The Approach of Mutual Diffusion Coefficients to Molecular Weight Independence in Semidilute Solutions of Polydisperse Dextran Fractions

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The mutual diffusion coefficients of dextrans in the molecular weight range of 6×10^3–2×10^6 are shown to converge to values between 6×10^{-11} and 8×10^{-11} m^2 s^{-1} in semidilute solutions. The approach to molecular weight dependence is analyzed in terms of factors contributing to mutual diffusion, namely the thermodynamic factor and the hydrodynamic factor. This analysis includes an extensive theoretical reappraisal based on an irreversible thermodynamic approach of the relationships between mutual diffusion, sedimentation, and tracer diffusion.

Introduction

The molecular weight independent properties of dextran solutions have been established in studies of the concentration dependence of the dextran sedimentation coefficient[1] and of the diffusion of tritiated water in dextran solutions.[2] The early studies of Ogston and Woods[1] on dextran sedimentation lead to the realization of transient polymer network structures occurring in semidilute solutions. This concept has later been adopted in the theoretical work of de Gennes et al.[3] The importance of polymer segments in governing the polymer dynamical properties is investigated in this study with respect to the mutual diffusion of dextran in semidilute solutions. This analysis is used to reappraise both theoretically and experimentally the relationships between mutual diffusion, sedimentation, and tracer diffusion.

Theory

(A) Comparison of Equations. The mutual diffusion coefficient, D_1, which characterizes the relaxation of the concentration gradient of solute (component 1) in solvent (component 2) is frequently expressed in the following form[4-7]

$$D_1 = (c_1/f)(\partial\mu_1/\partial c_1) \tag{1}$$

where f is a frictional factor, μ_1 the chemical potential per mol of 1, and c_1 the concentration of 1 in moles per liter. The development of eq 1 in terms of an expression for $(\partial\mu_1/\partial c_1)$ as an osmotic pressure virial expansion has led to various expressions for D_1[4-7] which differ with respect to the varying powers of a $(1 - \phi_1)$ term, where $\phi_1 = c_1V_1$ is the volume fraction of component 1 and V_1 is the partial molar volume of 1 (assumed to be independent of concentration), included in the function for D_1. Further confusion arises as other equations for D_1 described as a function of μ_1 have been derived;[2,8-12] their source of variance appears to reside in the definition of the frictional factor and frame of reference. These equations also differ in the powers of the $(1 - \phi_1)$ term. We shall proceed to reassess the expression for D_1 in the light of the different approaches that have been taken so far.

We assume that measurement of the flux J_1 with respect to the cell-fixed frame of reference yields $(D_1)_v$ corresponding to the diffusion coefficient in a volume-fixed frame of reference.[13-15]

The diffusion coefficient in a binary system for a volume-fixed frame has been derived by Bearman[9] as

$$(D_1)_v = (D_2)_v = \frac{(1 - \phi_1)c_1}{f_{12}}\left(\frac{\partial\mu_1}{\partial c_1}\right)_{T,p} \tag{2}$$

where T is the temperature, p the pressure, μ_1 is the chemical potential of 1, f_{12} the frictional coefficient defined as[16] (for similar formations see ref 17 and 18)

$$-(\partial\mu_1/\partial x) = f_{12}(u_1 - u_2) \tag{3}$$

and where u_i is the velocity of i, using the relationships for the diffusional flux

$$J_i = c_iu_i \tag{4}$$

and

$$\sum_{i=1}^{2} V_i(J_i)_v = 0 \tag{5}$$

Identical relationships to these have been used by Vrentas and Duda[11] and Comper et al.[2] Equation 2 could also be obtained through the use of the dissipative function $T\sigma = J_1(\partial\mu_1/\partial x) + J_2(\partial\mu_2/\partial x)$ where σ is the rate of entropy production per unit volume and by using $J_1 = L_{11}Y_1$ where Y_1 is the conjugate force $(= (1 - \phi_1)^{-1}\,\partial\mu_1/\partial x)$.[19-21]

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The relationship utilized by Yamakawa,[7] namely eq 1, does not include the $(1 - \phi_1)$ term which could imply that the diffusion coefficient in his treatment has been derived on the basis of a solvent-fixed frame of reference. Vrentas and Duda[11] suggest that Yamakawa's frictional coefficient, f, has been defined in the following form

$$-(\partial\mu_1/\partial x) = fu_1 \tag{6}$$

which may suggest that $u_2 = 0$ in eq 3 as associated with the solvent-fixed frame. It is to be noted, however, that while Yamakawa's definition of f is vague and that eq 6 has been criticized,[11] Kops-Werkhoven et al.[12] have used a similar form of eq 6 in their derivation for a volume-fixed frame, i.e.

$$-\partial\mu_1'/\partial x = f'u_1 \tag{7}$$

where μ_1' is the chemical potential of 1 per gram and f' is the corresponding frictional coefficient. Using eq 4 and 5 in eq 3 we equate chemical potential terms in eq 3, 6, and 7 to give

$$f_{12} = f(1 - \phi_1) = f'(1 - \phi_1)M_1 \tag{8}$$

The preference for the use of f_{12} over that of f or f' is that the former frictional coefficient is frame-independent whereas the other frictional coefficients are not. A source of ambiguity may arise if the frame-dependent frictional coefficients are not clearly defined as is possibly the case in Yamakawa's treatment.

An alternative expression for $(D_1)_v$ that has been rigorously derived is given as[8,10,12]

$$(D_1)_v = \frac{L}{(1 - \phi_1)}\left(\frac{\partial\mu_1'}{\partial C_1}\right)_{T,p} \tag{9}$$

where L the phenomenological coefficient, given by $L = (1 - \phi)^2 c_1 M_1^2/f_{12}$, has been derived from a general expression for entropy production when expressed as the sum of all independent forces and flows that maintain the Onsager reciprocal relations between phenomenological coefficients and C_1 is the mass concentration of 1.

(B) Evaluation of $(D_1)_v$. (1) Sedimentation. A prediction of magnitude of $(D_1)_v$ in eq 2 requires knowledge of both f_{12} and $(\partial\mu_1/\partial c_1)_{T,p}$. An estimate of f_{12} may be made from sedimentation velocity experiments where the sedimentation coefficient, $(s_1)_v$, in a volume-fixed frame is given by[12,22]

$$(s_1)_v = (1 - \rho v_1)(1 - \phi_1)M_1/f_{12} = (1 - \rho v_1)M_1/f \tag{10}$$

where ρ is the density of the solution and v_1 the partial specific volume of 1. Equation 10 has the form that is commonly used.[5,23] A number of investigators have experimentally shown that f in eq 10 and f in eq 1 are similar in magnitude.[24,25]

(2) Osmotic Pressure. Some caution must accompany the evaluation of the $(\partial\mu_1/\partial c_1)_{T,p}$ term in eq 2. Certainly its unambiguous evaluation could be made from its direct measurements by osmotic pressure at constant solution pressure p. However, measurements of activity coefficients are not normally made in this way but are performed with a fixed chemical potential of the solvent μ_2 in the solution phase. It may be shown, when the ratio of isothermal to osmotic compressibility is considerably less than one,[12,20] that

$$\left(\frac{\partial\mu_1}{\partial c_1}\right)_{T,p} = (1 - \phi)\left(\frac{\partial\mu_1}{\partial c_1}\right)_{T,\mu_2} = \frac{1}{c_2^2 M_2 V_2}\left(\frac{\partial\mu_1}{\partial m_1}\right)_{T,p} \tag{11}$$

where m_1 is the molality of 1. Substitution of this equation into eq 2 gives

$$(D_1)_v = (m_1/f_{12})(\partial\mu_1/\partial m_1)_{T,p} \tag{12}$$

This equation may be further developed in terms of osmotic virial coefficients. The partial derivative of osmotic pressure (Π) measured at constant temperature and pressure may be expressed[26]

$$\left(\frac{\partial\Pi}{\partial m_1}\right)_{T,p} = \frac{M_2}{V_2}m_1\left(\frac{\partial\mu_1}{\partial m_1}\right)_{T,p} = RT\frac{M_2}{V_2}(1 + \beta_{11}m_1 + \beta_{111}m_1^2 + \ldots) \tag{13}$$

(Kurata's nomenclature[26] for virial coefficients has been adopted in eq 13). Rearrangement of eq 13 and substitution into eq 12 gives

$$(D_1)_v = (RT/f_{12})(1 + \beta_{11}m_1 + \beta_{111}m_1^2 + \ldots) \tag{14}$$

where R is the universal gas constant.

For measurements at constant T and μ_2 the partial derivative of osmotic pressure (Π^*) is given by[26]

$$\left(\frac{\partial\Pi^*}{\partial C_1}\right)_{T,\mu_2} = C_1\left(\frac{\partial\mu_1}{\partial C_1}\right)_{T,\mu_2} \tag{15}$$

$$= QM_1RT \tag{16}$$

where

$$Q = \frac{1}{M_1} + 2A_2^{os}C_1 + 3A_3^{os}C_1^2 + \ldots \tag{17}$$

and A_2^{os} and A_3^{os} are termed the standard osmotic second and third virial coefficients defined by the relation

$$\Pi^*/RT = C_1/M_1 + A_2^{os}C_1^2 + A_3^{os}C_1^3 + \ldots \tag{18}$$

Using eq 15 and 17 in eq 2 gives

$$(D_1)_v = RT(1 - \phi_1)^2 QM_1/f_{12} \tag{19}$$

or with eq 8

$$(D_1)_v = RT(1 - \phi_1)QM_1/f \tag{20}$$

Note that eq 20 is identical with that obtained by Yamakawa.[7] The major concern associated with his treatment is the ambiguity of his definition of the frictional coefficient term and/or the reference frame.

Evaluation of osmotic pressure or the Q term in eq 17 is often performed through the use of a limited number of virial coefficients to generate a truncated virial expansion. This is an inherently inaccurate procedure as ideally the evaluation should proceed to concentration terms in the power series that converge to zero or certainly less than the change in magnitude that the inclusion of a $(1 - \phi_1)$ function may have on $(D_1)_v$. If this is not the case, inclusion of the $(1 - \phi_1)$ term would be irrelevant. Certainly, for virial coefficient analysis of dextran, severe errors are probably associated at the third virial coefficient level as higher-order coefficients have not been evaluated. Therefore, an estimate of $(D_1)_v$ must be performed by approximation. A summary of the complete diffusion equations come from eq 14

$$(D_1)_v = (RT/f_{12})(1 + \beta_{11}m_1 + \beta_{111}m_1^2 + \ldots)$$

and eq 17 in eq 19

$$(D_1)_v = [RT(1 - \phi_1)^2/f_{12}][1 + 2A_2^{os}M_1C_1 + 3A_3^{os}M_1C_1^2 + \ldots] \tag{21}$$

The $(1 - \phi_1)$ terms that appear in eq 21 come from (1) the conversion of the molal concentration scale to mass (or molar) concentration scale together with (2) the conversion of chemical

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potential terms evaluated at constant μ_2 as compared to those evaluated at constant p. The relationships between virial coefficients in eq 14 and 21 given by Kurata[26] indicate that to the third order in concentration terms the m_1 expansion is greater than the C_1 expansion. Clearly then eq 14 is preferred in the evaluation of $(D_1)_v$ for truncated expansions together with overcoming the decrement associated with the $(1 - \phi_1)^2$ factor in front of the C_1 expansion. If only standard osmotic virial coefficients are available then rather than using eq 21 we suggest that a better approximation of $(D_1)_v$ may be made by conversion of eq 14 to a mass concentration scale

$$(D_1)_v = RT(M_1/f_{12})(1/M_1 + 2A_2C_1 + 3A_3C_1^2 + ...) \quad (22)$$

where

$$A_2 = \beta_{11}/2c_2M_2(M_1)^2 \qquad A_3 = \beta_{111}/3(c_2M_2)^2(M_1)^3 \quad (23)$$

The virial coefficients A_2, A_3 may be related to the osmotic pressure by[2,26]

$$\Pi(1 - \phi_1) = RT\left(\frac{C_1}{M_1} + A_2C_1^2 + A_3C_1^3 + ...\right) \quad (24)$$

Equations 22–24 have been used previously[2] in dextran diffusional analysis assuming that $A_2 \simeq A_2^{os}$ and $A_3 \simeq A_3^{os}$.

(3) Tracer Diffusion. Other expressions for $(D_1)_v$ have assumed that the $1/f$ term in eq 1 or by implication the $1/f_{12}$ term in eq 2 is identical with the intradiffusion coefficient of the trace-labeled species in the absence of chemical potential gradients or concentration gradients in isobaric, isothermal systems.[27-29] The two parameters have been found to be quantitatively similar.[2,30,31] However, it should be noted that on theoretical grounds there is no general relation between these quantities[32] other than circumstances which give rise to the solutions being "regular"[9] which has been shown not to be the case for dextran solutions.[2]

For intradiffusion or tracer diffusion studies we designate the labeled component of 1 as 1*. We define the chemical potential as

$$\mu_i = \mu_i^\theta + RT \ln (c_i y_i/c^\theta)$$

where μ_{ic}^θ is the standard chemical potential of component i on the molar scale and c^θ denotes a standard value of molarity. Since 1 and 1* are identical, an intradiffusion experiment requires

$$y_{1^*} = y_1 \quad (25)$$

It is not difficult to show that by assuming $f_{12} = f_{1^*2}$ and the reciprocal relationship

$$c_i f_{ij} = c_j f_{ji} \quad (26)$$

gives

$$D_{1^*} = RT/(f_{1^*2} + f_{1^*1}(1 + c_{1^*}/c_1))$$

which reduces to

$$D_{1^*} = RT/(f_{12} + f_{1^*1}) \quad (27)$$

for $c_{1^*} << c_1$.

The justification of the assumption $f_{12} = f_{1^*2}$ comes from using the reciprocal relationship eq 26 and with the knowledge that $\partial\mu_2/\partial x$ and u_2 are zero which gives $f_{21}/c_1 = f_{21^*}/c_{1^*}$ (see also Tyrrell[21]). Note that it is not commonly recognized eq 27 can only be derived on the condition that eq 25 holds, which would not be the case for infinite dilution.

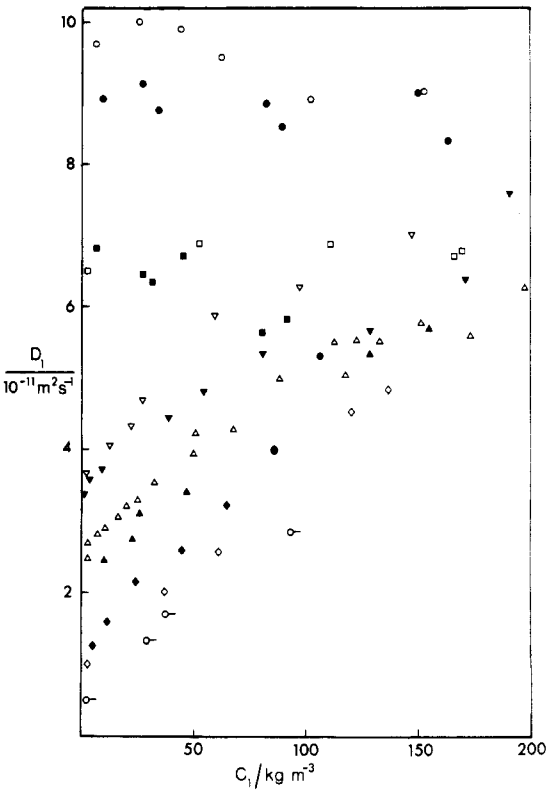

Figure 1. The mutual diffusion coefficient D_1 of dextran as a function of the mean concentration for dextran T10 (○), T20 (□), T70 (▽), FDR7783 (△), T500 (◇), and T2000 (○–). Empty symbols are values of the mutual diffusion coefficient obtained by schlieren analysis of boundary relaxation in the analytical ultracentrifuge; filled symbols are values of the mutual diffusion coefficient obtained dynamic light scattering. Some of the data for dextrans T10, T20, T70, and FDR7783 have been obtained from Preston et al.[30]

Experimental Section

Materials. The polymer dextran samples dextran T10 ($\bar{M}_n$ = 0.6 × 10⁴, $\bar{M}_w$ = 1.04 × 10⁴), T20 ($\bar{M}_n$ = 1.65 × 10⁴, $\bar{M}_w$ = 2.04 × 10⁴), T70 ($\bar{M}_n$ = 3.95 × 10⁴, $\bar{M}_w$ = 6.95 × 10⁴), FDR7783 ($\bar{M}_n$ = 12.03 × 10⁴, $\bar{M}_2$ = 15.82 × 10⁴), T500 ($\bar{M}_n$ = 30.3 × 10⁴, $\bar{M}_w$ = 51.7 × 10⁴), and T2000 ($\bar{M}_w \sim 2.0 \times 10^6$) were supplied by AB Pharmacia (Uppsala, Sweden). $\bar{M}_n$ and $\bar{M}_w$ are the number average and weight average molecular weights as supplied by the manufacturer. The physicochemical properties of these dextran fractions have been previously analyzed.[30]

Stock solutions of dextrans of known moisture content were made up by weight in either double distilled water or in 0.15 mol dm^{-3} NaCl. To convert dextran concentrations to a mass/solution volume scale we have used a dextran partial specific volume of 0.6 $cm^3\ g^{-1}$ (ref 2).

Methods. Mutual Diffusion Coefficients. Mutual diffusion coefficients were measured by either measurement of diffusion in a Beckman Model E analytical centrifuge at 20 °C using the schlieren optical system or by a dynamic light scattering technique. The details of these techniques and methods of analysis have been described previously.[30]

Sedimentation Coefficients. Sedimentation coefficients were measured at 44 000 rpm at 20 °C in the analytical ultracentrifuge by use of the schlieren optical system and monitoring the movement of the maximum peak height.[27]

Results

The concentration dependence of the mutual diffusion coefficient of dextrans in the molecular weight range from 6 × 10³ to 2 × 10⁶ is shown in Figure 1. The diffusion coefficients have been measured in solutions covering a concentration range from 1 to 200 kg m^{-3}. The two techniques used to measure these coefficients, namely the classical schlieren method and dynamic

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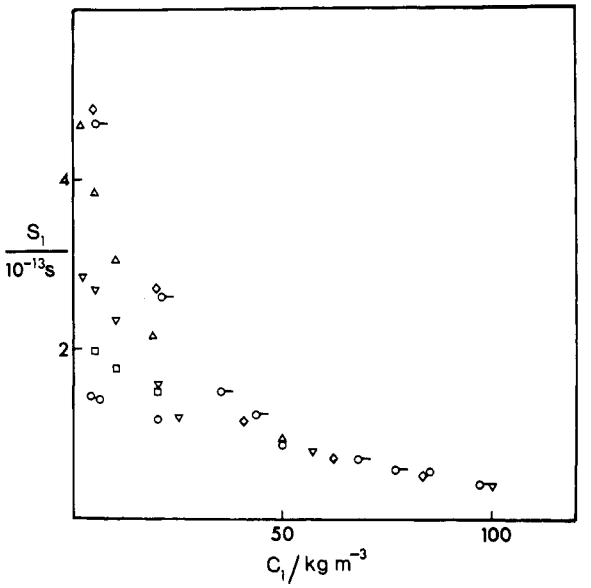

Figure 2. The sedimentation coefficient, s_1, as a function of concentration of dextran T10 (○) T20 (□), T70 (▽), FDR7783 (△) T500 (◇), and T200 (○–).

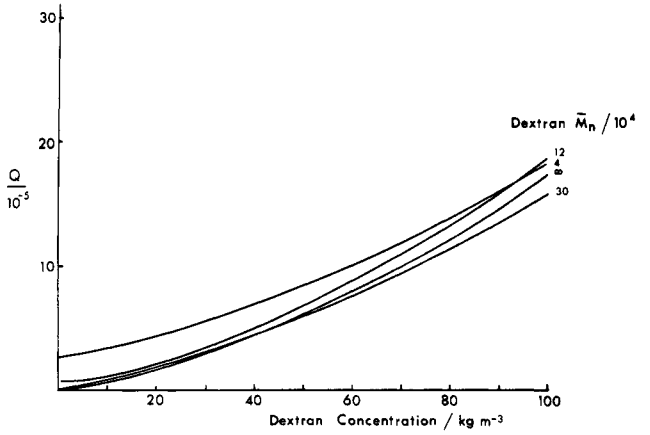

Figure 3. Calculated values of the virial expansion of Q (eq 17) as a function of concentration for dextrans of different molecular weight. The virial coefficients, measured for concentration up to approximately 100 kg m^{-3}, have been previously summarized.[30] Virial coefficients from cross-linked dextran $\bar{M}_n(\rightarrow \infty)$, i.e. Sephadex beads, have been obtained from Edmond et al.[33] The figure is modified from ref 34.

light scattering, have shown good agreement. Dextrans with molecular weights $\bar{M}_w > 7 \times 10^4$ exhibit a marked concentration dependence of D_1; with increasing concentration the value of D_1 increases. On the other hand, for dextrans with $\bar{M}_w = (1\text{–}2) \times 10^4$ the value of D_1 is essentially constant or may decrease with concentration for the low molecular weight sample dextran T10. At high dextran concentrations the diffusion coefficients appear to converge to a constant value, in the range of (6–8) × 10^{-11} m^2 s^{-1}, irrespective of the dextran molecular weight.

In Figure 2, the sedimentation coefficient for these dextran fractions appear to converge to a molecular weight independent value at dextran concentrations greater than 50 kg m^{-3}.

Discussion

It is of interest to analyze eq 10 and 22 to understand the contribution of the various parameters leading to the molecular weight independence of $(D_1)_v$ and s_1. We have previously shown that for dextrans with $\bar{M}_w > 70 \times 10^3$ the virial expansion Q in eq 17 evaluated to the third power in concentration is essentially molecular weight independent for concentrations up to 100 kg m^{-3} (Figure 3); at dextran concentration of 60 kg m^{-3} there was an ±11% variation about the mean Q value and at 100 kg m^{-3} the variation was ±7.5%. These compare with the variation about the mean D_1 (Figure 1) at 60 kg m^{-3} dextran of ±44% and at 100

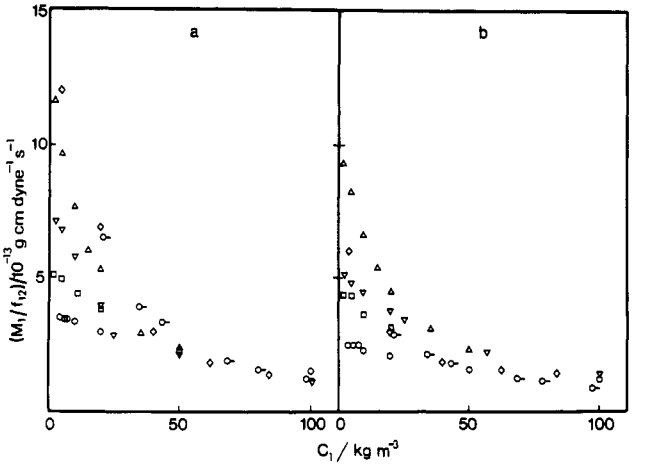

Figure 4. Calculated values of M_1/f_{12} obtained through eq 10 for sedimentation experiments (a) and eq 22 for mutual diffusion experiments (b) as a function of dextran concentration for dextran T10 (○), T20 (□), T70 (▽), FDR7783 (△), T500 (◇), and T2000 (○–).

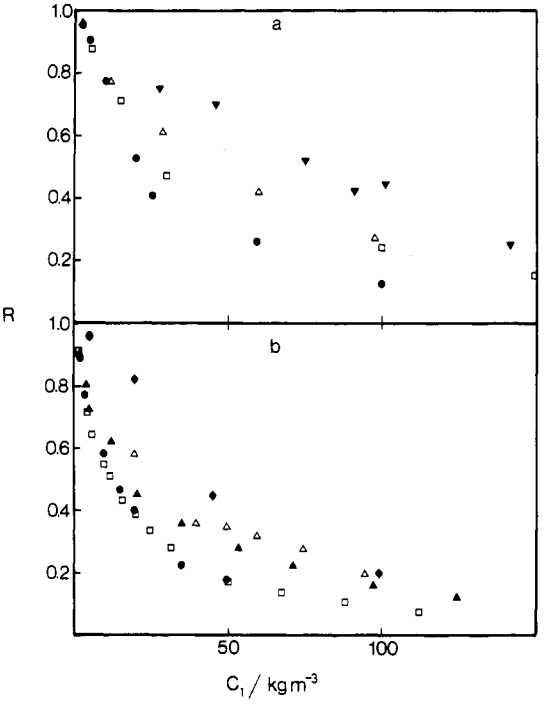

Figure 5. The reduced dynamic quantity (R) plotted as a function of dextran concentration for (a) dextran T70 and (b) dextran FDR7783 and dextran T170 ($\bar{M}_w$ = 170 000). The reduced quantities are f_{12}^0/f_{12} (□) from mutual diffusion[30] using eq 22, f_{12}^0/f_{12} from sedimentation velocity (●) using eq 10, $f_{12}^0/f_{12} + f_{1^*1}$) from tracer intradiffusion[30] (△) (Laurent et al.[28] data for FDR7783 (♦)) using eq 27 and D_s^0/D_s from NMR techniques for dextran T70[25] (▼) and dextran T170[39] (▲).

kg m^{-3} of ±32%. In assuming that $A_2 \simeq A_2^{os}$ and $A_3 \simeq A_3^{os}$ in eq 22 then the apparent slow convergence of D_1 to molecular weight independence at high dextran concentrations is due to the similar slow convergence of the M_1/f_{12} term in eq 22 (Figure 4b).

It is clear from the sedimentation data in Figure 2 that the M_1/f_{12} evaluated from eq 10 is molecular weight independent in the dextran concentration range of 60 to 100 kg m^{-3} (Figure 4a). This behavior may establish its difference from M_1/f_{12} evaluated from diffusion (Figure 4b). In terms of absolute values M_1/f_{12} from sedimentation is higher than that obtained from diffusion (Figure 4). The differences which are reflected in the extrapolated M_1/f_{12} values at infinite dilution (Table I) appear to be related to the polydispersity of the preparation; namely, the ratio of f_{12}(diffusion)/f_{12}(sedimentation) is similar to the ratio of $\bar{M}_w/\bar{M}_n$ for each preparation; since $\bar{M}_n$ was used for diffusional analysis it seems more appropriate to use $\bar{M}_w$ for sedimentation analysis. In light of these differences it is difficult to draw conclusions as

TABLE I: Comparison of Extrapolated Values of M_1/f_{12} (from Figure 4) to Infinite Dilution for both Sedimentation and Diffusion Measurements

dextran type	$\bar{M}_n$/ 10^4 g mol^{-1}	$\bar{M}_w/\bar{M}_n$	$(M_1/f_{12})_{c_1\to 0}$/ 10^{-13} g cm dyn^{-1} s^{-1} sedimentation	diffusion	f_{12}^m/f_{12}^s [a]
T10	0.6	1.73	3.78	2.47	1.53
T20	1.65	1.24	5.20	4.65	1.12
T70	3.95	1.76	7.32	5.25	1.39
FDR7783	12.03	1.32	12.20	10.30	1.18
T500	30.30	1.70	14.53	7.0	2.07

[a] f_{12}^s and f_{12}^m are the frictional coefficients from sedimentation and mutual diffusion, respectively.

to whether the M_1/f_{12} values from the two techniques are the same as has been found for less polydisperse polymer fractions.[25,35]

Certainly the approach to molecular weight independence of the M_1/f_{12} term does point to the possibility that it reflects dynamic properties of the polymer segment in semidilute solution rather than the individual molecule. Therefore, we would predict that the diffusion of the polymer segment in the dextran gel (i.e. Sephadex) (when elastic constraints are low) would be similar to that found in semidilute solution as its Q value is similar (Figure 3). These correlations have already been experimentally established for solute diffusion in semidilute solutions and gels of polyacrylamide,[36] polystyrene,[37] and gelatin.[38]

Some consideration has been given to the relationship of f_{12} to the intradiffusion coefficient D_{1*}. This has been a controversial area where, on the one hand, it has been assumed that $D_{1*} = RT/f_{12}$ (as compared to eq 27) and, on the other hand, various authors are critical of this assumption based on theoretical grounds.[2,25,32]

Comparison of values of f_{12}^0/f_{12} from mutual diffusion (eq 22) and sedimentation (eq 10) where the superscript zero denotes infinite dilution, $f_{12}^0/(f_{12} + f_{1*1})$ from tracer intradiffusion, and D_s/D_s^0 from NMR spin-echo techniques where D_s is the self-diffusion coefficient are shown in Figure 5 for dextrans T70 and FDR7783. For both dextrans there is good agreement between the reduced quantities obtained from mutual diffusion and from sedimentation; the values from tracer diffusion tend to be higher at higher concentration. Excellent agreement is found between Callaghan and Pinder's[39] self-diffusion study of dextran T170 in D_2O by NMR and tracer diffusion of FDR7783 whereas some difference is seen in the self-diffusion measurements of dextran T70 by NMR at 75 °C and corrected to 25 °C[25] to those made by tracer diffusion (Figure 5a). The conclusions drawn from these comparisons are that f_{12} from mutual diffusion and sedimentation are similar and that f_{1*1} is relatively small and negative in sign as compared to f_{12}.

A further outcome of this work is the possibility that if f_{12} represents a coefficient describing solute–solvent exchange across the boundary in a volume-fixed frame then the tracer diffusion measurement (being similar to f_{12} since $f_{1*1} \to 0$ in eq 27) may only represent an incomplete diffusion process or exchange (i.e. solute–solvent exchange) as governed by eq 25 which requires solute–solute exchange.

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Statistical Mechanics of Bolaform Electrolytes

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Bolaform electrolytes are a simple type of polyelectrolyte in which charges are separated by a chain of atoms in the polyion. This paper applies the methods of statistical mechanics to obtain thermodynamic properties for bolaform electrolytes. In particular, the linearized Poisson–Boltzmann equation is solved for an ellipsoidal model of a bolion. The electrostatic potential is then used to calculate thermodynamic properties. A comparison with available experimental activity coefficient data shows good agreement with the theory at low concentrations.

Theory and Model Formulation

Bolaform electrolytes are a peculiar type of polyvalent electrolyte in which the charged sites are separated by a chain of atoms within the ion. In this work we will mostly be interested in divalent bolions. Examples of such ions are disulfonates and diquaternary ammonium ions. These ionic compounds were named by Fuoss[1] and it is known that dilute solutions of bolaform salts have markedly different thermodynamic properties from those of normal (simple) electrolytes such as calcium chloride or copper(II) sulfonate. Very little theoretical work has been done on this problem since the original work by Rice and Nagasawa.[2] In this paper we will present a model for bolaform electrolytes and solve the Debye–Hückel equation exactly for this ionic system. We will also compare our theory with experimental activity coefficient data on real aqueous bolaform salts.

The ionic model that we shall use to represent the bolaform ions in solution consists of a uniform fluid with dielectric constant ϵ. The bolaform ion is immersed in this fluid. The other ions in the system are imagined to be charges with zero size.

We assume that the potential external to the ion of interest is satisfied by the linearized Poisson–Boltzmann equation

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