Test of 'scaling laws' describing the concentration dependence of osmotic pressure, diffusion and sedimentation in semidilute macromolecular solutions

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Data of osmotic pressure, diffusion and sedimentation in semidilute macromolecular solutions are systematized with regard to scaling laws. The observed main features are: (a) the concentration dependence of the osmotic pressure both at good and theta solvent conditions is in excellent agreement with that predicted by the scaling laws. (b) The concentration dependence of the mutual diffusion coefficient D_m could not uniquely be described by a simple scaling law. A difference in concentration dependence between D_m and the cooperative diffusion coefficient was observed for polystyrene under good solvent conditions. (c) The concentration dependence of the permeability coefficient (related to sedimentation) and the sedimentation coefficient were for most of the systems in close agreement with that predicted by the scaling laws.

INTRODUCTION

Up to 1972 the mean field picture was the prevailing theory. This theory, initiated by Flory[1], was successful in describing properties of dilute solutions of flexible polymers but failed for semidilute (entangled) solutions[2–4]. Furthermore, the behaviour in the dilute and semidilute solution regions was not logically linked. In order to avoid this inadequate description a new approach[2–6], based on an analogy between polymer and magnetic systems, describing static and dynamical properties of both dilute and semidilute solutions was proposed recently. In each regime well-defined patterns of behaviour were found and a rigorous link between the two regimes was established. From this picture, scaling laws, characterizing polymer solutions, emerged; the existence of these characteristic laws was inferred also from experimental work[2–8].

The concentration dependence of the osmotic pressure, π, the diffusion coefficient, D, and the permeability coefficient, λ (related to the sedimentation coefficient) has been formulated in terms of scaling laws[2,6,9,10]. However, these power laws have to our knowledge not been tested in a comprehensive study of experimental data. The principal aim of the present investigation is to determine the concentration dependence of π, D and λ, respectively, in the semidilute regime by utilizing scaling concepts, and to compare the experimental exponents, determined from a large amount of data, with those predicted. Therefore, a systematic study of existing experimental data covering both good and poor solvent conditions was undertaken. Before the results are presented and discussed the theoretical background is summarized.

THEORY

Concentration regimes

In dilute macromolecular solutions the solute molecules will be distinct and the dynamical situation is governed mainly by the intrinsic properties of the individual molecules. As the concentration increases, the intermolecular interactions will become more and more dominating and gradually the molecules will be in a state of more or less permanent contact. According to Simha[11], who considered solutions of flexible macromolecules, this incipient overlap of polymer coils should occur at $c^* = 1/[\eta]$ where $[\eta]$ is the limiting viscosity number (intrinsic viscosity). The significance of this concentration to separate different concentration regions has been manifested from recent sedimentation velocity measurements[12–15]. These investigations also demonstrate the difficulty in defining unambiguously a concentration which separates the dilute and semidilute domains. Upon a further increase in concentration the entanglement effects must be considered; eventually the statistical subunit density is homogeneous throughout the solution. The concentration c^+ where a uniform distribution of segments prevails can for instance be defined by[16–18]

$$c^+ = \frac{M}{N_A \langle S^2 \rangle^{3/2}} \tag{1}$$

where M is the molar mass (kg/mol), $\langle S^2 \rangle$ is the mean-square radius of gyration and N_A is Avogadro's constant. This concentration has been regarded as a critical concentration separating the dilute and semidilute domains. In the semidilute

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domain the entangled polymer solutions have been considered to behave like polymer networks with a finite lifetime[9,19,20]. The cross-over region (from incipient overlap to uniform segment density) has been observed from experiments to be smooth and to be centred roughly at c^+.

Scaling laws

Our present understanding of the organization in an entangled polymer solution is based on scaling hypotheses. The fundamental parameter in the scaling law picture is the screening length, ξ, which is dependent on concentration and temperature but independent of molecular weight and is of utmost importance in the description of both static and dynamical properties of semidilute solutions[2].

The screening length concept for a polymer solution in the semidilute range was introduced by Edwards[21]. In an entangled solution, where the chains are pictured to have contact (entanglement) points, the average distance between adjacent contact points is defined by a characteristic length, namely the screening length ξ. The parameter ξ may be interpreted as the distance beyond which there is no excluded volume effect between any two segments of the chain and can be defined by the following relation[21]

$$\xi = \left(\frac{l^2 n}{12 c N_A v}\right)^{1/2}; \qquad c > c^+ \tag{2}$$

Here c is the concentration (mass/volume) of the solute. The other quantities refer to the statistical subunit of the equivalent Gaussian chain; l^2 is the mean-square length, n the (molar) mass and v the excluded volume.

Using dynamical scaling, de Gennes has shown that the concentration dependence of ξ is given by[2,9]

$$\xi \sim c^{-m} \tag{3}$$

where

$$m \equiv \frac{\nu}{\nu d - 1} \tag{4}$$

Here d is the dimensionality of space and ν is a characteristic exponent. For good solvent conditions ν is the Flory exponent[1] for the excluded volume, and assumes the value 0.60 for $d = 3$, leading to $m = 0.75$. At theta conditions ν is a 'tricritical' exponent[22,23] with the value 0.50 and hence $m = 1$. Thus equation (3) can be written

$$\xi \sim \begin{cases} c^{-0.75} \text{ (good solvent conditions)} \\ \\ c^{-1.0} \text{ (theta conditions)} \end{cases} \tag{5}$$

These values of the exponents have been confirmed by recent small-angle neutron scattering experiments[2,24].

Osmotic pressure

The average number of contact (entanglement) points is proportional to $1/\xi^3$, (ξ may be regarded as the average distance between contact points). Since it can be argued generally that π/T measures the number of contact points[2], the osmotic pressure π can be expressed as[2,9]

$$\pi \simeq \frac{k_B T}{\xi^3} \tag{6}$$

where k_B is Boltzmann's constant and T is the absolute temperature. By combining equations (5) and (6) the following power laws for the osmotic pressure in the semidulite region are obtained[2]

$$\pi \sim \begin{cases} c^{2.25} \text{ (good solvent conditions)} \\ \\ c^{3.0} \text{ (theta conditions)} \end{cases} \tag{7}$$

For good solvent conditions the mean field theory due to Flory and Huggins predicts the value 2 for the exponent m^1. Although the difference between the value 2.25 and the mean field value 2 is not very large it is well visible in carefully performed experiments (see *Table 1*). Furthermore, this difference has a profound meaning which has been discussed previously[2,3]. On the other hand, the predicted scaling behaviour at theta conditions ($\pi \sim c^3$) is essentially identical with the mean field prophecy for the theta point.

Diffusion

The principle of quasielastic light scattering has been amply described in the literature[25–27]. By using this technique different dynamic regions are accessible[9,28]. The parameters which define these regions are concentration (dilute or semidilute solution), the coil radius of gyration, and momentum transfer [$|\underline{q}| = (4\pi/\lambda)\sin\theta/2$, $|\underline{q}|$ is a function of the scattering angle θ and the incident wavelength λ]. It can generally be maintained that when the dimensionless quantity $qR \ll 1$, where R is a characteristic length[9], the scattering is related to 'macroscopic' properties of the system, such as the overall translational motion of the chains, whereas when $qR \gg 1$ the scattering is governed by the 'local' properties (internal motions). In order to discuss the dynamic regimes in more detail a schematic sketch, introduced by a de Gennes[9], has been displayed in *Figure 1*, showing the ranges of concentration and momentum transfer for the predicted existence of the different types of modes.

In region 1 the diffusion of individual coils is detected and the diffusion coefficient is dependent on molecular weight but depends only slightly on concentration.

The diffusion process in region 2 corresponds to a superposition of centre of mass (translational) motion and coil deformations.

The diffusion behaviour in regime 3 is characterized by the cooperative diffusion coefficient, D_c, (independent of molecular weight) which is associated with network deformations and is given by[9]

$$D_c = \frac{k_B T}{6\pi\eta_0\xi} \tag{8}$$

where η_0 is the viscosity of the solvent. The scaling hypothesis for good solvent conditions yields consequently the following concentration dependence of D_c

$$D_c \sim c^{0.75} \tag{9}$$

Experimental evidence for this dynamical correlation has been observed recently[8,28,29]. However, the experimentally determined exponent was found to be somewhat smaller than the predicted one.

Region 4 may be interpreted as the domain where mutual diffusion motion (or centre of mass translational diffusion

Table 1 Compilation of osmotic pressure data for various polymer–solvent systems in the semidilute concentration region. a_π indicates the slope (above c^+) in a lg–lg plot of the osmotic pressure versus concentration

Polymer	Solvent	Molecular weight	Temperature °C	a_π	Remarks	Ref
Poly(γ-benzyl-L-glutamate)	Chloroform	9.80×10^4	29	2.1_6		52
	N,N-dimethylformamide	1.60×10^5	45	2.1_1		53
Poly(dimethyl siloxane)	Cyclohexane	1.22×10^5	20	2.2_2		54
		4.93×10^5	20	2.1_5		55
	n-Heptane	1.40×10^5	35	2.2_6		56
			50	2.3_2		
	n-Hexane		20	2.2_8		
			50	2.2_1		
	n-Nonane		20	2.3_7		
			50	2.2_5		
	n-Octane		20	2.2_9		
			35	2.2_8		
			50	2.2_3		
Polyisobutene	Benzene	9.00×10^4	24.5	3.2	θ_u = 24.5°C	57
	Cyclohexane	9.00×10^4	8	2.3_4		57
			30	2.2_4		
	n-Heptane	9.94×10^4	0	2.1_3	LCST = 174°C	58
			20	2.1_3		
			40	2.3_4		
			60	2.3_6		
	n-Hexane	9.94×10^4	0	2.1_4	LCST = 129°C	58
			20	2.1_4		
			40	2.1_4		
	n-Pentane	9.94×10^4	0	2.2_6	LCST = 73°C	58
			20	2.2_0		
Poly(methyl methacrylate)	Acetone	9.56×10^4	25	2.1_1		59
		1.61×10^5	30	2.1_9		60
	Benzene	4.33×10^5	30	2.4_0		60
	2-Butanone	1.01×10^5	25	2.0_9		59
	1,2-Dichloroethane	8.45×10^4	25	2.4_7		61
	Dioxane	8.45×10^4	25	2.3_2		61
	Ethyl acetate	1.04×10^5	25	2.1_3		59
	Toluene	8.98×10^4	25	1.9_5		59
Polystyrene	2-Butanone	8.50×10^4	10	2.2_9	θ_L = 146°C	62
			25	2.3_6		
			40	2.4_4		
			55	2.5_2		
		9.72×10^4	10	2.3_2		63
			50	2.5_0		
		5.25×10^5	27	2.0_6		64
			49	2.3_0		
		5.50×10^5	25	2.2_6		59
	Chlorobenzene	9.84×10^4	25	2.2_1		65
	Cyclohexane	1.17×10^5	37	2.7	θ_u = 35°C	59
		4.40×10^5	34	2.9		65
	Dioxane	9.73×10^4	25	2.1_5		66
	Ethyl acetate	1.15×10^5	25	2.0_6		59
		5.25×10^5	27	2.0_2		64
			49	2.0_5		
	Ethyl benzene	9.72×10^4	10	2.1_1		67
			35	2.1_1		
			60	2.1_1		
Polystyrene	Toluene	1.33×10^4	30	2.2_7		68
		2.45×10^4	40	2.1_3		69
		1.19×10^5	25	2.2_5		59
		4.21×10^5	40	2.1_8		68
		5.25×10^5	27	2.2_6		64
			69	2.2_6		
	trans-decalin	3.96×10^5	20	2.8	θ_u = 20.8°C	70
			25	2.1_5		
			30	2.0_6		
			35	2.0_8		
			40	2.1_5		
Poly(vinyl acetate)	2-Butanone	3.00×10^5	10	2.1_0		54
			45	2.1_7		
	1,3,5-Trichloropropane	2.70×10^5	15	2.3_1		54
			50	2.2_2		
Dextran	Water	3.74×10^5	25	2.3_9		71
Haemoglobin	Water (phosphate buffer)	6.70×10^4	–	2.2_6		72
Polyoxyethylene	Water	4.35×10^4	25	2.1_4		71
Poly(vinyl pyrrolidone)	Water	2.79×10^4	25	2.1_4		71

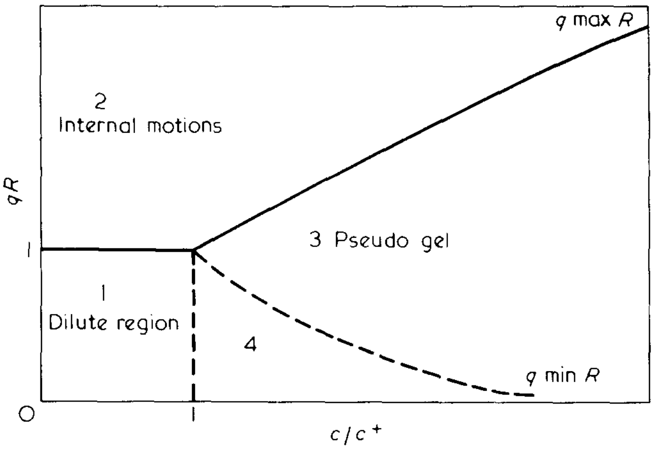

Figure 1 A schematic representation of the different dynamical regimes

motion) of the polymer chains are observable. The diffusion process is described by the relaxation of a concentration gradient. By choosing small enough angles θ (q values) it is always possible to arrange the centre of mass translational motion to dominate the Doppler-broadened spectrum. However, it should be emphasized that the interpretation of the experimental data in terms of diffusion coefficients is based upon theoretical models.

Most of the earlier quasielastic light scattering (QELS) measurements dealing with semidilute solutions[30–35] were conducted in region 4. It was demonstrated experimentally[30,32] that the mutual (translational) diffusion coefficient, D_m, obtained by classical techniques, i.e. by establishing an artificial concentration gradient and observing the relaxation of this gradient with time, was identical with that obtained by QELS measurements over an extended concentration interval*.

The diffusion data systematized in this paper are mutual (translational) diffusion data. The interest has been directed toward a quantitative determination of the concentration dependence of D_m for various polymer–solvent systems in the semidilute regime.

Sedimentation

At concentrations $c > c^*$ the sedimentation process is principally governed by the flow of solvent through, instead of mainly around, the polymer coils. This behaviour has been described by utilizing the permeability concept[36,37]. The notion of permeability was first introduced by Darcy in connection with the flow of liquids through a porous material[38].

Mijnlieff and Jaspers[37] considered the analogy between the sedimentation of a polymer in a solvent and the permeation of solvent through a porous plug of material. They derived, using irreversible thermodynamics, the following relation between the sedimentation coefficient and the permeability coefficient k

$$k = \frac{\eta_0 s}{c(1 - \bar{v}_2/\bar{v}_1)} \tag{10}$$

where η_0 is the solvent viscosity, s is the sedimentation coefficient at solute concentration c and $\bar{v}_1$ and $\bar{v}_2$ are the partial specific volumes of solvent and solute, respectively.

Quite recently, Brochard and de Gennes[10] derived by using the two-fluid model[9] and the analogue of Darcy's law a permeability coefficient λ of the same type as that of Mijnlieff and Jaspers

$$\lambda = \frac{g}{6\pi c \xi} \tag{11}$$

where g can be expressed as

$$\frac{c}{g} = \frac{1}{\xi^3} \tag{12}$$

Hence λ can be related to ξ as

$$\lambda \sim \xi^2 \tag{13}$$

By introducing equation (5) the scaling laws for the permeability coefficient can be written as[10]

$$\lambda \sim \begin{cases} c^{-1.5} \text{ (good solvent conditions)} \\ c^{-2.0} \text{ (theta conditions)} \end{cases} \tag{14}$$

In this work the permeability coefficients were calculated from sedimentation measurements. Therefore equation (10), which only contains experimentally observable quantities, was used for the evaluation of the permeability coefficients.

The concentration dependence of the sedimentation coefficient can also be predicted from dynamical scaling laws[10] stating that

$$s \sim \frac{c\xi^2}{\eta_0} \sim \begin{cases} c^{-0.50} \text{ (good solvent conditions)} \\ c^{-1.0} \text{ (theta conditions)} \end{cases} \tag{15}$$

RESULTS AND DISCUSSION

Osmotic pressure

Typical plots of lg π vs lg c are given in *Figure 2*. The corresponding exponents a_π (above c^+) are listed in *Table 1*, together with exponenents for other polymer–solvent systems. The curves depicted in *Figure 2* may be analysed in the following way. The initial part of the curves are practically linear up to c^*, followed by an upward curvature; at still higher concentrations (above c^+, indicated by vertical broken lines) a change to a new linear region with a different slope is observed. The initial slope is approximately 1 for theta systems, which is consistent with recent theory[23,24]. (This can also be observed from the common virial expression). The cross-over between dilute and semidilute regimes occurs roughly around c^+. The cross-over is smooth for good solvents, whereas for theta solvents the transition is more marked (see *Figure 2*). These observed features are in qualitative agreement with the theoretical predictions[16,17].

In *Table 1*, exponents (the slope above c^+ in a lg–lg plot of π vs. c) for a large number of various polymer–solvent systems have been compiled. These data can be represented by the following power law dependencies

$$\pi \sim \begin{cases} c^{2.22 \pm 0.12} \text{ (good solvent conditions)} \\ c^{2.9} \text{ (theta conditions)} \end{cases} \tag{16}$$

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* These diffusion coefficients are equal only when the samples are monodisperse.

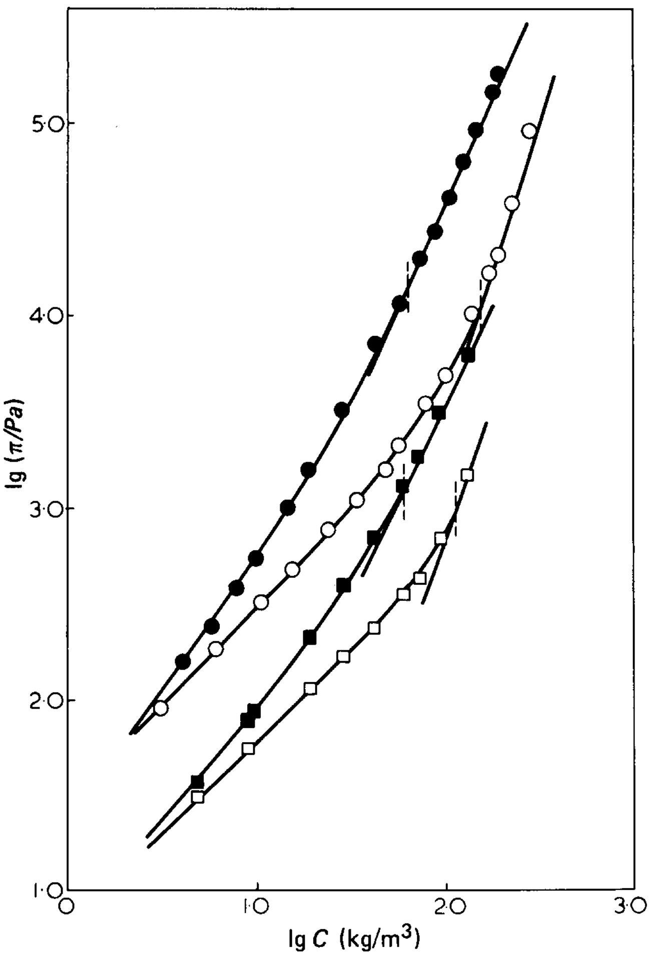

Figure 2 Typical lg–lg plots of the osmotic pressure versus concentration for the systems indicated: ○, Polyisobutene (M = 90 000)/benzene at 24°C (theta conditions)[57]; ●, Polyisobutene (M = 90 000)/cyclohexane at 30°C[57]; □, Polystyrene (M = 396 000)/*trans*-decalin at 20°C (theta conditions)[70]; ■, Polystyrene (M = 396 000)/*trans*-decalin at 35°C (approaching good solvent conditions)[70]

These exponents (the value is the average value of the exponents in *Table 1*, the standard deviation is given) are in excellent agreement with those predicted from the scaling laws (see equation 7). Furthermore, it can be concluded that the exponent related to good solvent conditions is definitely larger than 2 (the mean field value) and in fact close to 2.25, as expected from the scaling law picture.

It is interesting to note that the value of the exponent for the system polystyrene/*trans*-decalin decreases considerably when the temperature is removed only a few degrees from the theta temperature (see *Table 1*). This probably indicates a rapid transition from poor to good solvent conditions.

It may be concluded from the large amount of data that the universality of the scaling hypothesis is confirmed for the osmotic pressure.

Diffusion

In order to demonstrate the concentration dependence of the mutual (translational) diffusion coefficient, D_m, in a quantitative way, a lg–lg representation of D_m vs. c has been illustrated in *Figure 3* for some specific systems. The typical features as revealed by *Figure 3* can be described as follows. The curves representing good or moderately good solvent conditions (A, B and C) are smooth lines which are curved up to a concentration in the vicinity of c^+ and then practically straight from there onwards. A closer inspection of the curves shows that the slopes (above c^+) of curves A and B are approximately the same, confirming the conjecture that D_m is independent of the molecular weight in this concentration region. The slope of the linear part of curve C is somewhat smaller, probably due to the fact that the solvent 2-butanone is a poorer solvent than toluene.

For theta conditions (curve D), on the other hand, the diffusion behaviour is totally different. The most significant finding for this situation is that D_m decreases with concentration until a minimum value is attained at $c \approx c^+$; upon further increase in concentration the value of D_m increases almost linearly (in a lg–lg plot of D_m vs. c) with a slope of approximately 1. (If *Table 2* is scrutinized one can observe that this slope decreases as the temperature is removed from the *UCST*.) In this connection it should be mentioned that the minimum of the curve is located roughly at a concentration corresponding to the maximum of the phase equilibrium curve[39].

The exponents, a_D, compiled in *Table 2*, were calculated from the slope of curves (the linear part above c^+) analogous to those presented in *Figure 3*. The data have been obtained from both QELS experiments, conducted in region 4 of *Figure 1*, and gradient diffusion measurements (i.e. an artificial concentration gradient is formed and the disappearance of this gradient with time is followed).

A scrutiny of the exponents reveals some characteristic features, which can be summarized as follows. For the system polystyrene/2-butanone, where 2-butanone (in the interval 0°–25°C) is a moderately good solvent for polystyrene, D_m increases with concentration approximately as $c^{0.3}$. Under good solvent conditions, the exponent is higher, namely 0.43 (a calculated average value from *Table 2*, for polystyrene in good solvents), indicating a stronger concentration dependence. In this connection it is interesting to compare this value (0.43) with that obtained from QELS measurements, performed in region 3 of *Figure 1* (pseudo-gel domain), on the systems polystyrene–benzene[8,28] and

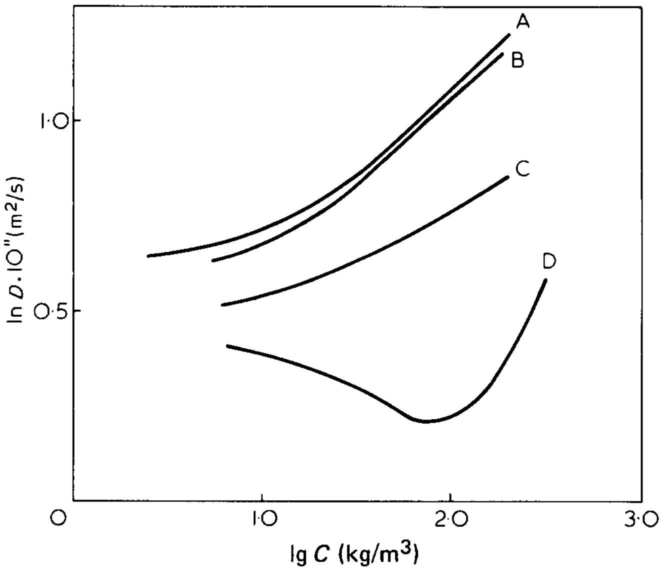

Figure 3 Lg–lg representation of the mutual diffusion coefficient versus concentration for the following systems: (a) Polystyrene (M = 110 000)/toluene at 25°C[45]; (b) Polystyrene (M = 200 000)/toluene at 21°C[30]; (c) Polystyrene (M = 670 000)/2-butanone at 25°C[31]; (d) Polystyrene (M = 180 000)/cyclohexane at 40°C (close to theta conditions)[73]

Table 2 Compilation of mutual diffusion data for various polymer–solvent systems in the semidilute region. a_D indicates the slope (above c^+) in a lg–lg plot of the mutual diffusion coefficient versus concentration

Polymer	Solvent	Molecular weight	Temperature °C	a_D	Remarks	Ref
Polystyrene	2-Butanone	2.00×10^5	0	0.23	θ_L = 146°C; QELS	31
		3.92×10^5	0	0.32		
		6.70×10^5	0	0.33		
		2.00×10^5	25	0.33		31
		3.92×10^5	25	0.28		
		6.70×10^5	25	0.33		
		2.00×10^5	50	0.26		31
		3.92×10^5	50	0.38		
		6.70×10^5	50	0.35		
	Cyclohexane	1.80×10^5	28	1.9	UCST = 26°C; 'Gradient diff.'	73
			40	0.92	θ_u = 35°C	
			50	0.57		
	Ethylbenzene	1.80×10^5	20	0.43	'gradient diff'	73
			40	0.42		
			60	0.45		
	Tetrahydrofuran	4.11×10^5	25	0.50	QELS	35
Polystyrene	Toluene	2.00×10^5	21	0.46	QELS	30
		1.10×10^5	25	0.47	'gradient diff.'	45
		1.80×10^5	30	0.39		73
Dextran	Water	7.00×10^4	25	0.22		74
	Water	1.54×10^5	20	0.3		43
Hydroxypropyl cellulose	Water	7.30×10^4	25	0.4	'good solv. cond.'	44
			37	~0	θ_L = 41°C	44
Poly(ethylene glycol)	Water	6.00×10^3	25	0.35	'gradient diff.'	74
		2.00×10^4	25	0.33		74
Poly(vinyl pyrrolidone)	Water	2.10×10^5	25	0.5		75
Serum albumin	Acetate buffer	–	25	~0	QELS	32
	Water	6.90×10^4	20	~0	'gradient diff.'	42
	Saline solution	6.90×10^4	25	~0	QELS	32

polystyrene–ethyl acetate[29]. The cooperative diffusion coefficient, D_c, could in these cases be represented by the power law $D_c \sim c^{0.67 \pm 0.01}$. This value is not too far from the value (0.75) predicted by the scaling law concept (see equation 9). However, the value 0.67 is significantly larger than 0.43, indicating that the concentration dependence of the cooperative diffusion coefficient is noticeably higher than that for the mutual (translational) diffusion coefficient. Incidentally, one should mention that measurements on the system polystyrene–benzene also were carried out for $qR \gg 1$ (region 2 in *Figure 1*)[28]; the corresponding exponent was in this case 0.42. This is a further indication of that the concentration dependence may be different, depending on in which dynamical regime the measurements are executed.

The concentration dependence of D_m for the polymer in aqueous solution (see *Table 2*) is of the same order of magnitude as for the polystyrene solutions, except for serum albumin and hydroxypropyl cellulose (theta conditions) which both show a negligible concentration dependence of D_m. The determination of the variation of D_m with concentration is somewhat ambiguous in the case of the water soluble polymers, principally because of relatively large polydispersity effects and aggregate formations. Therefore these data are not further examined. However, one may mention in passing that the dynamical behaviour of water soluble polymers is in general difficult to interpret, mainly due to the existence of hydrogen bond interactions between polymer and solvent. Furthermore, water is generally a relatively poor solvent for these polymers.

From the results presented here it seems not to be possible to describe the mutual (translational) diffusion coefficient by a general scaling law.

Another parameter which is important for the physical understanding of a diffusion process is the self-diffusion coefficient, D_s. This coefficient characterizes the random motion of an individual solute molecule; the process has qualitatively been described by a theoretical model[40]. Data in the literature[41–45] indicate that D_s at concentrations above c^+ decreases with concentration as c^{μ}, with $\mu \approx -1$. However, from one investigation dealing with proteins[46], μ was found to be considerably smaller ($\mu \approx -1.7$). A thorough examination of these results is beyond the scope of the present paper.

Sedimentation

Figure 4 shows lg–lg representations of the permeability coefficient, k, vs. c for polystyrene solutions under various thermodynamic conditions. The thermodynamic situation is for the system polystyrene–cyclopentane changed from very poor (5°C) (close to the upper critical solution temperature, *UCST*) to mediocre solvent conditions (40°C). Some interesting features should be observed. The permeability coefficient is monotonously decreasing as the concentration increases. However, for all the curves, except that representing the situation close to *UCST*, a transition domain beginning at approximately c^* (indicated by vertical dashed lines) is discernible. Above this concentration (of incipient overlap) the curves can be represented by straight lines with different slopes depending on the 'goodness' of the solvent (see *Table 3*). On the other hand, for polystyrene in cyclopentane close to the *UCST* the curve is linear over the entire concentration interval with a much smaller slope. This implies that the sedimentation coefficient is almost independent of concentration; this behaviour has been discussed recently[14,15].

The exponents (a_p and a_s) collected in *Table 3* have been evaluated from the linear part (above c^*) of curves analogous to those presented in *Figure 4* (i.e. lg–lg plots of k and s,

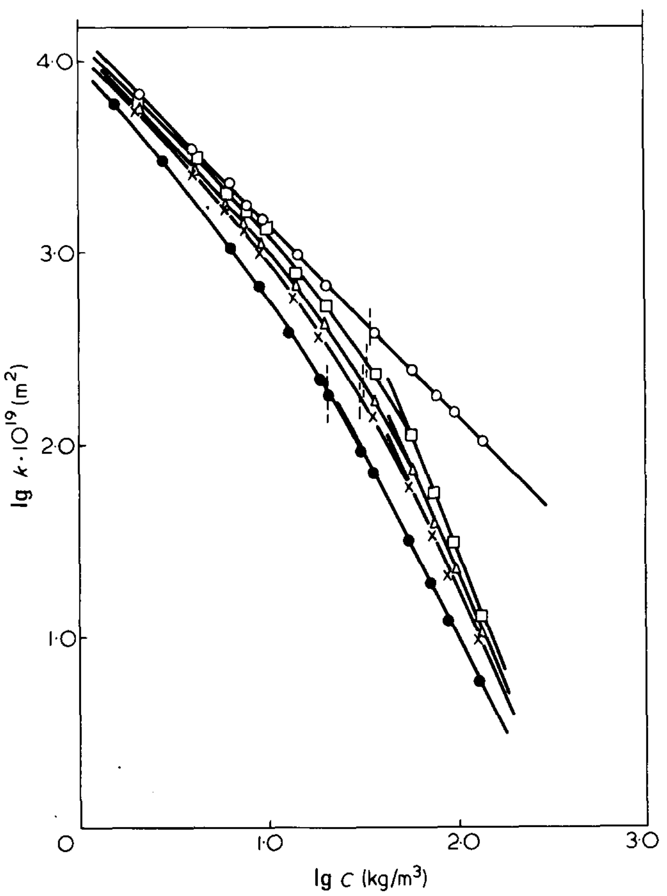

Figure 4 Lg–lg plots of the permeability coefficient as a function of concentration for polystyrene (M = 111 000)[15,45] in the solvents indicated: ○, cyclopentane at 5°C (~UCST); □, cyclopentane at 11°C; △, cyclopentane at 20°C (theta conditions); x, cyclopentane at 40°C; ●, toluene at 25°C (good solvent conditions)

respectively, vs. c). For most of the polymer–solvent systems the concentration dependence of the permeability coefficient and the sedimentation coefficient may be described by the following power laws

$$k \sim \begin{cases} c^{-1.0} \text{ (good solvent conditions)} \\ \\ c^{-2.0} \text{ (theta conditions)} \end{cases} \tag{17}$$

$$s \sim \begin{cases} c^{-0.7} \text{ (good solvent conditions)} \\ \\ c^{-1.0} \text{ (theta conditions)} \end{cases} \tag{18}$$

These exponents are in very good agreement with those predicted (see equations 14 and 15). However, some of the systems diverge from this pattern of behaviour and will therefore be scrutinized below.

(a) The most significant finding is that k and s are proportional to c^{-1} and c^0, respectively, at *UCST*. This remarkable observation can neither be confirmed nor contradicted, since no scaling laws or small-angle neutron scattering experiments have yet been reported for this crucial temperature. Furthermore, the exponents representing conditions not too far from *UCST* show also anomalous behaviour (see *Table 3*).

(b) For the system poly[2-(triphenylmethoxy)ethyl methacrylate]/toluene (good solvent conditions) the corresponding exponent is larger (–2.0) than the predicted one (–1.5), in fact identical with that predicted for theta conditions (see equation 14). This result may be explained by the following qualitative arguments. The polymer PTEMA has been found to be branched[47,48]. A branched polymer is generally characterized by the fact that the molecular dimensions (e.g. radius of gyration) are smaller than those for the corresponding linear polymer and that the average segment density within the polymer coils is far higher than that for its linear analogue. Thus, the PTEMA molecules can be expected to display a relatively compact conformation in solution, which also has been observed[13,49]. Therefore, it is not unlikely that PTEMA in toluene shows similar sedimentation and permeability behaviour as a linear polymer at theta conditions, since one of the crucial differences between a good and a theta system is that the polymer coils in a theta solvent are more compact than in a good solvent.

(c) The exponents (a_p and a_s) for the system poly(γ-benzyl L-glutamate)/dimethyl formamide (PBLG/DMF) are significantly larger than those predicted. However, the PBLG molecules display a rigid rod-like structure. Furthermore, these molecules may be apt to show alignment effects during the sedimentation process, which complicates the sedimentation behaviour (see reference 50). From these facts and the fact that the scaling laws have been deduced under the assumption that the polymer chains are completely flexible, the observed divergence is not unexpected.

(d) For the polymers in aqueous solution and for cellulose nitrate in acetone the exponent a_p is consistently somewhat larger than that for the synthetic polymers in good solvents (e.g. polystyrene in toluene). The former systems are characterized by certain common properties. The polymers are in general more polydisperse and less flexible than the synthetic polymers. Moreover, the solvents (water and acetone) are polar which may imply that dipole–dipole interactions can exist between polymer and solvent. These differences may to some extent explain the differences between the values of the exponents. Furthermore, in a recent investigation on poly(ethylene oxide) in water[51] the exponent a_s was found to be somewhat larger than predicted which is consistent with the above finding.

(e) The reason for the anomalous small value of the exponents (a_p and a_s) for the system ficoll/water has not been established. However, a possible cause of these small exponents may be that molecules of ficoll display a very compact spherical structure in water.

From the results presented above one can observe that there are some systems whose exponents are not entirely consistent with those predicted from equation (14). However, this does not obstruct the scaling laws from being a powerful tool in the analysis of the concentration dependence of the permeability and sedimentation coefficients.

CONCLUSIONS

The results presented in this paper are based on literature data of osmotic pressure, diffusion and sedimentation measurements performed in the semidulute region. The concentration dependence of the parameters π, D_m, k and s was systematised and analysed in terms of scaling laws. The most significant findings were the following:

(1) The exponent which expresses the concentration dependence of π was in excellent agreement with that predicted from the scaling laws, both for good and theta sol-

Table 3 Compilation of sedimentation data for various polymer–solvent systems. a_p and a_s indicate the slopes (above c^*) in lg–lg plots of the permeability coefficient and the sedimentation coefficient, respectively, versus concentration

Polymer	Solvent	Molecular weight	Temperature °C	a_s	a_p	Remarks	Ref.
Polyisobutene	n-Octane	1.90×10^6	25	−0.6	−1.6		76, 77
Poly(methyl methacrylate) (PMMA)	Toluene	1.40×10^6	25	−0.8	−1.7		13
Poly[(2-triphenylmethoxyethyl) methacrylatel (PTEMA)	Toluene	1.00×10^6	25	−1.0	−2.0	Branched polymer	
		1.35×10^6	25	−1.0	−2.0	Branched polymer	
Polystyrene	Cyclohexane	3.90×10^5	27	~0	−1.0	UCST	14
			31	−1.2	−2.2		
			35	−1.1	−2.0	$\theta_u = 35°C$	
	Cyclopentane	1.10×10^5	5	~0	−1.0	UCST	15
			11	−1.5	−2.4		
		2.04×10^4	20	−1.0	−2.0	$\theta_u = 20°C$	
		1.10×10^4	20	−1.2	−2.0	$\theta_u = 20°C$	
		3.90×10^5	20	−1.0	−2.0	$\theta_u = 20°C$	
		9.50×10^5	20	−0.9	−1.9	$\theta_u = 20°C$	
		1.10×10^5	40	−1.1	−1.9	close to theta cond.	
	Toluene	1.10×10^5	25	−0.8	−1.7		45
Polystyrene	Toluene	3.90×10^5	25	−0.7	−1.6		78
		1.80×10^6	25	−0.7	−1.6		
	trans-decalin	3.90×10^5	20	−0.8	−1.9	$\theta_u = 20.8°C$	12
		1.80×10^6	25	−1.0	−2.0	near to theta cond.	78
		3.90×10^5	30	−0.9	−1.9		12
			40	−0.8	−1.7	approach. good solv. cond.	
Poly(α-methylstyrene) (PAMS)	Cyclohexane	1.00×10^6	35	−1.0	−2.0	$\theta_u = 35°C$	37
		6.50×10^6	35	−1.0	−1.9	$\theta_u = 35°C$	
	Toluene	1.00×10^6	25	−0.7	−1.6		37
		6.50×10^6	25	−0.7	−1.6		
Poly(γ-benzyl-L-glutamate)	Dimethylformamide	3.20×10^5	25	−0.3	−1.3	a rod-like structure	50
Dextran	Water	4.00×10^4	25	−0.4	−1.4		79
		5.00×10^5	25	−0.5	−1.5		75
DNA	Water	$(5–6) \times 10^6$	25	−0.5	−1.5	a rod-like structure	80
Ficoll	Water	4.00×10^5	25	−1.3	−2.2	compact structure	50
Hydroxyethyl cellulose	Water	1.50×10^5	25	−0.5	−1.5		50
Hydroxypropyl cellulose	Water	7.30×10^4	25	−0.5	−1.5		81
			34	−0.6	−1.6		
			40	−0.7	−1.7	$\theta_L = 41°C$	
Cellulose nitrate	Acetone	3.50×10^5	20	−0.5	−1.5		82
		5.00×10^5	20	−0.4	−1.4		83
Serum albumin	Water	6.90×10^4	20	−0.4	−1.3		42

vent conditions. The mean field theory, on the other hand, was inadequate to describe the behaviour at good solvent conditions. It may be concluded that the collected data support the universality of the scaling hypothesis.

(2) The mutual diffusion data could not unambiguously be characterized by simple scaling laws. However, D_m for polystyrene in good solvents, for instance, showed a well-defined pattern of behaviour. The observed concentration dependence of D_m in this case was much smaller than that of the cooperative diffusion coefficient under similar solvent conditions. This indicates that the concentration dependence is phenomenologically related to the dynamical regime in which the actual experiments are conducted.

(3) The exponents which express the concentration dependence of k and s, respectively, were in close agreement with those predicted from the scaling laws for all but a few polymer–solvent systems. Most of these divergences could be explained, e.g. by the fact that the systems did not satisfy the conditions on which the theoretical model is based. However, the anomalous observations at the *UCST* emphasize the necessity of thorough experimental and theoretical investigations at this critical temperature.

Finally it can be concluded from the present study that the scaling law concept is a unique aid to describe and interpret the concentration dependence of different static and dynamical parameters in the semidilute regime.

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REFERENCES

1 Flory, P. J., 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, N. Y., 1953

2 Daoud, M., Cotton, J. P., Farnoux, B., Jannink, G., Sarma, G., Benoit, H., Duplessix, R., Picot, C. and de Gennes, P. G. *Macromolecules* 1975, **8**, 804

3 de Gennes, P. G. *Israel J. Chem.* 1975, **14**, 154

4 de Gennes, P. G. *J. Polym. Sci. (Polym. Lett. Edn)* 1977, **15**, 623

5 de Gennes, P. G. *Phys. Lett.* 1972, **A38**, 339

6 des Cloiseaux, J. *J. Phys. (Paris)* 1975, **36**, 281

7 Cotton, J. P., Farnoux, B. and Jannink, G. *J. Chem. Phys.* 1972, **57**, 290

8 Adam, M. and Delsanti, M., *Macromolecules* 1977, **10**, 1229

9 de Gennes, P. G. *Macromolecules* 1976, **9**, 587, 594

10 Brochard, F. and de Gennes, P. G. *Macromolecules* 1977, **10**, 1157

11 Weissberg, S. G., Simha, R. and Rothamn, S. *J. Res. Nat. Bur. Stand.* 1951, **47**, 298; see also Simha, R. and Utracki, L. A. *Rheol. Acta* 1973, **12**, 455

12 Nyström, B. and Roots, J. *Eur. Polym.* 1978, **14**, 551

13 Nyström, B., Sundelöf, L. -O., Petrus, V. and Bohdanecký, M. to be published

14 Sundelöf, L. -O. and Nyström, B. *Chem. Scr.* in press

15 Nyström, B., Roots, J. and Bergman, R. *Polymer* 1979, **20**, 157

16 Cotton, J. P., Farnoux, B., Jannink, G. and Ober, R. *J. Phys.* 1973, **A6**, 951

17 Cotton, J. P., Farnoux, B., Jannink, G. and Strazielle, C., *J. Polym. Sci. (Polym. Symp.)* 1973, **42**, 981

18 Candau, F., Strazielle, C. and Benoit, H., *Eur. Polym. J.* 1976, **12**, 95

19 Ferry, J. D., 'Viscoelastic properties of polymers', Wiley, New York, N. Y., 1970

20 Janeschitz-Kriegel, H., *Adv. Polym. Sci.* 1969, **6**, 170

21 Edwards, S. F., *Proc. Phys. Soc.* 1966, **88**, 265

22 de Gennes, P. G., *J. Phys. (Paris), Lett.* 1975, **36**, L-55

23 Daoud, M. and Jannink, G., *J. Phys. (Paris)* 1976, **37**, 973

24 Cotton, J. P., Nierlich, M., Boué, F., Daoud, M., Farnoux, B., Jannink, G., Duplessix, R. and Picot, C., *J. Chem. Phys.* 1976, **65**, 1101

25 Pecora, R., *J. Chem. Phys.* 1964, **40**, 1604

26 Cummins, H. Z. and Swinney, H. L., *Progr. Optics* 1970, **8**, 133

27 Chu, B., 'Laser Light Scattering', Academic Press, New York, 1974

28 Adam, M., Delsanti, M. and Jannink, G. *J. Phys. (Paris), Lett.* 1976, **37**, L-35

29 Munch, J. P., Candau, S., Herz, J. and Hild, G. *J. Phys. (Paris)* 1977, **38**, 971

30 Pusey, P. N., Vaughan, J. M. and Williams, G., *J. Chem. Soc. Faraday 2*, 1974, **70**, 1696

31 Baily, D., King, T. A. and Pinder, D. N., *Chem. Phys.* 1976, **12**, 161

32 Phillies, G. D. J., Benedek, G. B. and Mazer, N. A. *J. Chem. Phys.* 1976, **65**, 1883

33 Geissler, E. and Hecht, A. M. *J. Chem. Phys.* 1976, **65**, 103

34 Hecht, A. M. and Geissler, E., *J. Chem. Phys.* 1977, **66**, 1416

35 Mandema, W. and Zeldenrust, H., *Polymer* 1977, **18**, 835

36 Fessler, J. H. and Ogston, A. G., *Trans. Faraday Soc.* 1951, **47**, 667

37 Mijnlieff, P. F. and Jaspers, W. J. M., *Trans. Faraday Soc.* 1971, **67**, 1837

38 Darcy, H., Les fontaines publiques de la ville de Dijon, 1856

39 Rehage, G., Ernst, O. and Fuhrmann, J., *Discuss. Faraday Soc.* 1970, **49**, 208

40 de Gennes, P. G., *J. Chem. Phys.* 1971, **55**, 572

41 Keller, K., Canales, E. and Yum, S. I., *J. Phys. Chem.* 1971, **75**, 379

42 Kitchen, R. G., Preston, B. N. and Wells, J. D. *J. Polym. Sci. (Polym. Symp.)* 1976, **55**, 39

43 Laurent, T., Sundelöf, L. -O., Wik, K. and Wärmegård, B., *Eur. J. Biochem.* 1976, **68**, 95

44 Bergman, R. and Sundelöf, L. -O., *Eur. Polym. J.* 1977, **13**, 881

45 Roots, J., Nyström, B., Porsch, B. and Sundelöf, L. -O., in press

46 Riveros-Moreno, V. and Wittenberg, J., *J. Biol. Chem.* 1972, **247**, 895

47 Otoupalová, J., Tuzar, Z., Bohdanecký, M. and Hudeček, S., *Collect. Czech. Chem. Commun.* 1973, **38**, 870

48 Dolezalová, M., Petrus, V. and Bohdanecký, M., *Collect. Czech. Chem. Commun.* 1977, **42**, 1960

40 Dolezalová, M., Petrus, V., Tuzar, Z. and Bohdanecký, M., *Eur. Polym. J.* 1976, **12**, 701

50 Sundelöf, L. -O. and Nyström, B., *J. Polym. Sci. (Polym. Lett. Edn)* 1977, **15**, 377

51 Langevin, D. and Rondelez, F., *Polymer* 1978, **19**, 875

52 Okamoto, A., Kubo, K. and Ogino, K., *Bull. Chem. Soc. Jpn* 1974, **47**, 1054

53 Kubo, K., Kubota, K. and Ogino, K., *Polymer* 1976, **17**, 919

54 Browing, G. V. and Ferry, J. D., *J. Chem. Phys.* 1949, **17**, 1107

55 Kuwahara, N., Okazawa, T. and Kaneko, M., *J. Polym. Sci.* 1969, **C23**, 543

56 Sugamiya, K., Kuwahara, N. and Kaneko, M., *Macromolecules* 1974, **7**, 66

57 Flory, P. J. and Daoust, H., *J. Polym. Sci.* 1957, **25**, 429

58 Okazawa, T. and Kaneko, M. *Polym. J.* 1971, **2**, 747

59 Vink, H., *Eur. Polym. J.* 1974, **10**, 149

60 Kuwahara, N., Oikawa, T. and Kaneko, M. *J. Chem. Phys.* 1968, **49**, 4972

61 Leonard, J. and Daoust, H. *Can. J. Chem.* 1967, **45**, 409

62 Nakajima, A., Hamada, F., Yasue, K., Fujisawa, K. and Shiomi, T. *Makromol. Chem.* 1974, **175**, 197

63 Flory, P. J. and Höcker, H., *Trans. Faraday Soc.* 1971, **67**, 2258

64 Schick, M. J., Doty, P. and Zimm, B. H. *J. Am. Chem. Soc.* 1950, **72**, 530

65 Leonard, J. and Daoust, H., *J. Phys. Chem.* 1965, **69**, 1174

66 Krigbaum, W. R. and Geymer, D. O. *J. Am. Chem. Soc.* 1959, **81**, 1859

67 Höcker, H. and Flory, P. J., *Trans. Faraday Soc.* 1971, **67**, 2270

68 Kuwahara, N., Okazawa, T. and Kaneko, M., *J. Chem. Phys.* 1967, **47**, 3357

69 Hansen, J. and Hvidt, A. *J. Chem. Soc. (Faraday Trans. 2)* 1973, **69**, 881

70 Roots, J. and Nyström, B. *Eur. Polym. J.* 1978, **14**, 773

71 Vink, H. *Eur. Polym. J.* 1971, **7**, 1411

72 Adair, G. S. *Proc. Roy. Soc. (London) A* 1928, **120**, 573

73 Rehage, G. and Ernst, O. DECHEMA-Monographie 1964, **49**, 157

74 Kitchen, R. G. *Thesis*, Monash University, Clayton, Victoria, Australia, 1975

75 Sundelöf, L. -O., unpublished data

76 Nyström, B. and Sundelöf, L. -O., *Chem. Scr.* 1976, **10**, 16

77 Nyström, B., unpublished

78 Nyström, B., Porsch, B. and Sundelöf, L. -O., *Eur. Polym. J.* 1977, **13**, 683

79 Acosta, R., Nyström, B. and Sundelöf, L. -O., to be published

80 Peacocke, A. R. and Schachman, H. K., *Biochim. Biophys. Acta* 1954, **15**, 198

81 Nyström, B. and Bergman, R., *Eur. Polym. J.* 1978, **14**, 431

82 Campbell, H. and Johnson, P., *Trans. Faraday Soc.* 1944, **40**, 221

83 Jullander, I., *Arkiv Kemi, Mineral. Geol.* 1944, **21A**, No 8