data by Outer, Carr and Zimm[22] and by Krigbaum and Carpenter[20] for the mean square radius of gyration $\langle s^2 \rangle$ of polystyrene in cyclohexane; data of Outer, *et al.*, for the sample of $M_w = 16.1 \times 10^5$ give $a_0 = 7.31 \times 10^{-9}$ and $b_0 = 1.03_7 \times 10^{-9}$ and data of Krigbaum, *et al.*, for the sample of $M_w = 32.0 \times 10^5$ yield $a_0 = 6.72 \times 10^{-9}$ and $b_0 = 1.17_8 \times 10^{-9}$.

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(22) P. Outer, C. I. Carr and B. H. Zimm, *J. Chem. Phys.*, **18**, 830 (1950).

The value of a_0 may also be calculated from the value for $[\eta]_\Theta$, provided the value of X, and hence that of $XF_0(X)$, is available and the heterogeneity factor q_w can be determined. As noted above, a value 1.04 is obtained for q_w of our polystyrene sample from data for M_w and M_z. To find the required value of X the following procedure may be used here. First we substitute the value of a_0 deduced above from A_2' data into equation 7 to calculate M_0; a value of 563 is obtained. Introduction of this M_0 value, together with the a_0 and b_0 given in equation 17, into equation 9 then yields $X = 11.4$. Because the function $XF_0(X)$ varies very slowly for $X > 10$, this value of X may be substituted to determine the required value for $XF_0(X)$. By interpolation from the values given in Table I of reference 12 a value 1.02 is found for $XF_0(X)$ at $X = 11.4$. Substitution of $q_w = 1.04$, $XF_0(X) = 1.02$, $M_w = 7.84 \times 10^5$ and $[\eta]_\Theta = 0.684$ (dl./g.) (see Table I) into equation 10 and solution for a_0 then yields

$$a_0 = 7.01_6 \times 10^{-9} \qquad (18)$$

By substitution for z from equation 5, equation 8 may be written in the form

$$[\eta]/[\eta]_\Theta = 1 + p(X)(6/\pi)^{1/2}(b_0/a_0)^3(M_w)^{1/2}[1 - (\Theta/T)] \qquad (19)$$
$$+ \text{ higher terms}$$

From this we may derive the relation

$$b_0^3 = (\pi/6)^{1/2}a_0^3\, p(X)^{-1}(M_w)^{-1/2}\, Q_0 \qquad (20)$$

where Q_0 is the tangent of a plot for $[\eta]/[\eta]_\Theta$ *versus* $1 - (\Theta/T)$ at $1 - (\Theta/T) = 0$. Thus if we determine Q_0 by evaluating the initial tangent of the curve shown in Fig. 4 and substitute for a_0 from equation 18, a value may be obtained for b_0; the necessary value for $p(X)$ may be interpolated from Table II of reference 12 to give 1.50_5. The value we obtained for Q_0 is 8.30. Substitution of these values into equation 20 leads to

$$b_0 = 1.15_9 \times 10^{-9} \qquad (21)$$

The values of a_0 and b_0 obtained in this way from intrinsic viscosity data compare favorably with those derived above from A_2' data, suggesting that our A_2' and $[\eta]$ data are entirely consistent.

The agreement of the a_0 values deduced from two different sources may be somewhat fortuitous, because there is a considerable uncertainty in determining a_0 from A_2' data. The value of b_0 from $[\eta]$ is about 7% higher than that from A_2'. When the former b_0 value is substituted into equation 4, we find for the initial tangent of the curve for A_2' *versus* $1 - (\Theta/T)$ a value which is about 24% higher than that determined from the experimental curve This difference between predicted and observed initial slopes is probably beyond the error in experimental determinations of A_2'.

In general, the intrinsic viscosity $[\eta]$ can be measured quite accurately, provided rate of shear corrections are negligible. Therefore the value, 8.30, obtained for Q_0, the tangent of the curve for $[\eta]/[\eta]_\Theta$ *versus* $1 - (\Theta/T)$ at $1 - (\Theta/T) = 0$, is presumably fairly correct. This is even emphasized because the curvature at the point $1 - (\Theta/T) = 0$ is almost negligible. Accordingly, we see from equation 20 that the accuracy of the b_0 value determined from $[\eta]$ data depends mainly on the accuracy of the quantity $a_0^3p(X)^{-1}(M_w)^{1/2}$. We believe that the value for M_w obtained here is fairly accurate because of the negligible scattering of our data for $1/M_{app}$ at the Flory temperature. The two a_0 values derived above differ by less than 0.2% from one another. Therefore, assuming that the correct value of a_0 is in between, use of the above a_0 value for $[\eta]$ introduces a vanishingly small error into b_0. Thus so far as the present data are concerned, it is likely that the factor $p(X)$ is mainly responsible for the discrepancy noted above. There are good reasons which lend support to this view. First, in the theory of Kurata and Yamakawa no heterogeneity effect is explicitly taken into account in the derivation of $p(X)$; such an effect has been considered here by merely replacing M by M_w. Second, their derivation contains several approximations which admittedly lead to somewhat incorrect values of $p(X)$. For example, if we use an equation developed recently by Stockmayer and Albrecht,[23] values are obtained for $p(X)$ which are about 10% higher than those calculated by Kurata and Yamakawa in the region of large X.[24] Anyway, at present it appears extremely difficult and even almost hopeless to attempt to derive the correct expression for $p(X)$ by taking heterogeneity of the polymer into account. For this reason it is appropriate for practical purposes that we regard $p(X)$ as an empirical function and determine its values from suitable experiments. One way to proceed is to utilize an explicit relation between A_2' and $[\eta]$, derived as follows.

Equation 4 may be rewritten

$$1 - A_2'/\{(2\pi/3)N_A b_0^3[1 - (\Theta/T)]\} = 2.865z - 18.51z^2 + \ldots \qquad (22)$$

From equation 8 we have

$$[\eta]/[\eta]_\Theta - 1 = p(X)z - \ldots \qquad (23)$$

These two equations may be combined to give

$$[\eta]/[\eta]_\Theta - 1 = [p(X)/2.865](1 - A_2'/\{(2\pi/3)N_A b_0^3[1 - (\Theta/T)]\}) + \ldots \qquad (24)$$

This indicates that the required value of $p(X)$ may be obtained from the tangent at the origin of a plot for $[\eta]/[\eta]_\Theta - 1$ *versus* $1 - A_2'/\{(2\pi/3)N_A b_0^3[1 - (\Theta/T)]\}$. This plot may be constructed from the smooth curves of Figs. 2 and 4, using for b_0 the value determined above from A_2' data. Figure 6 shows the plot so obtained. The initial tangent of this curve is found to be 0.61, giving a value 1.75 for $p(X)$. This $p(X)$ is 16% higher then the value 1.50_5 which was estimated above

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(23) W. H. Stockmayer and A. C. Albrecht, *J. Polymer Sci.*, **32**, 251 (1958).

(24) Personal communication: Professor M. Kurata, University of Kyoto, Kyoto, Japan.

for $X = 11.4$ from Table II of reference 12.[25] It should be noted that this method of determining $p(X)$ can be utilized independently of a_0. Since, however, the initial slope of the curve shown in Fig. 6 is rather sensitive to the choice of b_0, the value of $p(X)$ thus obtained should be accepted with some reservation; as mentioned before, the accuracy of the b_0 value obtained by applying equation 14 to A_2' data may be less than might be desired. With this empirically determined $p(X)$ we may calculate b_0 from equation 20 in exactly the same manner as described above. The result is

$$b_0 = 1.10_2 \times 10^{-9} \qquad (25)$$

which stands in better agreement with the b_0 deduced from A'_2 data than does that datum which is obtained from $[\eta]$ by using the theoretical $p(X)$ value.

To see how well the values for a_0 and b_0 derived from viscosity data reproduce the temperature dependence of A_2' in the vicinity of the Flory temperature, they are substituted into equation 4 to calculate A_2' as a function of $1 - (\Theta/T)$. In Fig. 2 the calculated values are compared with experimental data. The agreement of theory and experiment is fairly satisfactory in the range such that $|1 - (\Theta/T)| < 0.01$. This range corresponds to ±3° about the Flory temperature, 34.2°, and to ± 0.05 about $z = 0$. Outside of this range the calculated curve diverges to a greater and greater extent from experimental results, indicating that the theory of Kurata and Yamakawa is really applicable only in the very vicinity of the Flory temperature. This conclusion had already been reached by Kurata and Yamakawa[12] from a detailed analysis of light scattering data[20,22] for higher molecular weight polystyrenes in cyclohexane.

To summarize, we may conclude that our sedimentation equilibrium and viscosity data not only fit well into the scheme of the Kurata theory for dilute polymer solutions but also yield for the molecular parameters, a_0, b_0 and M_0, values which may be compared favorably with those deduced from light scattering experiments. This implies that so far as the temperature range near the Flory point is concerned, the sedimentation equilibrium method may be used as satisfactorily as the light scattering method for studying thermodynamic interactions in dilute polymer solutions. In this connection, we should like to emphasize the fact that for sedimentation equilibrium experiments we need not be concerned with the familiar difficulties in light scattering experiments such as preparing optically clear solutions. In osmotic pressure experiments difficulty usually arises from the selection of an "ideal" semi-permeable membrane. In the sedimentation equilibrium experiment the molecular weight range which may be studied is unlimited in principle; it may be adjusted to molecular weight range by changing the speed of rotation. The chief disadvantage of the sedimentation method is probably that for any given solution it may take a considerable period of time to reach sedimentation equilibrium at a speed of rotation which is suitable for the evaluation of the experiment.

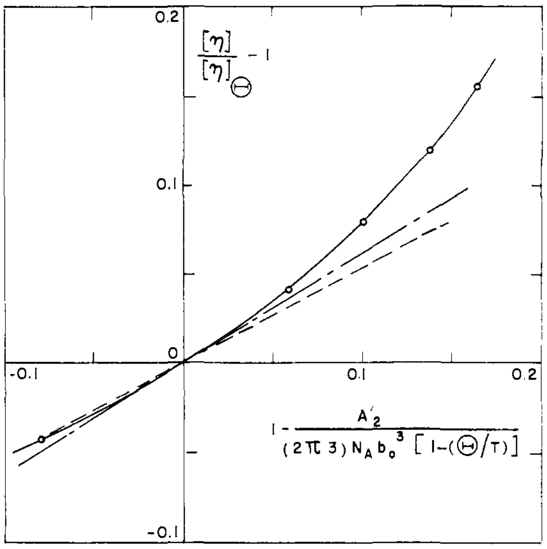

Fig. 6.—Plots for $([\eta]/[\eta]_\Theta) - 1$ *versus* $1 - A_2'/\{(2\pi/3) N_A b_0^3[1 - (\Theta/T)]\}$. N_A is the Avogadro number, and b_0 is a parameter determined from the tangent at $1 - (\Theta/T) = 0$ of the smooth solid line in Fig. 2. Dashed line is the tangent for the solid line, and chain line is the corresponding tangent expected with the theoretical $p(X) = 1.50_5$ for $X = 11.4$.

Finally, our data are applied to calculate the pair interaction entropy parameter, ψ_1, which appears in the theories of dilute polymer solutions by Flory and his associates.[10] It is readily shown that ψ_1 is related to the parameter b_0 by the equation

$$\psi_1 = (V_1/\bar{v}^2)(2\pi/3)N_A b_0^3 \qquad (26)$$

where $\bar{v}$ is the partial specific volume of polymer and V_1 is the molar volume of solvent. Introduction of $b_0 = 1.07_8 \times 10^{-9}$ (see equation 16), $V_1 = 110$, and $\bar{v} = 0.950$ into equation 26 yields

$$\psi_1 = 0.192 \qquad (27)$$

This is in good agreement with the value 0.19 ± 0.05 deduced by Krigbaum and Carpenter[20] from light scattering measurements for a polystyrene of $M_w = 32.0 \times 10^5$ in cyclohexane. These values show considerable discrepancy from the value 0.36 ± 0.03 which was reported by Krigbaum[16] from osmotic pressure measurements on several lower molecular weight polystyrenes in the same solvent. However, in an article which has just appeared Krigbaum and Geymer[26] have made use of their osmotic pressure measurements and additional information about the Flory temperature to obtain a revised value, $\psi_1 = 0.23$. If the polymer is monodisperse, one would expect both light

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(25) The referee has been kind enough to point out that the Flory–Fox assumption,[10] $[\eta]/[\eta]_\Theta = \alpha^3$, when combined with a proper evaluation of α, leads to $p(X) = 1.91$ for large X. The α is one of the parameters in the Flory–Fox intrinsic viscosity–molecular weight relationship.

(26) W. R. Krigbaum and D. O. Geymer, THIS JOURNAL, **81**, 1859 (1959).

scattering and osmotic pressure to yield the same value for ψ_1, because ψ_1 is the parameter which should be characteristic of a given polymer–solvent pair. Some difference may appear between values from these two types of experiment when the polymer is polydisperse, as is always the case with the polymer samples which are currently available.

In this connection we may note that Kurata, Utiyama and Tamura[27] have recently derived a value $1.13_7 \times 10^{-9}$ for the parameter b_0 from osmotic pressure experiments for a polystyrene fraction in cyclohexane. When this value of b_0 is substituted into equation 26, we obtain for ψ_1 a value 0.226, in good agreement with the value from our sedimentation experiments. The ψ_1 data of Krigbaum and associates[20,26] from osmotic pressure and light scattering are now also consistent. In order to see whether this kind of agreement is merely apparent further experimental studies by light scattering, osmotic pressure, sedimentation equilibrium, and so forth must be undertaken with a variety of polymer–solvent systems.

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(27) M. Kurata, H. Utiyama and M. Tamura, unpublished data.