THE APPLICATION OF LIGHT SCATTERING TO THE INVESTIGATION OF PREFERENTIAL ADSORPTION EFFECTS IN QUASI-TERNARY SYSTEMS

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ABSTRACT

The study of preferential adsorption in quasi-ternary systems by means of light scattering is reviewed and a brief description of the theoretical treatment of multicomponent systems is given. The thermodynamic interpretation of preferential adsorption is then discussed and the effect this phenomenon has on the measurement of polymer molecular weight and coil size, and on the second virial coefficient of the solutions is outlined. Examples of systems exhibiting negative adsorption are mentioned and the application to biological systems is also illustrated.

INTRODUCTION

"Errors, like straws upon the surface flow,
He who seeks pearls must dive below".
John Dryden.

The study of binary systems solvent [1] polymer [3] by light scattering is a well established and extensively documented technique which has provided an impressive amount of information on the dilute solution properties and conformations of all kinds of macromolecules. It is convenient to develop the theoretical analysis of such systems from the fluctuation theory as suggested by Smoluchowski[1] and Einstein[2] who considered that the scattering of light within a small volume element in a liquid and a solution arises from local density and concentration fluctuations. An extension of this theory by Debye[3] led to the well known light scattering equations which allow us to calculate molecular weights, chain dimensions and thermodynamic parameters relevant to the polymer-solvent system in question:

$$\frac{H'[(\partial n/\partial c_3)_{T,P}]^2 c_3}{\Delta \tau} = \frac{1}{M_3 P(\theta)}\left[1 + \frac{c_3}{RT}\left(\frac{\partial \mu_3^e}{\partial c_3}\right)\right] = \frac{1}{M_3 P(\theta)} + 2A_2 c_3 \quad (1)$$

with the reciprocal particle scattering factor:

$$P(\theta)^{-1} = 1 + [16\pi^2/3(\lambda')^2]\langle S^2 \rangle \sin^2 \theta/2 - \dots \quad (1a)$$

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and where H' is the optical constant, $\Delta\tau$ is the difference in turbidities between solution and solvent, the excess chemical potential of the polymer μ_3^e is defined by $\mu_3 = RT \log c_3 + \mu_3^e + \mu_3^\theta(T, P)$ for dilute solutions. $(\partial n/\partial c_3)_{T, P}$ is the refractive index increment, A_2 is the second virial coefficient, $\langle S^2 \rangle$ is the square of the radius of gyration and λ' is the wavelength of light in solution.

If we now consider a homogeneous three component system, equation 1 can no longer be rigorously applied because of the additional contributions from the interaction of the polymer with the third component.

There are several types of ternary system which are of interest, but as the theoretical treatment normally assumes that the polymer component is homodisperse—rarely, if ever, found in practice—we should perhaps refer to them as quasi-ternary systems. Several examples are listed below where the polymer component may be linear, branched or a copolymer.

(a)   solvent [1]   solvent [2]   polymer [3]
(b)   solvent [1]   non-solvent [2]   polymer [3]
(c)   solvent [1]   electrolyte [2]   polymer [3]
(d) non-solvent [1]   non-solvent [2]   polymer [3]
                                                    [cosolvent system]
(e)   solvent [1]   polymer [2]   polymer [3]

One might well ask the question: why use quasi-ternary systems which are more difficult to understand, and require a more complex combination of the various interaction parameters? There is perhaps no short answer to this other than the fact that mixed solvents are in many instances extremely useful from a practical and experimental viewpoint. For example, type (a) systems often exhibit a synergistic effect where the polymer molecule is thermodynamically more compatible with a mixture of the two solvents than with either component separately, and in the extreme case such as a type (d) system the polymer may not be soluble in either component separately but is soluble in a mixture of both i.e. a cosolvent action can be observed. Similarly type (b) systems form the basis of the fractional precipitation technique, widely used to obtain polymer fractions with a narrower molecular weight distribution than the parent sample. They are also used to obtain critical consolute mixtures when no single liquid can be found to act as a theta solvent for a polymer whose unperturbed dimensions are to be measured.

The addition of electrolytes to produce a type (c) mixture is usually essential when studying biological and synthetic polyelectrolytes if non ideality caused by charge effects is to be eliminated or minimised, and one finds examples of type (e) systems when complex formation betwen two proteins is investigated. In the synthetic field the question of polymer compatibilities is also receiving considerable attention and involves a type (e) mixture. However, only (a) and (b) will be considered in any detail here.

The additional contribution of the interaction between the second liquid, component [2], and the polymer means that extrapolation of light scattering data to zero concentration is no longer a simple function of the molecular

weight, and it is found that the molecular weight of a given polymer sample M_3, frequently varies from one mixed solvent medium to another. In some instances, such variations, which result in an apparent molecular weight M_3^*, may arise from aggregation of the polymer in the solvent mixtures[4], but in other cases they are caused by preferential adsorption of one of the components comprising the mixture, by the polymer. This latter phenomenon was first reported by Ewart et al.[5] while studying the systems benzene [1] methanol [2] polystyrene [3] and butanone [1] isopropanol [2] polystyrene [3]. They decided that the effect was caused by a change in concentration of the thermodynamically better solvent in the polymer domains. In simple terms the preferential adsorption of one liquid component by the polymer alters the local concentration of the mixture in the immediate vicinity of the polymer coil; a measurement of the refractive index increment now results in a value which differs from the correct one and depends on the refractive index of the adsorbed species. For instance if the three refractive indices are n_1, n_2 and n_3 respectively and if $n_3 > n_1$ and n_2 then the refractive index increment (dn/dc_3) will be decreased if the solvent with the higher refractive index is adsorbed, resulting in M_3^* larger than the correct molecular weight, while the reverse is true if the solvent with the lower refractive index is adsorbed.

A rigorous theoretical treatment of the problem has been provided most notably by Stockmayer[6] and also by Kirkwood and Goldberg[7] and others[8]. Stockmayer interpreted the turbidity of multicomponent solutions, in the absence of angular dissymetry of scattered light, in terms of fluctuations in the refractive index in a volume element V of solution containing 1 kg of solvent. Under conditions of constant temperature and pressure with component [1] fixed at 1 kg, we have:

$$\frac{H'V}{\Delta\tau} = \frac{a_{33}}{\Psi_3^2} \frac{[1 - (a_{23}^2/a_{22}a_{33})]}{[1 - (a_{23}/a_{22})\Psi_2/\Psi_3]^2} \tag{2}$$

with

$$\Psi_i = \frac{dn}{dM_i} = \frac{dn}{dc_i} \cdot \frac{M_i}{V}$$

and the activities

$$a_{ii} = \frac{1 + \beta_{ii}M_i}{M_i}; \; a_{ij} = \beta_{ij}$$

where M_i = moles of component i.

The components are expressed in weight molalities and it is much more convenient to restate the Stockmayer equation in the more commonly used concentration units (c) such as g/ml. Equation 2 (where subscripts, T and P for

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the partial derivatives are now understood and omitted) then becomes[9]:

$$\frac{H'[(\partial n/\partial c_3)_{c_2}]^2 c_3}{\Delta \tau} = \frac{1}{M_3\left[1 + \frac{(\partial n/\partial c_2)_{c_3}}{(\partial n/\partial c_3)_{c_2}}\left(\frac{\partial c_2}{\partial c_3}\right)_{\mu}\right]^2}$$

$$+ \frac{Vc_3\left(\beta_{33} + \left(\frac{\partial c_2}{\partial c_3}\right)_{\mu}\beta_{23}\right)}{M_3^2\left[1 + \frac{(\partial n/\partial c_2)_{c_3}}{(\partial n/\partial c_3)_{c_2}}\left(\frac{\partial c_2}{\partial c_3}\right)_{\mu}\right]^2} \qquad (3)$$

and if

$$\Omega = \left[1 + \frac{(\partial n/\partial c_2)_{c_3}}{(\partial n/\partial c_3)_{c_2}}\left(\frac{\partial c_2}{\partial c_3}\right)_{\mu}\right]$$

then,

$$\frac{Hc_3}{\Delta \tau} = \frac{1}{M_3^*} + \frac{2A_2 c_3}{\Omega^2} \qquad (4)$$

where M_3^* is the apparent molecular weight $= M_3\Omega^2$, $(\partial n/\partial c_3)_{c_2}$ is the conventional refractive index increment for the polymer in the liquid mixture expressed in ml/g, $(\partial c_2/\partial c_3)_{\mu}$ represents the adsorption of component [2] by the polymer and is negative when selective adsorption of [2] is absent, and the subscript μ indicates conditions of constant chemical potential of liquid components [1] and [2] throughout the system.

It is obvious from these equations that the measurements of polymer molecular weights by light scattering in mixed solvents can lead to erroneous values of M_3· and to obtain the true values of M_3 it is necessary to satisfy one or other of the following conditions:

(i) In a binary liquid mixture no dependence of M_3 on solvent composition will be observed if the components are an isorefractive pair. Thus Chinai et al.[10] used mixtures of butanone and isopropanol as a theta solvent for poly(methylmethacrylate), but a cautionary note has been sounded by Tuzar and co-workers[11] who emphasised that even when the refractive index difference between the two solvents is very small, the value of the molecular weight can be affected if a strong selective adsorption occurs, and cite as an example a polyamide dissolved in a mixture of water and tetrafluoro-propanol. One should mention at this point that use of an isorefractive solvent pair does not eliminate the possibility of preferential adsorption of one of the components, it merely makes the phenomenon impossible to detect, by light scattering methods.

(ii) The value of $(\partial c_2/\partial c_3)_{\mu}$ is a measure of the amount of component [2] which must be added to or removed from the system, per unit weight of component [3], in order to maintain a constant chemical potential as required, i.e. to keep the system in equilibrium with either the osmotic

equilibrium liquid or in the case of electrolytes, the Donnan equilibrium liquid. Thus:

$$(\partial n/\partial c_3)_\mu = (\partial n/\partial c_3)_{c_2} + (\partial n/\partial c_2)_{c_3}(\partial c_2/\partial c_3)_\mu \qquad (5)$$

where

$$\frac{1}{M_3} = \left\{ \frac{H'[(\partial n/\partial c_3)_{c_2} + (\partial c_2/\partial c_3)_\mu(\partial n/\partial c_2)_{c_3}]^2 c_3}{\Delta\tau} \right\}_{c_3 = 0} \qquad (5a)$$

The refractive index increment measured in the normal way is $(\partial n/\partial c_3)_{c_2}$ while equilibration of the polymer solution with the solvent mixture across a semipermeable membrane, followed by measurement of the refractive index increment of the equilibrated solution and solvent, will provide the correct value of $(\partial n/\partial c_3)_\mu$ necessary for the evaluation of the true molecular weight. Estimation of these two parameters together with $(\partial n/\partial c_2)_{c_3}$ allows the preferential adsorption to be calculated from equation 5.

The equilibration method was used by Stockmayer and Chan[12] when examining the solution behaviour of polyoxymethylene in mixtures of hexafluoroacetone and water. Polymer solutions were dialysed against the solvent through porous glass thimbles and subsequent refractive index increment measurements showed that there was a strong preferential adsorption of the mono-hydrate $(CF_3)_2 C(OH)_2$. Omission of this procedure would have resulted in a 30 per cent error in the molecular weights. Mauss et al.[13] were also careful to apply this equilibration technique in their light scattering investigation of the intercalation of proflavine in the DNA helix in aqueous solution, where adsorption of the dye on the macromolecule will alter the refractive index increment, and consequently the apparent molecular weight. As interpretation of the mechanism of adsorption of the dye by DNA required a knowledge of the mass per unit length, accurate molecular weight measurements were essential.

(iii) For certain type (c) systems, an extrapolation procedure can be used as described by Vrij and Overbeek[9] who showed that for a polyelectrolyte with a valency Z and a degree of dissociation α, in an aqueous electrolyte solution, the correction factor Ω' is given by

$$\Omega' = \left[1 - \alpha Z \frac{M_2}{M_3} \cdot \frac{(\partial n/\partial c_2)_{c_3}}{(\partial n/\partial c_3)_{c_2}} \right] \qquad (6)$$

They examined partially neutralized polymethacrylic acid in aqueous solutions containing various sodium halides at constant ionic strength and found that the magnitude of M_3^* was a function of the electrolyte used. The true M_3 was estimated by plotting $(M_3^*)^{\frac{1}{2}}$ against the molar refractive index increment of the salt, $M_2 (\partial n/\partial c_2)_{c_3}$ as shown in *Figure 1*. This is in effect an extrapolation to conditions involving a hypothetical electrolyte which has no influence on the refractive index, i.e. $(\partial n/\partial c_2)_{c_3} = 0$.
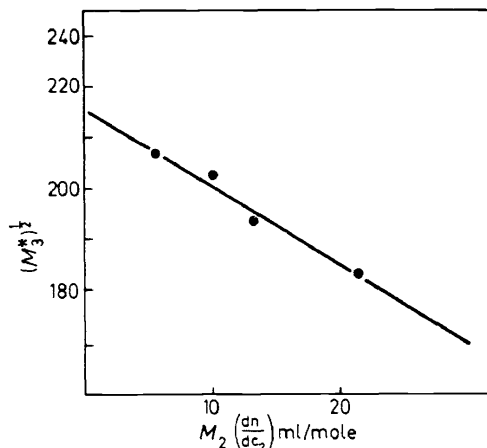
Figure 1. Square root dependence of M_3^*, for polymethacrylic acid, on the molar refractive index increment of the supporting electrolytes in aqueous solution. From right to left, NaI, NaBr, NaCl, NaF. (Vrij and Overbeek 1962).

PREFERENTIAL ADSORPTION PARAMETER

Although one can eliminate the effect of preferential adsorption it is often more interesting to examine the phenomenon itself in greater detail and to obtain a quantitative measure of the preferred interaction between the polymer and one of the components of the mixture. It can be seen from equations 3 and 4 that calculation of the apparent molecular weight M_3^* combined with a knowledge of the actual value of M_3 should provide a measure of the amount of the particular component preferentially adsorbed by the polymer. This can be expressed very simply by starting with the form first proposed by Ewart et al.[5] (replacing their α by λ^*):

$$\frac{H'[(\mathrm{d}n/\mathrm{d}c_3) + \lambda^*(\mathrm{d}n/\mathrm{d}\phi_1)]^2 c_3}{\Delta\tau} = \frac{1}{M_3} \tag{7}$$

which provides a qualitative interpretation of the observed behaviour in quasi-ternary systems at $c_3 = 0$. For an isorefractive solvent pair $(\mathrm{d}n/\mathrm{d}\phi_1) = 0$ while for a pure solvent $\lambda^* = 0$ hence M_3 is unaffected, but M_3 will be too small when $\lambda^* . (\mathrm{d}n/\mathrm{d}\phi_1) > 0$ and too large when $\lambda^* . (\mathrm{d}n/\mathrm{d}\phi_1) < 0$ assuming $(\mathrm{d}n/\mathrm{d}c_3)$ to be positive. Other combinations will affect M_3 in different ways. Equation 7 has been recast by Read[14] as:

$$\lambda^* = \left[\left(\frac{M_3^*}{M_3}\right)^{\frac{1}{2}} - 1\right]\left[\frac{(\mathrm{d}n/\mathrm{d}c_3)}{(\mathrm{d}n/\mathrm{d}\phi_1)}\right] \tag{8}$$

which can be related to Ω by

$$\lambda^* = [\Omega - 1]\left[\frac{(\mathrm{d}n/\mathrm{d}c_3)}{(\mathrm{d}n/\mathrm{d}\phi_1)}\right] \tag{8a}$$

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where the adsorption parameter $\lambda^* = (-d\phi_1'/dc_3)$ is in units of ml/g, while ϕ_1 and ϕ_1' are the volume fractions of component [1] in the bulk medium and in the domain of the polymer coils respectively. Strazielle and Benoit[15] extended the analysis by considering that in a quasi-ternary system the polymer molecule is encapsulated in a sphere of solvent containing $(N_1 + x_1)$ and $(N_2 + x_2)$ molecules of components [1] and [2], where N_1 and N_2 are the numbers in the absence of preferential adsorption, and x_1 and x_2 are the excess numbers related by:

$$x_1 \bar{V}_1 + x_2 \bar{V}_2 = 0 \tag{9}$$

where $\bar{V}$ is the partial molar volume. It was also assumed that the size of this sphere and the solution concentration were such that any preferential adsorption left the composition of the bulk mixture virtually unchanged. The final expression arrived at was:

$$M_3^* = M_3 \left[1 + \frac{x_1 V_1}{M_3} \left(\frac{dn/d\phi_1}{dn/dc_3} \right) \right]^2 \tag{10}$$

in which the adsorption coefficient λ^* is now $(x_1 V_1/M_3)$ and is a measure of the excess number of component [1] molecules adsorbed by each polymer molecule of molecular weight M_3. Both Read and Strazielle and Benoit found λ^* to be independent of the magnitude of M_3.

In the Stockmayer treatment, the selective adsorption coefficient is positive when component [2] is the species adsorbed.† In practical terms the sign is normally defined as being positive when $M_3^* > M$ as in equation 7. Thus in a co-solvent system where both components[16] are adsorbed such as propanol [1], water [2], poly(ethyleneglycolmonomethacrylate) [3], λ^* is positive when [1] is adsorbed and negative when [2] is adsorbed because $n_1 > n_2$. If then the liquid component with the larger refractive index is denoted as component [1] when $n_3 > n_1$ and n_2 the various forms of the adsorption parameter used by different authors can be interrelated as shown in *Table 1*.

Table 1 Nomenclature used by various authors to denote preferential adsorption in quasi-ternary systems.

Author	Ewart et al.	Read	Strazielle -Benoit	Stockmayer	Vrij-Overbeek
Preferential Adsorption Parameter	α	λ^*	$\dfrac{x_1 V_1}{M_3}$	$-\dfrac{V_2}{V_3} \bar{v}_3 \phi_1 \left(\dfrac{\partial m_2}{\partial m_3} \right)_\mu$	$-V_2 \left(\dfrac{\partial c_2}{\partial c_3} \right)_\mu$

The Strazielle–Benoit form for λ^* provides a means of evaluating the selective adsorption in relation to the excess number of molecules of a given

† A commonly used convention is to assign a positive value to the adsorption coefficient when the thermodynamically better solvent is adsorbed selectively by the polymer and negative value when the thermodynamically poorer liquid component (i.e. the one least expected to interact with the polymer) is adsorbed. Examples of this latter type are given later.

component in the polymer domain; Lange[17] has extended the concept to enable calculations of the number of molecules of a particular component which solvate the polymer in the absence of a third component. Lange first calculated λ^* in the usual way for a three component system as a function of the composition of the binary mixture and redefined the parameter as:

$$\lambda^* = \frac{V_m X_1 X_2}{M_0} \left(\frac{N_{1S}}{X_1} - \frac{N_{2S}}{X_2} \right) \tag{11}$$

where X is the mole fraction, M_0 the monomer molecular weight, V_m the molar volume of the binary mixture, and N_{1S}, N_{2S} are the numbers of molecules of components [1] and [2] in the solution shell surrounding the polymer per monomer unit. In the limit of $X_2 \rightarrow 0$ differentiation of (11) yields:

$$\frac{M_0}{V_1} \left(\frac{d\lambda^*}{dX_2} \right)_{X_2=0} = (N_{1S}^0)_{X_2=0} - \left(\frac{dN_{2S}}{dX_2} \right)_{X_2=0} \tag{12}$$

Lange then measured $M_0 V_1^{-1}(d\lambda^*/dX_2)$ from the limiting slope of the curve λ^* against X_2 for a number of benzene [1] precipitant [2] polystyrene [3] systems, in which the precipitants were members of a homologous series, and extrapolated this parameter to infinite M_2 as shown in *Figure 2*. In this way an
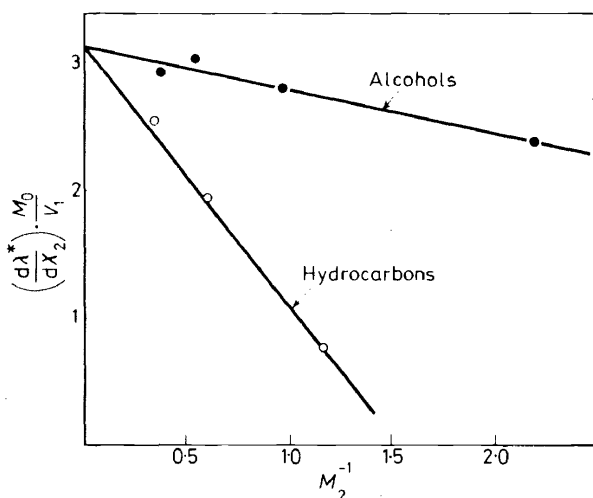

Figure 2. Estimation of the solvation of polystyrene by benzene (Lange 1964).

estimate of N_{1S}^0 for pure component [1] could be obtained and it was found that approximately three benzene molecules solvate every monomer unit of polystyrene dissolved in pure benzene. Further investigations on systems with paraffins and alcohols as precipitants revealed that for hydrocarbons the isomer with the lowest molar volume was adsorbed most strongly (i.e. the preferential adsorption of the benzene was lower), but that the size had

no effect when alcohols were the precipitants[18]. In both cases, the preferential adsorption of the benzene increases as the chain length of the precipitant increases as implied by the plot in *Figure 2*, and is virtually independent of temperature between 20–70°. A detailed analysis of the two solvent system benzene [1], butanone [2], polystyrene [3] was also attempted[19]. The amount of butanone which solvated the polymer in pure solvent [2], N_{2s}^0, was first calculated in a manner comparable to that for benzene. The preferential adsorption in the ternary system was then measured over the complete composition range and $(d\lambda^*/dX_1)_{X_1=0}$ estimated from the resulting curve.

A relation of the form:

$$N_{1s} = \left(\frac{dN_{1s}}{dX_1}\right)_{X_1=0} + \left[N_{1s}^0 - \left(\frac{dN_{1s}}{dX_1}\right)_{X_1=0}\right] X_1^2 \qquad (13)$$

was then assumed which is valid in the limits of $X_1 \to 0$ and $X_2 \to 0$. Hence N_{1s} could be calculated using:

$$\frac{M_o}{V_2}\left(\frac{d\lambda^*}{dX_1}\right)_{X_1=0} = \left(\frac{dN_{1s}}{dX_1}\right) - N_{2s}^0 \qquad (13a)$$

and substitution in equation 11 permitted analysis over the complete composition range. From this it was found that benzene was preferentially adsorbed over the entire range of compositions even though the molar volumes of the two species are almost equal.

THERMODYNAMIC INTERPRETATION OF λ^*

Stockmayer has defined the adsorption coefficient in terms of the chemical potential as:

$$\lambda^* = \frac{V_2}{V_3}\bar{v}_3\phi_1\left(\frac{\partial\mu_2}{\partial M_3}\right)_{T,P,\,M_2 M_3\to 0} \bigg/ \left(\frac{\partial\mu_2}{\partial M_2}\right)_{T,P,\,M_3\to 0} \qquad (14)$$

Starting from equation 14 Read used the Flory–Huggins theory to relate λ^* to the solvent composition when the interaction parameters χ_{ij} are known. Flory[20] has shown that the chemical potential of component [2] in a ternary mixture is given by

$$\frac{\mu_2 - \mu_2^0}{RT} = \ln\phi_2 + (1 - \phi_2) - l^{-1}\phi_1 + (\chi_{12}l^{-1}\phi_1 + \chi_{23}\phi_3)(\phi_1 + \phi_3)$$
$$- \chi_{13}l^{-1}\phi_1\phi_3. \qquad (15)$$

where $l = V_1/V_2$ and $\chi_{ij} = V_i\chi_{ji}/V_j$. By differentiating μ_2 with respect to M_2 and M_3 and eliminating terms in ϕ_3 Read derived the relation, suitably extended to incorporate χ_{ijj} and χ_{ijk} terms,

$$\lambda^* = \bar{v}_3\phi_1\phi_2$$

$$\times \frac{[(\chi_{12} - \chi_{123})(\phi_2 - \phi_1)l^{-1} - (\chi_{13} + \chi_{133}/2)l^{-1} + (\chi_{23} + \chi_{233}/2) + l^{-1} - 1]}{\phi_1 + l^{-1}\phi_2(1 - 2\chi_{12}\phi_1)}$$
$$\qquad (16)$$

The inclusion of χ_{ijj} and χ_{ijk} terms is not explicit in the Flory-Huggins theory although the authors recognized they might be necessary, and experimental evidence indicates the need for these higher terms for certain systems where the solution properties can best be accounted for if a quadratic dependence of χ on concentration is assumed. In the majority of quasi-binary liquid systems χ_{12} is sufficient to characterize the interactions so χ_{122} terms were dropped from equation 16. Similarly Read is of the opinion that $(\chi_{133}/2)l^{-1}$ and $(\chi_{233}/2)$ probably cancel out so that only the χ_{123} term remains significant. The need even for this term has been questioned by Strazielle and Benoit[21] who have suggested that only the binary interaction parameters are required, and they found that their experimental data for the system benzene [1], cyclohexane [2], polystyrene [3] are in good agreement with the predicted behaviour of λ^*. Read obtained equally good agreement for the same system using χ_{123}, but Strazielle and Benoit believe this is due to an overestimation of $(\mathrm{d}n/\mathrm{d}c_3)$ by Read. This system has also been studied by Yoshino and Tanzawa[22] using a diffusion method. Their data are compared with λ^* values calculated from the light scattering investigations shown in *Figure 3* and
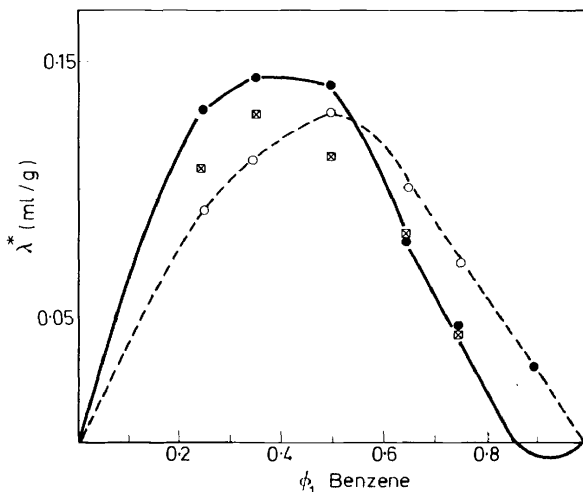

Figure 3. Variation of adsorption parameter with solvent composition in the system benzene [1], cyclohexane [2], polystyrene [3]. Data of Strazielle and Benoit —●—. Read —○—, Yoshino and Tanzawa —⊠—. Solid line calculated from equation 16 neglecting ternary interaction terms, broken line calculated from equation 16.

although neither curve is matched exactly, better agreement is obtained with the curve derived using only χ_{ij}. Lange[18] studied the same system but obtained λ^* much larger than those reported above. This was due to differences in the measured refractive index increments and subsequent correction of his values of $(\mathrm{d}n/\mathrm{d}c_3)$ brings his data in line with the Strazielle–Benoit curve. This lends further support to the suggestion that χ_{ijk} terms are unnecessary for this system.

Unfortunately equation 16 is not generally applicable and *Figure 4.1* shows the behaviour of λ^* in the benzene [1], heptane [2], polystyrene [3] system[23] in which heptane acts as a precipitant, producing a critical consolute mixture (measured by light scattering) when $\phi_1 = 0.44$, at which point $A^*_{2,LS} = 0$
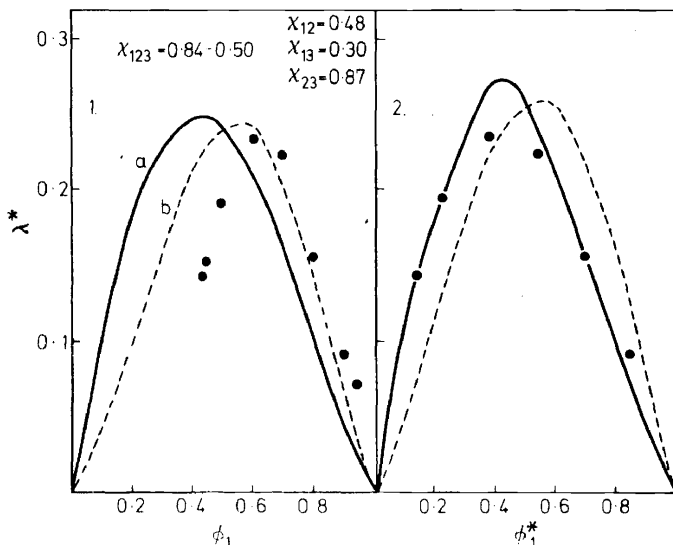

Figure 4. System benzene [1], heptane [2], polystyrene [3] (Cowie and Bywater 1966). Section 1: Broken line calculated from equation 16, solid line calculated using binary interaction parameters only. Section 2: as for section 1 except for replacement of ϕ_1 by equation 18 to give ϕ_1^*.

and $\lambda^* = 0.143$. The theoretical curve (a) was calculated using $\chi_{12} = 0.48$, $\chi_{13} = 0.30$ and $\chi_{23} = 0.87$.† The last value is unobtainable experimentally but Scott[24] and Tompa[25a] have shown that the composition of a solvent, non solvent, polymer mixture at the critical point is given by $\phi_3 = 0$ and:

$$l - 2l\phi_1^c\chi_{13} - 2l(1 - \phi_1^c)\chi_{23} + D\phi_1^c(1 - \phi_1^c) = 0 \qquad (17a)$$

$$D = 2\chi_{12}\chi_{13} + 2l\chi_{13}\chi_{23} - \chi_{12}^2 - \chi_{13}^2 - l^2\chi_{23}^2 \qquad (17b)$$

in the limit of infinite M_3, which allows calculation of χ_{23} from data obtained in the critical consolute mixture. Curve (b) was derived by incorporating χ_{123} which was estimated according to the method proposed by Blanks and Prausnitz[25]. This provides a better fit for the data in the initial region of low precipitant concentration but fails as the critical consolute mixture is approached. The loss of agreement below $\phi_1 \sim 0.6$ is probably caused by an alteration of the χ_{ij} parameters in the region $\phi_1 < 0.4$ where phase separation will begin to manifest itself. A better fit can be forced by adopting an empirical

† The interaction parameter χ_{13} was obtained by Tompa[25b] from vapour pressure measurements on solutions of low molecular weight polystyrene samples in benzene, χ_{12} was estimated from data in Landolt-Bornstein Vol. 2 Part IIa *Table 193*.

procedure. When $A^*_{2, L, S} = 0$, λ^* still has a finite value for the system, and there will be another mixture with a composition for which $\lambda^* = 0$. This can be identified either as the composition in which $A_{2, \pi} = 0$, or for which $[\eta]$. $M^{-\frac{1}{2}}$ is independent of $M^{\frac{1}{2}}$ (i.e. a Stockmayer–Fixman plot with zero slope) as reported by Dondos and Benoit[26]. If the value of ϕ_1 for this mixture is now referred to as ϕ_1^0, a new composition range can be defined by:

$$\phi_1^* = \frac{\phi_1 - \phi_1^0}{1 - \phi_1^0} \tag{18}$$

and substitution of ϕ_1^* and $\phi_2^* = (1 - \phi_1^*)$ in equation 16 produces the curves shown in *Figure 4.2*. This artificially imposes limits of homogeneity on the system and has no theoretical basis. The curve calculated by incorporating χ_{ijk} parameters is no longer the better fit, whereas the binary parameter curve is now an acceptable representation of the data.

The question of whether the χ_{ijk} parameters are or are not necessary, is an open one and probably depends on the system under investigation. Thus Zivny, Pouchly and Solc[27] have found that in benzene [1] methanol [2] poly-(methylmethacrylate) [3] the Flory–Huggins treatment is quite inadequate in providing the number of interaction parameters required to describe the system effectively and a ternary parameter was introduced. For rigorous testing of the theory, however, it is essential to have accurate activity data for the binary solvent mixtures and these must be carefully measured if anything other than an approximate correlation of selective adsorption and thermodynamic behaviour is required.

SECOND VIRIAL COEFFICIENT

It can be seen from equation 4 that the value of the second virial coefficient is also altered when selective adsorption occurs and the relation between the true ($A_{2, LS}$) and apparent ($A_2^*_{, LS}$) values, obtained from light scattering measurements is:

$$A^*_{2, LS} = A_{2, LS}\Omega^{-2} = A_{2, LS}M_3/M_3^* \tag{19}$$

The validity of this expression was tested by Fujita and his co-workers[28] who determined $A^*_{2, LS}$ for poly α-methylstyrene dissolved in mixtures of benzene and cyclohexane, then applied equation 19 to provide corrected values which were compared with $A_{2, \pi}$ measured after osmotic equilibration of the solutions. Their results, shown in *Figure 5* substantiate the validity of equation 19 for their system. Another aspect which illustrates the need to correct $A^*_{2, LS}$ is provided on examination of data for benzene [1] heptane [2] polystyrene [3][29]. Krigbaum[30] derived a semi-empirical relationship between A_2 and the root mean square end to end distance $(\bar{R}^2)^{\frac{1}{2}}$ and its unperturbed value $(R^2)^{\frac{1}{2}}_0$.

$$(\bar{R}^2)^{\frac{1}{2}} = (\bar{R}^2)^{\frac{1}{2}}_0 + 3(134/105)(3/2\pi)^{\frac{3}{2}}A_2M^2/N_A \tag{20}$$

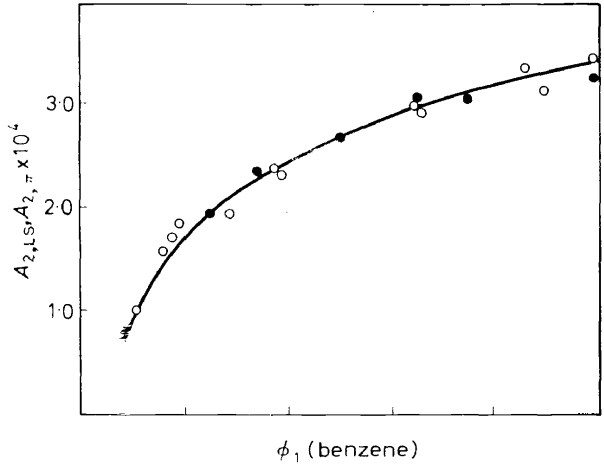It can be seen from *Figure 6*, that the linearity embodied in equation 20 is

Figure 5. Comparison of $A_{2,\pi}$ (—○—) and values of $A_{2,LS}$ (—●—) corrected by means of equation 19. (Okita *et al.* 1968).
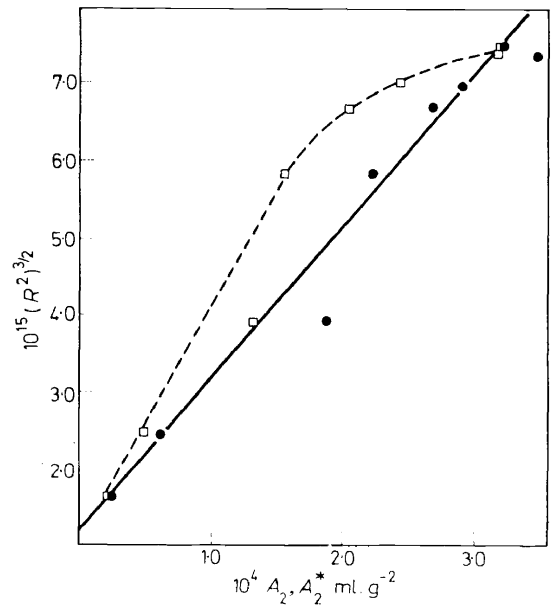

Figure 6. Dependence of $(R^2)^{3/2}$ on second virial coefficient corrected' (—●—) and uncorrected (—□—) for preferential adsorption effects. Measured in system benzene [1] heptane [2], polystyrene [3] and plotted according to equation 20. (Cowie 1968).

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obtained only when corrected values of $A_{2,LS}$ are used, while a curved plot results from $A_{2,LS}^*$

COIL SIZES

The application of the Krigbaum plot provides an estimate of the unperturbed dimensions of polystyrene in the benzene-heptane solvent pair, $\langle \bar{S}^2 \rangle_0^{\frac{1}{2}} = 438A$ compared with $447A$ calculated directly from light scattering. This leads us into the somewhat more ambiguous realm of polymer unperturbed dimensions in mixed solvents.

The fluctuation theory, used successfully to describe light scattering in quasi-ternary systems by Stockmayer and others, neglects the effects of angular dissymmetry of scattered light, and both inter- and intramolecular interactions in these systems. Yamakawa[31], has extended the distribution function theory developed by Zimm for two component systems, to describe the scattering in multicomponent systems, and in accounting for situations where angular dissymmetry is appreciable, he has proposed conditions under which molecular dimensions should be determined. These stipulate that if $0 \cdot 8 < M_3^*/M_3 < 1 \cdot 2$ then $\langle S^2 \rangle_0^{\frac{1}{2}}$ can be determined without being affected by selective adsorption; similarly $A_{2,LS}^*$ can be corrected simply by means of equation 19, if these conditions hold or the concentration of precipitant is low. As yet, no one has tested how rigorous these limits are, but it is felt that the assumptions involved may make them stricter than is necessary. A further point arising from this theory draws attention to the possibility that the mixture with $A_{2,LS}^* = 0$ may not co-incide with the Θ point except under the above conditions.

One can elaborate on this aspect by considering results reported by Benoit and Dondos[26] who derived Stockmayer–Fixman plots:

$$[\eta] \cdot M^{-\frac{1}{2}} = K_\Theta + 0 \cdot 51 B \Phi M^{\frac{1}{2}} \tag{21}$$

for various quasi-ternary systems in which preferential adsorption was both present and absent. Only for critical consolute mixtures in which $\lambda^* = 0$, was $[\eta]$ proportional to $M^{\frac{1}{2}}$ as required by equation 21. When $\lambda^* > 0$ the slope B, which is related to the excluded volume, was positive and approximately proportional to λ^*; a zero slope was attained at a lower solvent to non-solvent ratio. They explained their observations by assuming that the solvent composition in the interior of the coil is changed by selective adsorption thereby changing the nature of the intramolecular contacts in relation to the intermolecular interactions. From this, one can postulate the existence of two theta states, one for intermolecular interactions when $A_{2,LS}^* = 0$ and one for intramolecular interactions, when the chain is Gaussian i.e. $A_{2,\pi} = 0$. When preferential adsorption occurs, the apparent virial coefficient $A_{2,LS}^*$ for the particular solvent composition under consideration will be an average value of the solvent activities in the vicinity of the coil and in the bulk solvent. When the osmotic virial coefficient $A_{2,\pi}$ is measured the chemical potentials are equilibrated across the semipermeable membrane thereby changing slightly the solvent composition, so that $A_{2,\pi}$ will differ from $A_{2,LS}^*$ if there is selective adsorption.

Yamakawa proposed that the critical consolute mixture should be determined by osmotic or phase equilibrium techniques when there is strong

preferential adsorption, which assumes that the excluded volume will then be zero, whereas it may be finite for $A_{2,LS}^* = 0$. This could result in small chain perturbations in solutions for which $A_{2,LS}^* = 0$, but these are probably within experimental error for non polar polymers and systems in which λ^* is low.

Flory has suggested that variations in the unperturbed dimensions can be caused by specific interactions with the solvent and might be detected under Θ-conditions at a given temperature. This is particularly noticeable for polar polymers, but for non-polar polymers should be limited to differences in the order of 10 per cent. Molecular dimensions of a sample of polystyrene in several critical consolute mixtures have been determined at 35° thereby allowing $\langle S^2 \rangle_0^{\frac{1}{2}}$ measured in the single solvent cyclohexane to be used as reference[32]. The binary mixtures were chosen to cover a wide range of polarity measured in terms of the solubility parameter of the mixture:

$$\delta_m = 8 \cdot 1 \text{ to } 11 \cdot 4 \text{ [cal/ml]}^{\frac{1}{2}}$$

while the critical consolute mixtures were defined from the composition at which $A_{2,LS} = 0$, thus corresponding to conditions under which at least intermolecular interactions are eliminated. The coil sizes showed a slight dependence on solvent polarity, but were apparently unrelated to the magnitude of λ^* for the system, see *Figure 7*. Values of $\langle S^2 \rangle_0^{\frac{1}{2}}$ differed by less than ± 10 per cent from the value in cyclohexane, even for systems which exceeded the Yamakawa limit of $M_3^*/M_3 > 1\cdot2$. Benoit and Dondos[33] determined K_Θ for polystyrene in various mixtures using Stockmayer–Fixman plots, and
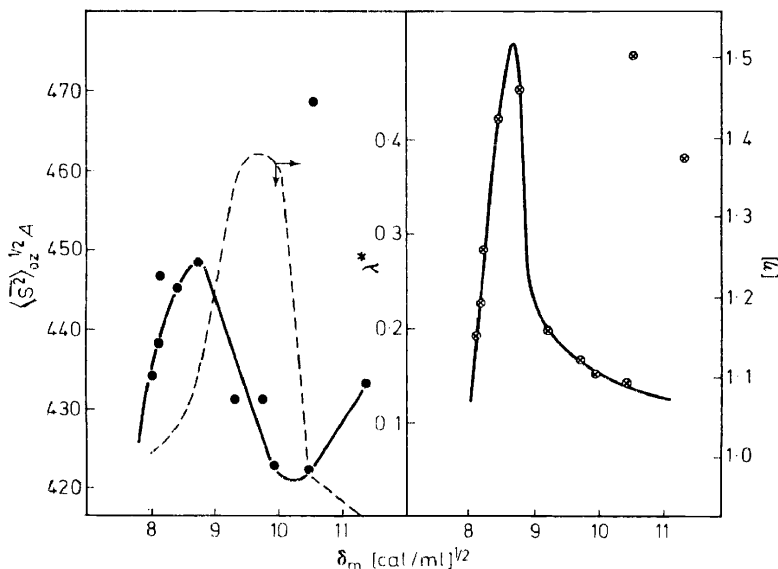

Figure 7. Unperturbed dimensions —●—, limiting viscosity number —⊗— and preferential adsorption parameter measured for polystyrene in several binary liquid mixtures of varying solubility parameter δ_m. (Cowie 1968).

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concluded that K_θ (mixture) was larger than K_θ (single liquid) when $\chi_{12} > 0$ and smaller when $\chi_{12} < 0$, but again the variations observed in coil sizes were within the ± 10 per cent limit. For a more polar polymer such as poly(vinyl-2-pyridine) the relative magnitude of K_θ was again dependent on χ_{12} but dimensional variations now exceeded 10 per cent and it is expected that effects will be magnified accordingly as the polymer polarity increases. The extrapolation procedures embodied in equations 20 and 21, should provide estimates of $\langle S^2 \rangle_0^{\frac{1}{2}}$ which, although reflecting specific solvent effects, should be free of possible perturbation by preferential adsorption. From the limited data available (and recognizing the limitations in the accuracy of these procedures) it would appear that for non-polar polymers dimensional variations are restricted to 10 per cent and in many instances should be within the limits of experimental error.

SYSTEMS EXHIBITING NEGATIVE SORPTION

In certain non-ionic systems adsorption of the poor solvent component [2] has been noted in mixtures containing low concentrations of [2]. This behaviour is predicted by the theoretical curve derived from the Flory–Huggins theory shown in *Figure 3* for polystyrene dissolved in high ratio benzene to cyclohexane mixtures, but was not demonstrated experimentally. Zivny, Pouchly and Solc[27] detected preferential adsorption of methanol in the range $\phi_1 = 0.8 - 1.0$ for benzene [1] methanol [2] poly(methylmethacrylate) [3], but an inversion soon occurred and benzene was adsorbed over the remaining composition range see *Figure 8*. This observation is also consistent with the 'cluster' model proposed by Suh and Liou[34] for quasi-ternary systems in which it is postulated that the polymer molecule dissolved in a mixture
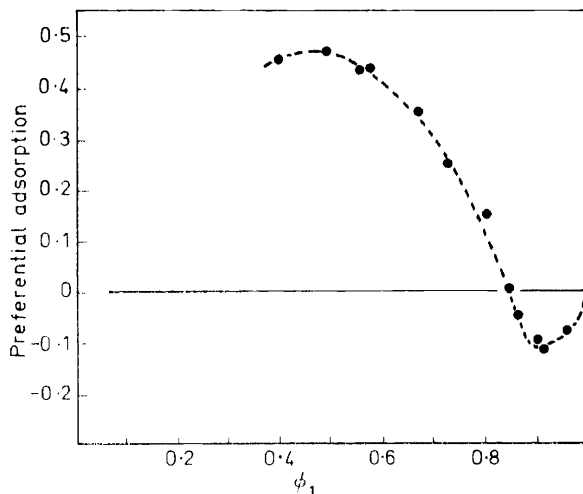

Figure 8. Preferential adsorption in system benzene [1], methanol [2], poly(methylmethacrylate) [3] (Zivny *et al.* 1967).

composed of good solvent [1] and strong precipitant [2] is surrounded mainly by solvent molecules. The polymer-solvent cluster then behaves like the good solvent alone in respect to interactions with the bulk mixture and this in effect suggests that the polymer is encapsulated in a protective layer of solvent. Various significant features arise as a result of the extension of this concept to phase equilibria one of which states that when the molar volume V_2 is less than V_1 and the solubility parameter of the solvent δ_1 is less than that of the polymer δ_3, i.e. the system under consideration here, then selective adsorption of the smaller component [2] is important at low concentrations of [2] in the binary phase, but decreases as the concentration of [2] increases, rapidly giving way to adsorption of component [1]. This is as observed. However, Suh states that the cluster model need only be applied when $(\delta_2 - \delta_3) > 2 \cdot 0$ and as we have seen in *Figure 3* need not be specially invoked to predict negative adsorption. Another example of negative sorption was reported by Shakhparanov et al.[35] for solutions of methylene chloride [1] methanol [2] secondary cellulose acetate [3] although the authors did not express this in terms of an adsorption parameter.

This system satisfies the conditions required for the cluster model, but has been interpreted in a different manner. On addition of methanol up to $\phi_2 = 0 \cdot 24$, M_3^* was observed to decrease, while $\langle S^2 \rangle^{\frac{1}{2}}$ decreased at low methanol concentrations then increased, and $A_{2,LS}^*$ tended to pass through a maximum value. The authors have taken this to indicate an initial breaking of hydrogen bonds in the incompletely esterified cellulose acetate resulting in an initial coiling following loss of some skeletal rigidity. Subsequently, coil expansion occurs by interaction of the liberated hydroxyls with methanol molecules. Further solvation ceases as the free hydroxyls all become shielded by the methanol and as ϕ_2 increases, solvent interaction with the esterified portion of the molecule decreases causing eventual phase separation. In this case, the negative adsorption is stimulated by the liberation of potential weak bonding sites and the molecule to all intents behaves somewhat like a copolymer. As the refractive indices n_1 and n_2 are very similar the selective adsorption must be quite large for it to be so readily detected.

APPLICATIONS TO BIOLOGICAL SYSTEMS

For proteins in aqueous electrolyte solutions it is possible to assess the degree of hydration of the macromolecule using preferential adsorption measurements. Thus, the hydration of DNA in the presence of NaCl and NaBr, calculated from selective adsorption studies is in good agreement with estimates from other methods[36].

An elegant application in the study of helix-coil transitions has been made by Marchal and Strazielle[37] who observed that a thermal transition from coil to helix occurs in the range 20–35° for poly (L benzyl glutamate) in a mixture of dichloracetic acid-heptane (0·55–0·45). This transition could be detected, not only by a conventional observation of dimensional changes, but also by the more unexpected variation of M_3^* as shown in *Figure 9*. This was interpreted as being due to a change in preferential adsorption as the conformation altered from a coil to a helix, and it was found that the helical structure adsorbed fewer DCA molecules than the coiled form. If heptane was replaced
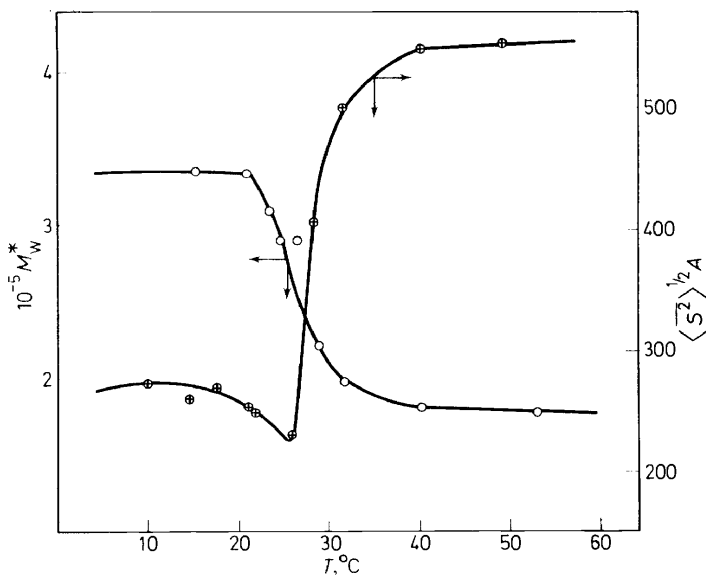
Figure 9. Helix-coil transitions of poly (L Benzyl glutamate) in dichloracetic acid (0·55)-heptane (0·45), showing variation of M^* (—O—) and $\langle S^2 \rangle^{\frac{1}{2}}$(—●—) as a function of temperature. (Marchal and Strazielle 1968).

by cyclohexanol no variation in M_3 was detected which supported the idea that the observed change in the DCA-heptane is a helix-coil transition and not aggregation.

CONCLUSIONS

Although the detailed interpretation of the behaviour of quasi-ternary systems is complicated by the need to consider additional thermodynamic interaction parameters, useful information can be elicited from the light scattering measurements once the complications are recognised. Indeed potential errors in molecular weight measurements can be turned to the advantage of the investigator and can be used to reveal the mode of inter-acation occurring between the polymer and the components of the mixture. The use of multicomponent systems is widespread and much remains to be done before a full understanding is achieved. It is hoped that the few examples given here may serve to illustrate the variety of problems which exist in this field and suggest other areas of exploration.

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