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On the Concentration Dependence of the Rates of Sedimentation and Diffusion of Macromolecules in Solution. Preliminary¹

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The concentration dependence of the osmotic pressure, rate of diffusion, and sedimentation velocity for solutions of high molecular weight solutes, on the basis of certain assumptions, have been shown to be interrelated. Experimental confirmation, however, has been lacking. Preliminary data are given in this article which satisfy these interrelationships, with fractions of cellulose acetate in acetone; however, more cooperative osmotic pressure, diffusion, and sedimentation experiments on a variety of well-defined systems are necessary to confirm the hypothesis.

If and when this additional confirmation is produced, the assumptions involved in the hypothesis may be con-

sidered correct; these are: (1) that the frictional coefficient in diffusion is the same (barring special cases of orientation during transport) as the frictional coefficient in sedimentation; and (2) that the driving force of diffusion is the gradient of the free energy of dilution of the system.

For solutions with no heat of mixing, the slight dependence of the diffusion constant on concentration has its molecular basis in the fact that the size and shape of the molecules affect the thermodynamic and hydrodynamic contributions to the variation of the diffusion rate to a comparable extent, and these contributions partially cancel one another. This is quantitatively so in the simple case of rigid spheres in an athermal solution.

A. INTRODUCTION

THE dependence of the rates of sedimentation and diffusion of solutes of high molecular weight on their concentrations in solution has long been of considerable empirical and theoretical interest. These rates, for example, have to be extrapolated to zero concentration in order for the Svedberg molecular weight equation to hold. It has been found that the sedimentation velocity is generally much more marked a function of concentration than the rate of diffusion, and that the dependence is more pronounced the more asymmetric the solute molecule. Certain independent empirical relations have been adduced to account for these rate variations with concentrations, and these generally satisfy the experi-

mental data. The purposes of this paper are to discuss the investigation of Beckmann and co-workers, who have related these rate dependences to one another and to the variation of the thermodynamic properties of the solution with concentration; to present experimental data substantiating their hypothesis; and to develop in more detail the explanation of these rate phenomena in the light of recent advances in the theory of solutions.

B. THEORY

A brief account of the pertinent theory of the ultracentrifuge is necessary in order to discuss the material covered in this article. More detailed general information may be found elsewhere.^{3,4}

¹ This paper was presented at the Twentieth Colloid Symposium, University of Wisconsin, May 1946.

² Du Pont Research Fellow, 1946-1947.

³ T. Svedberg and K. O. Pedersen, *The Ultracentrifuge* (Oxford University Press, London, 1940).

⁴ E. G. Pickels, *Chem. Rev.* **30**, 341 (1942).

When molecules in solution are acted upon by a centrifugal field of sufficient strength, the random Brownian motion, tending to keep the average concentration of the solution uniform, is partially overcome, and the molecules sediment in the direction of the field. The velocity of sedimentation is small and nearly constant, and, thus, the resultant force on each molecule is almost zero. That is, the weight minus the buoyant force may be taken as equal to the force of resistance for each molecule. For a gram-molecular weight of such molecules we have the relation:

$$M(1 - \bar{V}d)\omega^2x = fdx/dt. \quad (1)$$

M is the molecular weight of the solute of partial specific volume \bar{V} , moving with an average velocity dx/dt in a fluid of density d ; x is the distance from the axis of rotation and ω is the angular velocity with which the centrifuge rotor is spinning. The force of resistance acting on the molecule may be taken as proportional to the velocity with which the molecule moves in the fluid; the proportionality constant f , as written in Eq. (1), is called the molar frictional coefficient. The sedimentation constant, s , is defined as $(dx/dt)/\omega^2x$, and Eq. (1) may be put in the form:

$$s_c = M(1 - \bar{V}d_c)/f_{s,c}, \quad (1a)$$

where the subscript c indicates a finite concentration, and the subscript s refers to sedimentation. Many investigators⁵⁻¹¹ have found the sedimentation constant to be a quantity strongly dependent on concentration, and it is well understood that experiments must be performed at several concentrations, and the sedimentation constant extrapolated to infinite dilution. Empirically, it has been shown that for most high polymer solutions, and for solutions of asymmetric protein molecules, the sedimentation data fit the equation:

$$s_c = s_\infty/(1 + k_sc), \quad (2)$$

where k_s is a constant. It has been demonstrated that \bar{V} is essentially independent of concentration in dilute solutions.^{6,7} The problem of what value of d_c to use in Eq. (1a) is not yet settled: the appropriate value is probably in between that for the macroscopic density of the solution and the density of the pure solvent. In any event the magnitude, Δd , of the change of density in going from solvent to a dilute solution is generally small compared to the magnitude of k_s . *Therefore, when $k_s \gg \Delta d$, the dependence of s upon c is entirely caused by the variation of $f_{s,c}$ with c .*¹² If we write

$$f_{s,c} = f_{s,\infty}(1 + k_sc), \quad (3)$$

we then obtain Eq. (2) from Eq. (1a).

The Einstein gas law of diffusion:¹³

$$D_\infty = RT/f_{D,\infty} \quad (4)$$

holds at infinite dilution, where D_∞ is the diffusion constant extrapolated to zero concentration, R the gas constant, T the absolute temperature, and $f_{D,\infty}$ the molar frictional coefficient acting during the diffusion process. If $f_{D,\infty} = f_{s,\infty}$, combination of Eqs. (1a) and (4) yields the well-known Svedberg equation for molecular weights obtained with the aid of the velocity ultracentrifuge:

$$M = RTs_\infty/D(1 - \bar{V}d). \quad (5)$$

At any finite concentration, however, the gas law of diffusion cannot be expected to hold, except for ideal solutions. *If the driving force of the diffusion process is the gradient of the free energy of dilution of the system*, i.e., the gradient of $\Delta\bar{F}_1$, the partial molar free energy of the solvent in the solution minus the partial molar free energy of the solvent at infinite dilution, Onsager and Fuoss¹⁴ have shown that the diffusion constant at a finite concentration depends on the activity coefficient of the solute. Equivalently, since $\Delta\bar{F}_1 = -\pi\bar{V}_1$, giving the osmotic pressure of the solution by a convergent power series in the solute concentration:

$$\pi = (RT/M)c + Bc^2 + \dots, \quad (6)$$

¹² For solutions of symmetrical protein molecules, s_c varies more slowly with c than described by Eq. (2). This is probably due to the fact that Δd is beginning to make a significant contribution.

¹³ A. Einstein, *Ann. d. Physik* **17**, 549 (1905).

¹⁴ L. Onsager and R. M. Fuoss, *J. Phys. Chem.* **36**, 2689 (1932).

⁵ R. O. Carter, *J. Am. Chem. Soc.* **63**, 1960 (1941).

⁶ N. Gralen, *Inaugural Dissertation*, Uppsala (1944).

⁷ I. Jullander, *Arkiv. f. Kemi Min. Geol.* **A21**, 1 (1945).

⁸ M. Lauffer, *J. Am. Chem. Soc.* **66**, 1189 (1944).

⁹ H. Mosimann, *Helv. Chim. Acta* **26**, 61 (1943).

¹⁰ R. Signer and H. Gross, *Helv. Chim. Acta* **17**, 59, 335 (1934).

¹¹ K. G. Stern, S. Singer, and S. Davis, *Polymer Bull.* **1**, 31 (1945).

where B is a constant¹⁵ independent of the molecular weight of the solute, and \bar{V}_1 is the partial molar volume of the solvent, we may write:

$$D_c = (RT/f_{D,c})[1 + (2BM/RT)c]. \quad (7)$$

Most dilute solutions (up to concentrations of 1 percent or so) of solutes of high molecular weight have osmotic pressures that are satisfactorily represented by the first two terms in Eq. (6), and so Eq. (7) should represent their diffusion behavior.¹⁶⁻¹⁸

Assuming now that $f_{D,c} = f_{s,c}$, an assumption analogous to the one previously made for the frictional coefficients at zero concentration, we obtain Eq. (8):

$$\begin{aligned} D_c &= \frac{RT[1 + (2BM/RT)c]}{f_\infty(1 + k_s c)} \\ &= D_\infty \frac{[1 + (2BM/RT)c]}{1 + k_s c} \cong D_\infty(1 + k_D c). \quad (8) \end{aligned}$$

It has been found empirically that the diffusion constant generally varies linearly with concentration^{6,7,19} represented by the right side of Eq. (8); k_D is some small constant which is most often positive but may be negative, and which is somewhat a function of the molecular weight in a homologous series of polymers.⁷

According to this treatment of the problem, a modification of that credited to Beckmann and Rosenberg,^{19,20} the slight dependence of the diffusion constant on concentration is attributable to the balancing of two effects: the thermodynamic, usually tending to increase the diffusion constant at a finite concentration, and the hydrodynamic, always tending to decrease it.²¹ "In general, we should suppose that the effect of mutual influence of particles sedimenting

in a solution will be a retardation of the motion; . . . so that apparently for every molecule the frictional forces will become somewhat greater than they are for a single molecule in an unlimited field."²² The sign and magnitude of k_D depends on the relative magnitudes of the two factors. Moreover, the variation of the frictional coefficient with concentration should be the same during sedimentation and diffusion, and we expect the relation

$$[1 + (2BM/RT)c]/[1 + k_s c] = 1 + k_D c + \dots \quad (9)$$

It should be emphasized that k_s has not been made any the less empirical; it is still not derivable from molecular parameters except for spherical particles (see below). What this treatment does is to relate in a reasonable fashion the variations of osmotic pressure, rate of diffusion, and sedimentation velocity, with concentration in dilute solutions.

C. EXPERIMENTAL

One of the aims of this communication is to provide some experimental confirmation of the hypothesis just outlined by testing the validity of Eq. (9), through independent sedimentation, diffusion, and osmotic pressure measurements on the same systems. Unfortunately, heretofore there have been no published data in which all three types of experiments were performed on the same solutions. However, with some severe assumptions, the sedimentation data of Signer and Gross¹⁰ on unfractionated polystyrenes in chloroform may be subjected to analysis.

We take for the value of B in this system a modification of that reported by Boyer,^{23,24} obtained by swelling measurements. This value is somewhat dependent on the method of

during transport. Orientation must be avoided, so that this exception is trivial.

²² J. M. Burgers, in *Second Report on Viscosity and Plasticity* (Amsterdam, 1938), p. 178.

²³ R. F. Boyer, paper presented before the Columbia University meeting of the American Physical Society, January 1946; see also R. F. Boyer, *J. Chem. Phys.* **13**, 363 (1945). The μ value was given as 0.43; we have used 0.41 to correct for the effect of the cross-linking in the swelling measurements. In the Huggins theory for the osmotic pressures of polymer solutions,

$$B = (RT/V_1 \rho_2^2)(\frac{1}{2} - \mu),$$

where ρ_2 is the density of the polymer. For ρ_2 , the value 1.06 was used, and as a result $(2BM/RT) = 2.0 \pm 10^{-3}M$. V_1 is the molar volume of solvent.

²⁴ M. L. Huggins, *J. Chem. Phys.* **9**, 440 (1941).

¹⁵ Over a very wide range of molecular weights, however, theory predicts some variation of B with M .

¹⁶ T. Alfrey, A. Bartovics, and H. Mark, *J. Am. Chem. Soc.* **65**, 2319 (1943).

¹⁷ P. M. Doty and E. Mishuk, *J. Am. Chem. Soc.*, in press.

¹⁸ H. M. Spurlin, in *High Polymers*, Volume V (Interscience Publishers, Inc., New York, 1943), p. 910.

¹⁹ C. O. Beckmann and J. Rosenberg, *Ann. N. Y. Acad. Sci.* **46**, 209 (1945).

²⁰ A similar interrelationship was proposed by R. Simha at a meeting of the American Physical Society, Columbia University, New York, January 1946.

²¹ An exception will occur if the particles are oriented

TABLE I. Polystyrene-chloroform sedimentation data (Signer and Gross).

$\eta sp/c$	M	k_s	$2BM/RT$
110	1,100,000	1990	2200
47	550,000	1110	1100
24	270,000	523	540
5.6	80,000	83	160

preparation of the polymer,¹⁸ but this is disregarded here. For M we use the weight average values given by the authors: a number average is desirable, but there is no way to determine it from the given data. The assumption is made, moreover, that $k_D \ll 2BM/RT$, as is probably true for the higher molecular weight polystyrenes in chloroform. In toluene, a polystyrene fraction of molecular weight 200,000 gave a value¹⁹ of $k_D = 10$, which is relatively small (see Table I), and in chloroform, also a good polystyrene solvent, the value is probably similar.

With these assumptions: that k_D is negligible; that the value of B obtained from swelling measurements is applicable; and that the molecular weights of the unfractional polymers given by equilibrium centrifuge measurements are suitable for our purposes, we obtain the values listed in Table I. The close agreement between k_s and $2BM/RT$ is no doubt fortuitous, considering the assumptions made in order to employ the excellent sedimentation data. Nevertheless, the confirmation of the development given above is striking.

We have studied the behavior of four fractions of cellulose acetate in acetone. The samples of fractions 2, 9, and 15 were from the well-known fractions of Sookne and Harris;²⁵ fraction 2c was prepared by Dr. W. Badgley, from a different batch of cellulose acetate, but using a similar fractionation procedure.²⁶

Beckmann and Rosenberg¹⁹ have found $k_D = 0$ at 25°C for an acetone solution of another cellulose acetate fraction prepared by Badgley, with a molecular weight 100,000. Since k_D is not strongly a function of molecular weight, we may assume that $k_D = 0$ for our fractions dissolved in

acetone. The value of B at 27°C is available from the osmotic pressure measurements of Badgley²⁷ which were performed with a series of fractions; the slopes of the straight lines in the π/c against c graphs were the same within experimental error over a range of molecular weights 50,000–230,000.

The sedimentation measurements were performed with an air-driven ultracentrifuge; our installation is described elsewhere.¹¹ Several considerations, however, pertaining to the accuracy of the measurements are mentioned here.

The rotor, enclosed in a vacuum chamber, spins in an atmosphere of about 5-mm hydrogen gas, which serves to conduct away any heat generated during rotation to the cooling coils in the periphery of the chamber. A cold alcohol-water mixture is circulated through the coils during an experiment. The temperature of the rotor is determined by a thermocouple circuit, one junction of which is a silver leaf situated in the slip-stream of the spinning rotor. The slip-stream temperature was calibrated by observing the melting points of pure, low melting solids under experimental conditions, as suggested by Svedberg.³ The rotor temperature was found to be 2.5°–4.0° above the slip-stream temperature as recorded by a galvanometer deflection, over the temperature interval 20°–40°C. Since most of the experiments were run at one speed, 720 r.p.s., and the temperatures were always near 30°, the correction necessary to obtain the actual rotor temperature was about 3°. During a run, the temperature variation was less than 2°, and no convection effects were noticed.

The speed is measured stroboscopically with a Stroboskopt,²⁸ the light from which is reflected from the top surface of the centrifuge air turbine. This surface is half-covered with a dull black paint, the other half retaining a metallic sheen. Runs are performed only at a multiple of the calibrated reed frequency, and the speed is measured and manually maintained constant to within ± 10 r.p.s. without difficulty.

To calibrate the performance of the centrifuge, a 1 percent solution of bovine serum albumin in phosphate buffer was investigated. This protein is available in crystalline form from the Armour Company, Chicago, and was found to be electrophoretically and ultracentrifugally homogeneous. It was dissolved in phosphate buffer of pH 7.7, $\mu = 0.2$. A sedimentation experiment performed at 840 r.p.s. gave, when corrected to water at 20°,³ $S_w^{1\%} = 4.04$; values reported in the literature are 4.0, by Cohn *et al.*²⁹ and 4.06 by Lauffer.³⁰

²⁷ W. Badgley and H. Mark, J. Phys. Coll. Chem. **51**, 58 (1947).

²⁸ General Radio Company, Cambridge, Massachusetts.

²⁹ E. J. Cohn, J. A. Leutscher Jr., J. L. Oncley, S. H. Armstrong Jr., and B. D. Davis, J. Am. Chem. Soc. **62**, 3396 (1940).

³⁰ M. Lauffer, data published in F. W. Putnam, J. O. Erickson, E. Volkin, and H. Neurath, J. Gen. Physiol. **26**, 513 (1943).

²⁵ A. Sookne, H. Rutherford, H. Mark, and M. Harris, J. Research Nat. Bur. Stand. **29**, 123 (1942).

²⁶ W. Badgley, Ph.D. Thesis, Polytechnic Institute of Brooklyn, 1945. No chemical analyses were performed on fraction 2c; fractions 2, 9, and 15 analyzed for 38.6 percent acetyl.

The molecular weights of fractions 2, 9, and 15 were determined by osmotic pressure measurements, and of all four fractions by velocity ultracentrifuge and free diffusion measurements, with Eq. (5). Kraemer's value of $\bar{V}=0.68$ was utilized.³¹ The diffusion technique employed is described in a forthcoming publication;³² the experiments are performed in a modified Lamm diffusion cell³³ adapted to the Longworth-Tiselius apparatus,³⁴ and the second moment method of calculating the diffusion constant is employed.⁶

In our experiments, however, the base-lines of the diffusion curves were slightly skewed, because the optical apparatus was focused for water and not acetone solutions. Therefore, we preferred not to calculate k_D ; the curves we obtained appeared symmetrical, however, indicating a value of k_D very near zero.^{6,19}

Since the molecular weight distribution of the cellulose acetate fractions appears quite sharp, there is little question as to the experimental value of M to insert in Eq. (9). We have consistently used the value determined ultracentrifugally, however.

In the calculation of the sedimentation constant, there are several fine points that deserve consideration. Under the influence of the high pressures built up in the centrifuge cell during an experiment, the viscosity of acetone changes noticeably from its value at atmospheric pressure. This has been demonstrated by Mosimann and Signer.³⁵ In our experiments, however, the sedimenting boundary was observed for only a short distance in the cell, never beyond 6.30 cm from the axis of rotation. (The distance to the top of the cell is 5.77 cm.) Moreover, at 720 r.p.s. the pressures are much less than at 1150 r.p.s., the speed used in the calculations of Mosimann and Signer. Therefore, while the viscosity corrections were always made because of pressure, they never exceeded 4 percent. The variation of the density of solvent with pressure was even smaller.

³¹ E. O. Kraemer and W. D. Lansing, *J. Phys. Chem.* **39**, 153 (1935).

³² K. G. Stern, S. Singer, and S. Davis, *J. Biol. Chem.*, in press.

³³ O. Lamm, *Nova Acta Reg. Soc. Sci. Upsal.* **IV**, 10, 1 (1937).

³⁴ L. G. Longworth, *Ind. Eng. Chem. A. E.* **18**, 219 (1945).

³⁵ H. Mosimann and R. Signer, *Helv. Chim. Acta* **27**, 1123 (1944).

There is still another factor, however, which must be taken into account. It is well known that during sedimentation there occurs a dilution effect⁸ caused by the sector shape of the cell, and the continual increase in the centrifugal force with distance from the axis of rotation. The magnitude of this effect is given by the relation: $c_t = c_0(x_0/x_t)^2$, where c_t is the concentration of the solution at the distance x_t in the cell, c_0 is the initial concentration, and x_0 the distance to the top of the cell. If the sedimentation boundary is observed at 6.30 cm, the effective concentration of the solution will be 16 percent less than the original value, a serious effect in all cases where an appreciable concentration dependence of the sedimentation constant exists. In our experiments the average concentration during an experiment was never different by more than 8 percent from the original, and this average value was employed in evaluating the data. Under these circumstances, no systematic variation of the sedimentation constants during a run was observed.

In Fig. 1, the Philpot sedimentation diagrams³⁶ of the bovine serum albumin experiment, and of experiments on two of the cellulose acetate fractions, are reproduced. The results of our measurements are listed in the first three columns of Tables II, III, IV, and V and are represented graphically in Fig. 2. In Table VI are recorded

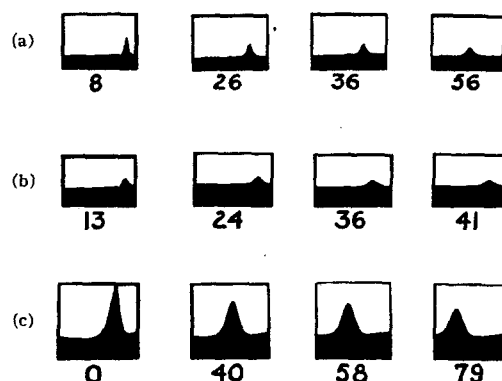


FIG. 1. Philpot sedimentation diagrams of: (a) fraction 2 in acetone at 0.181 percent; (b) fraction 9 in acetone at 0.167 percent; and (c) bovine serum albumin in phosphate buffer pH 7.7, $\mu=0.2$ at 1 percent. The ordinate of each diagram is the refractive index gradient in the solution, and the abscissa the distance in the cell. The numbers under the diagrams refer to the times in minutes after the first reference exposure.

³⁶ J. St. L. Philpot, *Nature* **141**, 283 (1938).

TABLE II. Fraction 15.

c_{av} g/100 cc	$s_{20} \times 10^{13}$	$(1/s_{20}) \times 10^{-12}$	η_{sp}/c^*
0.925	3.83	2.61	0.241
0.694	3.93	2.54	0.238
0.463	3.94	2.54	0.235
0.000	4.07**		0.230**

* Extrapolated from data of A. Sookne and M. Harris, Ind. Eng. Chem. **37**, 475 (1945).

** Extrapolated.

TABLE III. Fraction 9.

c_{av} g/100 cc	$s_{20} \times 10^{13}$	$(1/s_{20}) \times 10^{-12}$	η_{sp}/c^*
0.483	5.9	1.70	1.75*
0.344	6.3	1.59	1.64
0.243	6.8	1.47	1.56
0.230	6.5	1.54	1.55
0.173	6.7	1.49	1.50
0.173	6.6	1.51	1.50
0.117	7.2	1.39	1.45
0.000	7.5**		1.37**

* Interpolated in the data of A. Sookne and M. Harris, Ind. Eng. Chem. **37**, 475 (1945).

** Extrapolated.

the calculations concerning the validity of Eq. (9), with k_D taken as zero.

It is to be noted that while the deviations of k_s from $2BM/RT$ are within experimental error for all three fractions, the values of k_s are very closely proportional to the values of M . It may be possible, therefore, to ascribe the observed slight discrepancies to somewhat different values of B , resulting from the use of different batches of c.p. acetone in the osmotic pressure and ultracentrifugal measurements. For example, the values of B from the experiments of Sookne and Harris³⁷ are slightly lower than those of Badgley. Small differences in impurity content of the solvent might well account for a change in the osmotic pressure slope.

Consequently, the data presented above for the system cellulose acetate in acetone agree with the general development put forward in the early part of the paper. That many more systems should be measured goes without saying. Measurements on fractionated polystyrenes in a series of solvents, over a considerable range of B values are being initiated in our laboratories. Not until more data over a large interval of B and k_s values are obtained will the quantitative considerations given above be generally confirmed.

³⁷ A. Sookne and M. Harris, Ind. Eng. Chem. **37**, 475 (1945).

At the moment, however, the available data do agree with the hypothesis.

D. DISCUSSION

Up to this point no reference has been made to any of the theories concerning the value of B , the slope of the π/c against c lines, measuring the departure of the solution from the ideal. The quantitative interrelationships of the concentration dependences of the diffusion rate, the sedimentation velocity, and the osmotic pressure are independent of the interpretation placed upon B , only its magnitude being significant. However, in order to gain greater insight into the molecular parameters which so often cause the diffusion constant to be only lightly a function of concentration, some of these theories must be considered.

Many papers have been written in the past few years on the free energy of dilution of dilute macromolecular solutions, but for the particular purposes of this communication, two of the most recent are significant. Flory,³⁸ in a treatment which improves on previous calculations made with the quasi-lattice model of polymer solutions, and Zimm,³⁹ by the more rigorous and general method of molecular distribution func-

TABLE IV. Fraction 2.

c_{av} g/100 cc	$s_{20} \times 10^{13}$	$(1/s_{20}) \times 10^{-12}$	η_{sp}/c^*
0.329	7.4	1.35	4.08*
0.293	7.7	1.30	3.91
0.167	8.9	1.12	3.32
0.147	9.0	1.11	3.22
0.111	9.3	1.08	3.06
0.075	9.8	1.02	2.89
0.000	10.9**		2.75**

* Interpolated in the data of A. Sookne and M. Harris, Ind. Eng. Chem. **37**, 475 (1945).

** Extrapolated.

TABLE V. Fraction 2c.

c_{av} g/100 cc	$s_{20} \times 10^{13}$	$(1/s_{20}) \times 10^{-12}$	η_{sp}/c^*
0.353	7.5	1.34	5.20*
0.230	8.6	1.16	4.38
0.173	9.2	1.09	4.03
0.124	10.2	0.98	3.74
0.116	10.5	0.95	3.69
0.100	10.4	0.96	3.60
0.000	12.5**		3.05**

* Interpolated in the data of W. Badgley, private communication.

** Extrapolated.

³⁸ P. J. Flory, J. Chem. Phys. **13**, 453 (1945).

³⁹ B. H. Zimm, J. Chem. Phys. **14**, 164 (1946).

tions, come to roughly similar conclusions. Since the former treatment lends itself more readily to qualitative discussion, we will make more frequent use of it in the following paragraphs.

The free energy of dilution, $\Delta\bar{F}_1$, is made up of a heat and an entropy contribution:

$$\Delta\bar{F}_1 = \Delta\bar{H}_1 - T\Delta\bar{S}_1,$$

at constant temperature. In athermal solutions, $\Delta\bar{H}_1 = 0$, $\Delta\bar{F}_1 = -T\Delta\bar{S}_1$, and $\pi = T\Delta\bar{S}_1/\bar{V}_1$; moreover, the entropy of dilution may be calculated without the necessity for any weighting of certain molecular configurations because of energy considerations. Without going into any details, for which the reader is referred to the original publication, the osmotic pressure term which is quadratic in the solute concentration is proportional to a "swelling factor," s , the ratio of lattice cells pervaded by the solute molecule to the number of segments in the molecule. In other words, in an athermal solution, B is proportional to a factor which is determined by the shape and rigidity of the molecule: the more compact the molecule, the smaller the value of B . Therefore, the product BM is a function both of the shape and size of the solute particle.

Now, the decrement in the sedimentation velocity with increasing solute concentration is obviously a function of the dimensions and form of the solute molecules, since these variables determine the extent of intermolecular interference in kinetic processes.⁴⁰ In a crude manner, then, we can understand that in athermal solutions, the quantities k_s and $2BM/RT$, both depending on the size and shape of the dissolved molecules in approximately the same way, are often of the same order of magnitude.

This is actually the case for athermal solutions of spherical particles. A rigorous theoretical

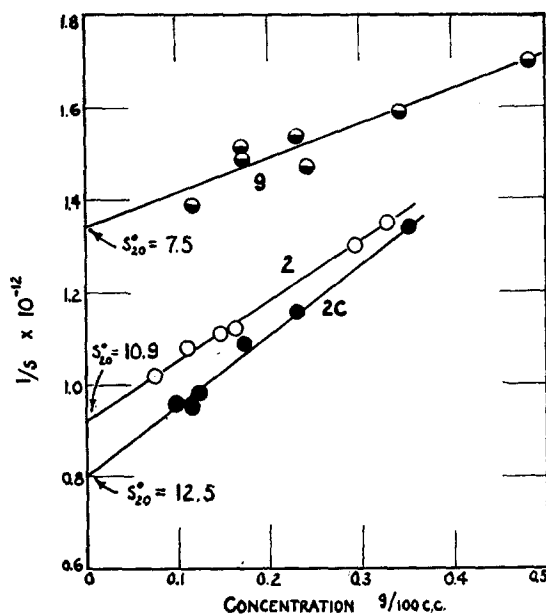


FIG. 2. Sedimentation data for three cellulose acetate fractions, 9, 2, and 2c, in acetone.

treatment of the problem of the concentration dependence of the sedimentation constant in such solutions is accredited to Burgers.⁴⁰ Since this paper is apparently not too well known as yet on this continent, a short section of it is quoted in the following paragraph.

"Under the influence of the field of flow produced by the falling particle A , the particle B is carried along with a velocity, the x -component of which is given by $u_m \dots$; whereas the particle A , in consequence of the disturbance due to the presence of B , experiences an induced velocity $u_i \dots$, which is of negative sign and thus evidently represents a retardation of the motion of $A \dots$. Hence when we now consider two particles both of which experience the action of the same gravitational force, they will acquire the same resultant velocity, $u_{res} = (F/8\pi\eta)(4/3a + u_m + u_i)$." Here F is the weight minus the buoyant force acting on the particle of radius a , in a medium of viscosity η . Assuming the medium extends indefinitely in all directions, everywhere possessing the same average number of particles per unit volume, summations over the particles are performed, and neglecting terms of higher order,

$$u_{res} = \frac{F}{6\pi\eta a} \frac{1}{1 + 6.875C_v},$$

TABLE VI. $B = 0.00125 \pm 0.00012$.

Fract.	s_{20}^0 $\times 10^{13}$	D_{20} $\times 10^{-7}$	Molecular weight				k_s
			Osm. ³⁷	Sed. and diff.	$2BM/RT$		
15	4.07	20.7	11,000	10,350	14 ± 2		6 ± 10
9	7.5	7.7	53,000	51,000	64 ± 6		56 ± 15
2	10.9	4.0	130,000	143,000	179 ± 17		143 ± 20
2c	12.5	3.4	—	194,000	243 ± 23		191 ± 25

⁴⁰ J. M. Burgers, Proc. Acad. Sci. Amsterdam **44**, 1045, 1177 (1941); **45**, 9, 126 (1942).

where C_v is the volume concentration of solute. Transforming this to the form of Eq. (2),

$$s_c = \frac{s_\infty}{1 + 6.875c\bar{V}},$$

\bar{V} being the specific volume of the solute, and c the concentration in grams/cc. Therefore, $k_s = 6.875\bar{V}$. Now from the theory of Zimm, for the osmotic pressure of athermal solutions of spherical particles, $2BM/RT = 8\bar{V}$ in the same units. Thus we see that theory predicts close correspondence, though not equality, of k_s and $2BM/RT$ for solutions of rigid spheres with no intermolecular forces present. The fact that k_D is relatively small for solutions of molecules quite different from rigid spheres suggests that this theoretical correspondence will be found to persist for molecules with a wide variety of configurations in athermal solutions.

In dealing with solutions for which $\Delta\bar{H}_1 \neq 0$, but is not large enough to alter significantly the shapes and distributions of the molecules from their characteristics in the athermal solution, it may be assumed as a first approximation²⁴ that the entropy and heat contributions to the free energy of dilution are independent, and that the entropy of dilution has the same value as it had in the previous case. For such solutions, according to the development just given, k_s should be of about the same magnitude as in the corresponding athermal solution, while k_D , a function of the free energy of dilution, should be somewhat different from its athermal value; larger

if $\Delta\bar{H}_1 < 0$, smaller if $\Delta\bar{H}_1 > 0$. The value of $\Delta\bar{H}_1$ is given by the relation:

$$\Delta\bar{H}_1 = \frac{\partial(\Delta\bar{F}_1/T)}{\partial(1/T)};$$

it may therefore be determined from the temperature dependence of the osmotic pressure.

For solutions with a large heat of mixing, where the heat and entropy of dilution are not independent, the quasi-lattice model becomes less significant, and the method of molecular distributions is at least hypothetically capable of predicting the osmotic pressure. However, the theory of the concentration dependence of the sedimentation constant for solutions of thread-like molecules is as yet so undeveloped that it is not profitable to attempt even qualitative correlations of k_s with the entropy of heat of dilution in such solutions. Moreover, there are practically no data concerned with this phase of the subject. Indeed, only in a very few polymer systems has the heat of dilution been determined. Evidently, investigations are required concerning the variation of k_s and k_D with $\Delta\bar{S}_1$ and $\Delta\bar{H}_1$ of solutions.

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