Appendix IV Viscous Flow and Sedimentation of Concentrated Dispersions of Particles (quoted from A.J. Rowe, mss. in preparation)

The hydrodynamic properties of dispersions of particles in fluids are quite well described at very high particle dilution, both for simple models (spheres, ellipsoids, rods) and for more complex models which may be represented as assemblies of simple models and the appropriate interaction tensors computed. Restricting outselves to the case of small particles (Brownian motion dominant) suspended in liquids, the work of Stokes, Einstein, Perrin, Simha, Broersma and others (for simple models) and of Kirkwood, Bloomfield and others (for assemblies) enables a reasonably accurate description to be given of the sedimentation and viscous flow properties of such suspensions to be given at 'infinite dilution'.

At real particle concentrations however, no theory has proved adequate, even for the simplest particle model - the sphere. The need for such a theory is evident in many fields: in my own field of Biochemistry it would be useful both for methodological purposes in characterising macromolecular properties and for the description of 'in vivo' systems, which are generally rather concentrated dispersions of macromolecular particles. I have been concerned to derive such a theory, relating the properties of suspensions of particles at real concentration to their 'infinite dilution' behaviour. In a recent paper (Rowe, 1977) a first part of such a theory was described: the extension of this theory to cover the case of high concentrations is now described.

The State of the Problem

It has long been noted that the concentration dependence of sedimentation and of reduced specific viscosity is finite even at high dilution, and remains nearly linear over moderate ranges of concentration:

(sedimentation) $s_c = s(1 - k_s c) \sim s(1 + k_s c)^{-1}$

(viscous flow) $\frac{\eta_{sp}}{c} = \left(\frac{\eta_{sp}}{c}\right)_{c \to 0} \cdot (1 + k_\eta c)$

A recently derived theory (Rowe, 1977) shows that

$$k = k_s = 2\bar{v}\left(\frac{\bar{v}_s}{\bar{v}} + (f/f_o)^3\right)$$

for compact particles, where $\bar{v}$ is the partial specific volume of the particle and f/f_o, the frictional ratio, is a parameter computable for simple models and for assemblies of sub-units. This theory is thus applicable to particles of <u>any</u> conformation. The values predicted for both spheres and other particles agree well with experimental evidence and with earlier theoretical predictions for spheres (Figure 52, Table 24).

At higher concentrations two further effects must be considered:

(i) mutually proximity of the particles affects the rate of energy dissipation at constant shear (the 'cloud effect' of Burgers). In general this poses a many-body problem which is not amenable to solution by classical techniques.

(ii) the critical packing fraction (ϕ_p) will be approached. Semi-empirical equations due to Mooney (1951), Dougherty and Kreiger (1972) and others describe the viscosity of suspensions of spheres in terms of ϕ_p.

A New General Approach

The theory applicable to high dilutions (Rowe, 1977) was based on the supposition that <u>only</u> a 'frame-of-reference' effect need be considered in this case. Derived in terms of sedimentation, it is shown that the latter must be unchanged with concentration in a frame of reference defined by the solvent in return flux (i.e. solvent not transported or convected with the particles). The equation above then follows from the relation between the defined frame of reference and the cell-fixed frame of reference in which measurements are normally made.

To extend this approach to higher concentrations we re-define the problem by considering the system to consist of a large but finite number of volume elements, each element small in comparison to a particle. These volume elements can be classified as elements of disjoint sets V1....V4, shown in a Venn diagram for two particles (Figure 53).

Among interesting properties which may be noticed are that

(i) Sets V1, V3 can be classified into sub-sets $v1_1 - v1_n$, $v3_1 - v3_n$, for n particles in the system

(ii) $v1_i \cap v1_j = \Phi$; but $v3_i \cap v3_j \neq \Phi$

(iii) In Newtonian flow, the magnitude of the flow vector of the solvent at any point in the system is defined by the fraction of the volume elements in the vicinity of that point classified as in $V2 \cup V3$ in relation to those in $V4 \cup V2 \cup V3$

(iv) $v1_i \cap V2 \neq \Phi$: more completely V2 is partitioned into the disjoint subsets V2a and V2b, where $v1_i \cap V2a = \Phi$; $v1_i \cap V2b \neq \Phi$: and ϕ_p, the critical packing volume of the particles, determines the relative number of elements in V2a and V2b $\{\phi_p = 1;\ V2a = \Phi\}$.

On the assumptions that n is large, and that the elements in V3 are located randomly in $V3 \cup V4$, then a simple finite probability space can be constructed, enabling us to calculate the number of elements in V1....V4, and hence the quantity g c in

$$\frac{s_c}{s} = \frac{\eta_{sp}/c}{(\eta_{sp}/c)_{c \to 0}} = (1 - gc)$$

since $V1 \cup V2 \cup V3 = gc$.

The result is given by

$$\frac{gc - z}{1 - z} = \Phi = (kc - 2c\bar{v}_s) - \sum_{i=2}^{i=\infty} (i - 1)(\Phi^{i} - \Phi^{i+1})$$

where $z = 2c\bar{v}_s - \frac{1}{\phi_p} (c\bar{v}_s)^2 (1 - Q)_+$; $Q = (1 - \phi_p)/\phi_p$

which for almost all cases simplifies to

$$gc = \frac{kc - \frac{2\phi_p - 1}{\phi_p^2} (c\bar{v}_s)^2}{kc - 2c\bar{v}_s + 1}$$

where $k = k_s$ or k_η ; $\bar{v}_s$ = specific volume of the hydrodynamic particle.

This equation predicts rather accurately the high-shear viscosity of latex spheres over the entire concentration range (Figures 54 - 58). It is applicable only to Newtonian flow, but is free of arbitrary or empirical constants. The treatment used has some affinity with the widely used approach involving transient doublets, triplets, etc. (i = 2 in the above summation refers to 'doublet' interaction, etc.), but as no particle model is employed, the results should be general for all particles. The ϕ_p term would often be difficult to estimate, but computer simulation shows that an exact knowledge of ϕ_p is unimportant except at the highest concentrations

Figures 54 – 58 demonstrate the success of the theory in predicting known properties of sedimentation and viscous flow at real concentrations.

Table 24. Various theoretical estimates and a practical estimate for k_2, the second coefficient in the expansion for η_{rel} in terms of Φ (volume fraction)

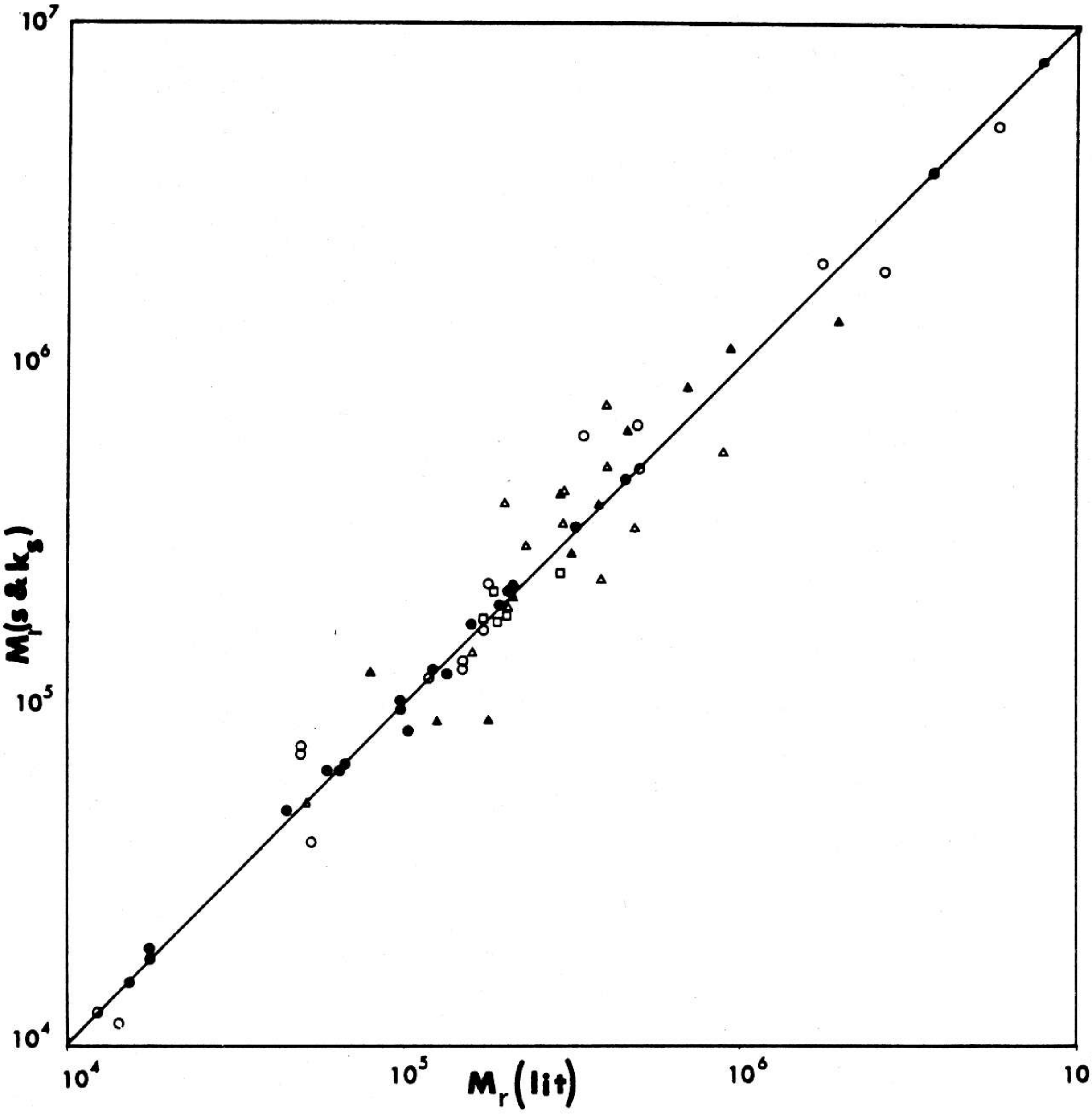
$$\eta_{rel} = 1 + k_1\Phi + k_2\Phi^2 + \ldots\ldots\ldots\ldots$$

Estimate for k_2	Author
7.5	Vand (1948)
9.15	Manley & Mason (modification of Vand) (1954)
7.5	Kynch (1956)
14.1	Gold (1937)
12.6	Simha (modification of Gold) (1952)
7.6	Batchelor & Green (1972)
10.0	Rowe (1977)
'about 10'	Cheng & Schachman data on PSL spheres (1955)

Figure 52.

Empirical data and the equation for transport-concentration dependence (Rowe 1977), at high solute dilution. The equation enables M_r (molecular weight) values to be calculated from s and k_s only. The agreement found between values for M_r computed thus and M_r values from the literature (various methods) is good evidence for the applicability of the equation to a wide range of systems.

Solute	$\frac{M_r(s+k_s)}{M_r(lit)}$	Standard error	Symbol
Proteins, nucleic acids, viruses	1.02	0.01	●
Cellulose derivatives in CUAM	1.01	0.09	○
Cellulose derivatives in ACETONE	0.97	0.10	△
Levans (aqueous)	0.99	0.04	□
Poly(methylymacrylate) in ETHYL ACETATE	1.05	0.08	▲



10^7
10^6
10^5
10^4
$M_r(s \& k_s)$
10^4
10^5
10^6
10^7
$M_r(lit)$

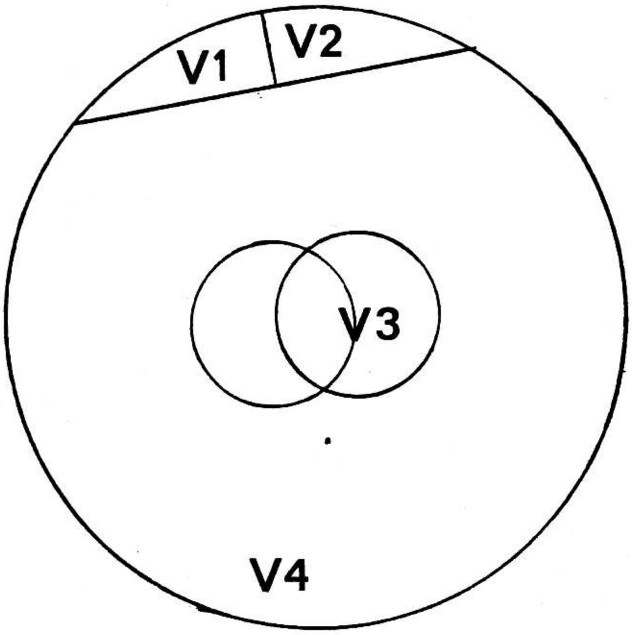


Figure 53. Venn diagram showing the volume elements for two particles in solution

V1 – particle volume

V2 – particle co-volume

V3 – solvent frictional forward flux

V4 – solvent return volume flux

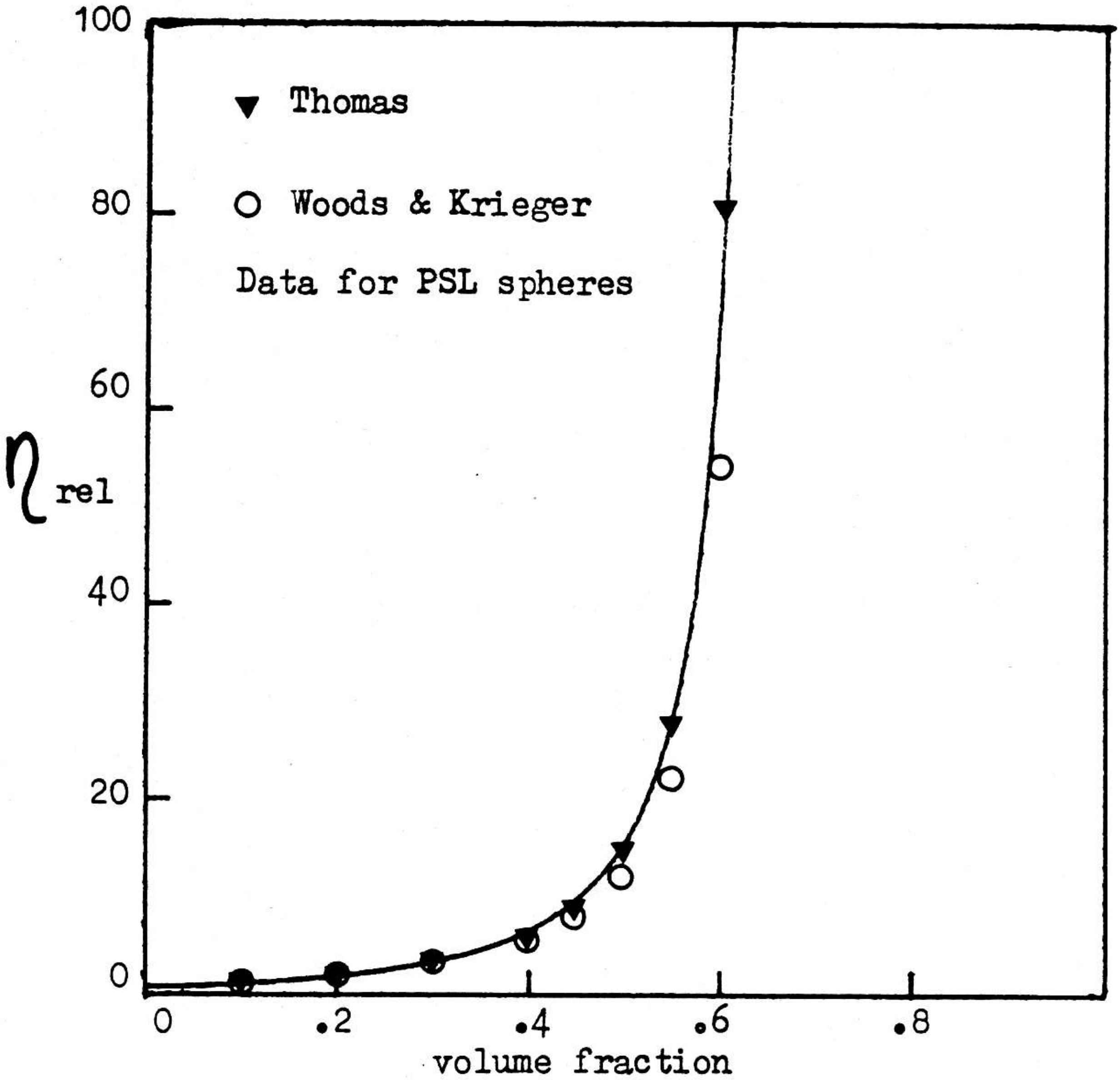


Figure 54. Relative viscosity of spheres as a function of volume fraction. Predicted line, for $k_\eta = 4$, $\bar{v}_s = 1$, $\phi_p = 0.64$. Experimental data points are also shown

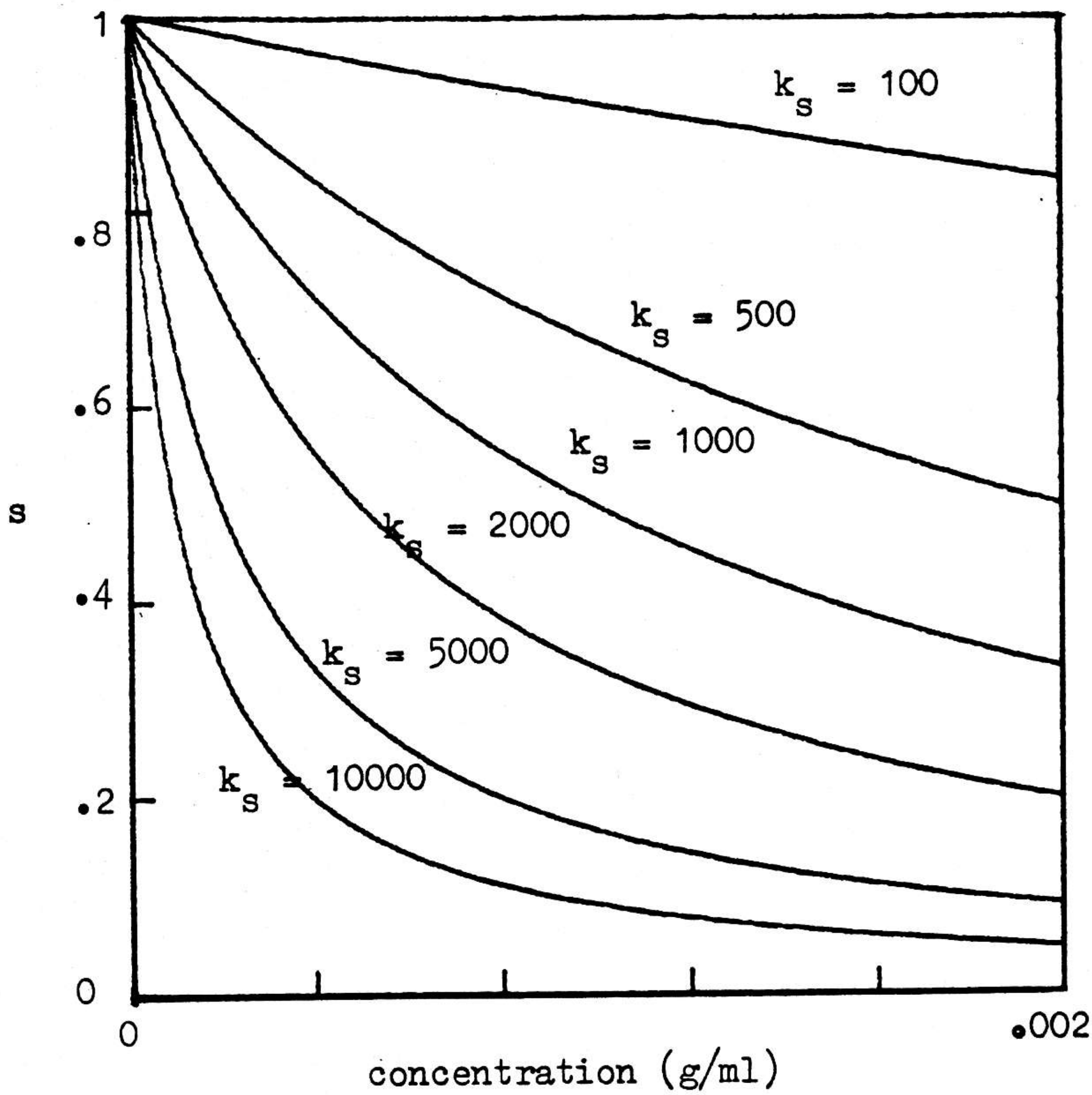


Figure 55. For highly asymmetric particles the sedimentation coefficient falls very steeply with concentration, to reach a relatively constant 'plateau' value. Computed curves.

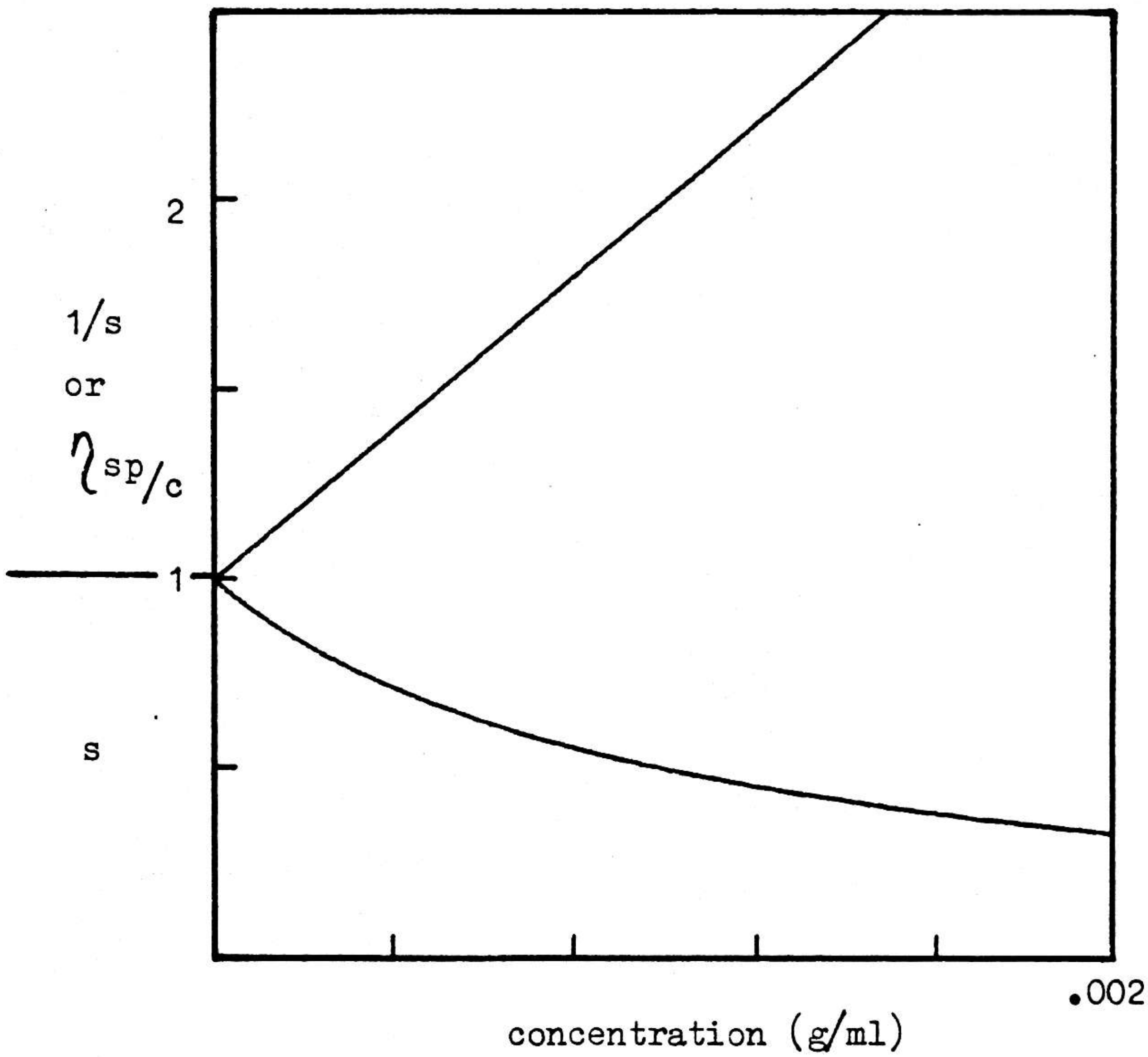


Figure 56. Viscosity/sedimentation coefficients as a function of concentration for $k_s(k_\eta) = 1000$, $\bar{v}_s = 1$. The 1/s plot is linear, whilst the direct plot is markedly curved. Computed curves.

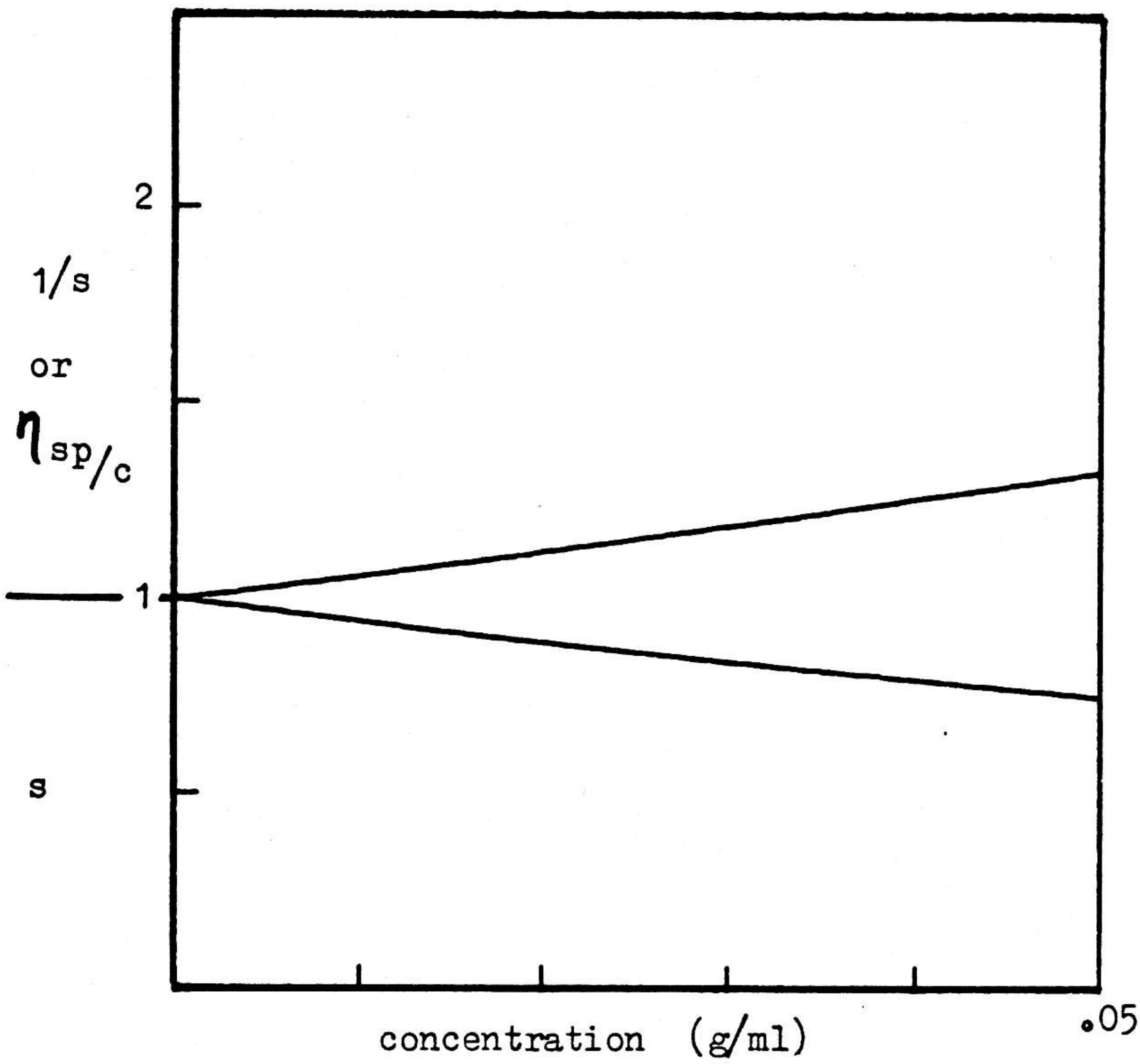
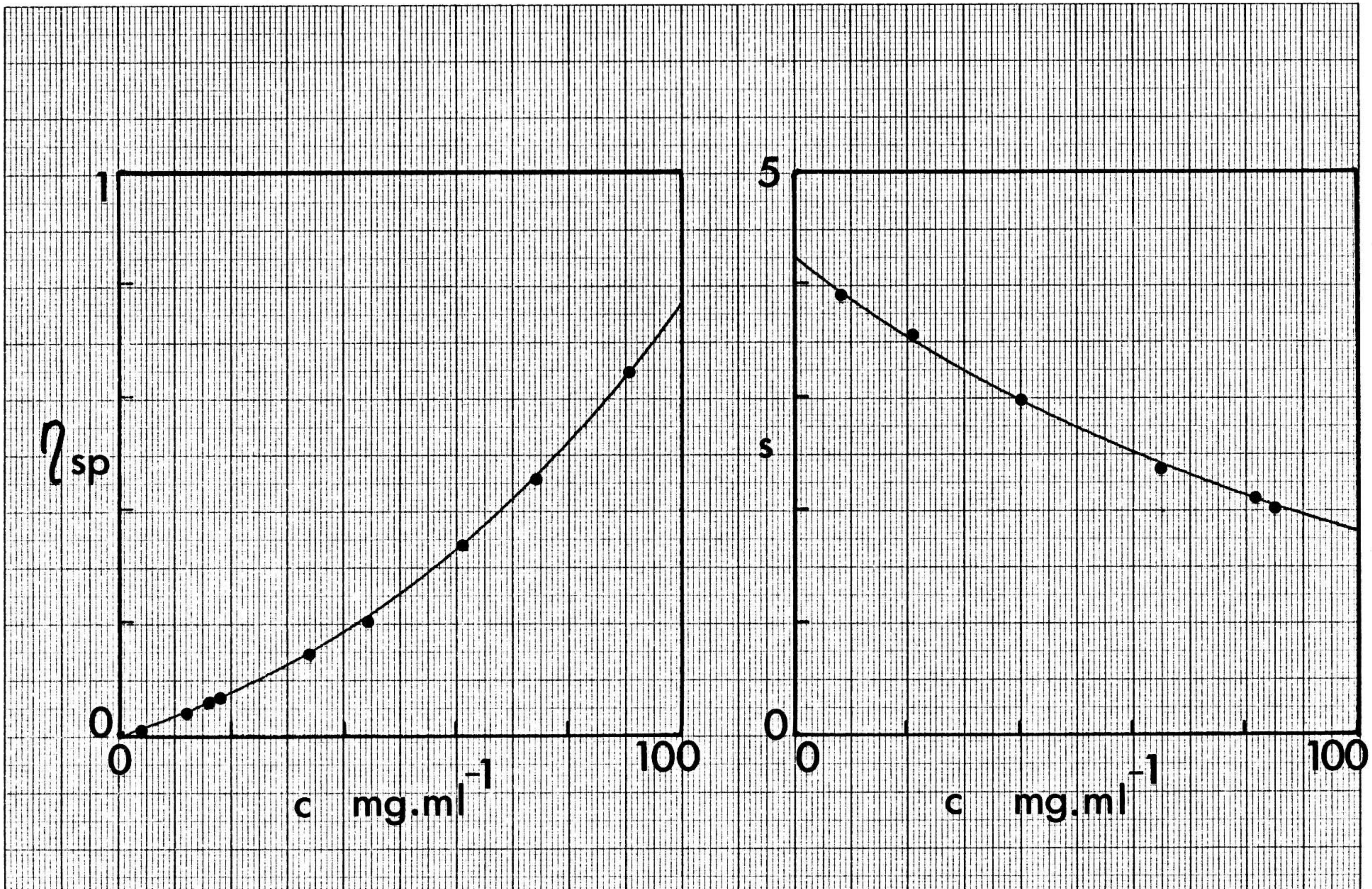


Figure 57. Viscosity/sedimentation coefficients as a function of concentration for $k_s(k_\eta) = 6$. Both plots are reasonably linear over this concentration range. Computed curves.

Figure 58. Hydrodynamic data for Bovine serum albumin fitted using the new general equation for transport at all solute concentrations



Bovine Serum Albumin

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