On the possibility of quantitative evaluation of the polymer–solvent interaction from the Huggins viscosity constant

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We discuss the possibility of evaluation of the 'goodness' of solvents for polymers and eventually of the extent of association in polymer–solvent systems from the Huggins constant, as a function of the viscosity expansion factor. However, this method does have some problems and therefore an analogous method has been suggested, i.e. the dependence of the Huggins constant on the slope of Heller's relationship. For non-associating systems, this dependence is defined by a generalized linear equation, which, unlike the dependence on expansion factor, is independent of both the polymer and its molecular weight. For associating systems, this dependence is described by a quadratic function. Its steepness is dependent on both the polymer and its molecular weight. Numerical evaluation from the above-mentioned information is thus very simple.

(Keywords: dilute polymer solutions; Huggins viscosity constant; polymer–solvent interaction; polymer association)

INTRODUCTION

Knowledge of the magnitude of polymer–solvent interactions, and particularly of the 'goodness' of a solvent for a given polymer, is very important for the investigation of the properties of polymers and their solutions and also for technological applications, e.g. adhesives, surface finishes, man-made leathers, fibres, etc. The goodness of solvents has hitherto been determined by either the Hildebrand solubility parameter δ (ref. 1) or the Flory–Huggins interaction parameter χ (refs. 2–6).

In the first case it is necessary to know solubility parameters of both the solvent, δ_1, and the polymer, δ_2. A general rule for non-polar systems is that the solvent is better when its δ_1 values is closer to δ_2. In polar systems, contributions of dispersive forces, dipole moments and hydrogen bonds to the total δ value[7–12] should be taken into account. The solubility parameter can thus be used only for a rough estimation of the goodness of a solvent, without claiming particular reliability of the conclusions drawn.

Another possible variable for the characterization of the goodness of solvents is the interaction parameter χ, expressing the measure of deviations of actual solutions from ideal ones. This value can be determined by several methods, which are, however, mostly experimentally demanding and time-consuming. The reliability of the results obtained is more or less influenced by simplifying assumptions, adopted for the calculation. Moreover χ is dependent on both the polymer concentration and molecular weight, and information provided about the specific interactions in the solution is of no particular interest[13–15]. Solvents, obviously different in quality, yield quite close values and thus the resolving capability is low. Comparison of results obtained by various methods and/or experimenters is thus fairly difficult[13,16–18].

There are also other quantities that are dependent on the goodness of solvents. Among them is the Huggins viscosity constant, which can be determined quite easily and, because of its interesting properties, seems to be suitable for direct determination of the goodness of a particular solvent.

THEORETICAL

The dependence of viscosity η of dilute polymer solutions on concentration C can be described by a polynomial in the form[15,19]:

$$\eta = \eta_0(1 + a_1C + a_2C^2 + \ldots) \qquad (1)$$

where η_0 is the viscosity of the pure solvent. Equation (1) is generally presented in the form:

$$\eta = \eta_0(1 + [\eta]C + k'[\eta]^2C^2 + \ldots) \qquad (2)$$

where $[\eta]$ is the intrinsic viscosity and k' is the dimensionless Huggins viscosity constant. Neglecting terms with third and higher powers of concentration yields the well known Huggins (H) equation. Other semiempirical equations, like those of Kraemer (K), Heller (HE), Martin, Staudinger and Heuer (MSH), and Schulz and Blaschke (SB), etc., are also used for processing of viscosimetric data.

As mentioned in other monographs[15,20] and confirmed by numerous experimental results[21–25], the Huggins constant is independent of the molecular weight of the polymer. Its value is influenced only by the goodness of the solvent. Because in some papers[26–28] more or less pronounced dependence of the Huggins constant on molecular weight of the polymer is claimed, it seems to be convenient to discuss both problems in more detail.

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Dependence of k′ on the goodness of solvent

In systems with good solvents, where polymeric chains are solvated to the highest degree and polymer–solvent forces are dominant, observed values of the Huggins constant[15,20,24,27,29–33] were between 0.3 and 0.4, and in some cases even lower[27,34].

With decreasing goodness of the solvent, the Huggins constant increases steadily, up to about 0.55 for θ conditions[27]. Literature data for the Huggins constant in the θ state are, however, quite variable: Spychaj *et al.*[35] give for polystyrene $k_{HE}^{\theta}=0.45$; Cvetkov *et al.*[36] and Bohdanecký *et al.*[37] give for acidolytic polyamide-12 $k_{H}^{\theta}=0.5$; Bohdanecký and Tuzar[23] give for poly(ethylene glycol methacrylate) $k_{HE}^{\theta}=0.58$; Sakai[30,38] claims for flexible polymers the interval $k'^{\theta}=0.5$ to 0.7; Nikonov[39] for polycaproamide give $k_{H}^{\theta}=0.9$, $k_{MSH}^{\theta}=0.73$ and $k_{SB}^{\theta}=0.70$; and Howard *et al.*[27] give for poly(tetrahydrofuran) $k_{H}^{\theta}=0.96$ and $k_{SB}^{\theta}=0.66$, and for polyamide-6 $k_{H}^{\theta}=0.55$ and $k_{SB}^{\theta}=0.46$.

The above short survey shows the wide variance of both the k_{H}^{θ} values and the Huggins constants determined from other relationships, although the k'^{θ} value is supposed to be a universal constant, independent of the polymer, its molecular weight and solvent[40,41]. It can thus be logically deduced that the higher values of the Huggins constant obtained are not the true values in the θ state, but can obviously be attributed to the presence of supermolecular configurations and/or associates in solution. This is confirmed by the results of Bohdanecký[21], who, for poly(methyl methacrylate) prepared by radical polymerization, for poly(vinyl chloride) and for polyamide-6, found k_{H}^{θ} values between 0.7 and 1.1.

The sensitivity of the Huggins constant to the presence of supermolecular structures is equally well documented by the results of other studies. For example, Trachtenberg and Korostyleva[42] found for acrylamide copolymer with styrene in toluene the value $k_H=1.33$; Hernández-Fuentes *et al.*[43] for poly(methyl methacrylate) in acetonitrile and chlorobutane found $k_H=2.0$; Šebenda and Králíček[33] for hydrolytic polyamide-6 found $k_H=4.75$; Pavlova *et al.*[44] found for poly(methyl methacrylate) in tetrachloroethane $k_H=12.0$; and for the same system Lánská and Šebenda[45] found a value as high as $k_H=19$. More complex studies of the dependence of the Huggins constant on the solvent system were published by Moore[46] and Berger[47].

Dependence of k′ on the molecular weight of the polymer

As mentioned above, the Huggins constant is not supposed to be dependent on the molecular weight of the polymer. This is, however, in disaccord with the experimental results of some investigators. In some cases the dependence of k' on $\bar{M}_w$ is not pronounced[21,48,49] and seems to be within the experimental error[27,46].

The results of other investigations are much more conclusive. Rafler and Reinish[50] studied hydrolytic polyamide-6 in a phenol–tetrachloroethane (1:1) mixture and, with increasing degree of polymerization P_n from 21.5 to 155, observed a drop of k_H from 2.37 to 0.5. For acidolytic polyamide, such a dependence was not observed. Lánská *et al.*[28] found for hydrolytic polyamide-12 a decrease of k_{MSH} from 3.46 to 0.36, when $\bar{M}_w$ of the polymer was increased from 3.5×10^3 to 3.9×10^4. No such dependence was observed for the acidolytic polymer.

It can thus be expected that the Huggins constant will be molecular-weight-dependent only in polymers easily associating in solution, either by the effect of strong ionic or polar interactions or by the effect of hydrogen bonds.

Functional dependences of the Huggins constant

From the above survey it is evident that the Huggins constant can be conveniently used for direct evaluation of the goodness of a solvent for a given polymer. It can easily be shown that the Huggins constant is independent of the numerical value of the initial polymer concentration in the dilute solution and is thus not influenced by errors resulting, for example, from an inaccurate value of the concentration, following from impurity of the polymer[51]. There is still the problem of the independent variable to which the Huggins constant could be correlated.

The dependence usually found in the literature is k' as a function of the cube of the viscosity expansion factor α_η^3. For non-associating systems its plot is a convex curve on which $\alpha_\eta^3=1$ corresponds to k'^{θ}; with increasing α_η^3, k' decreases to a value of about 0.25. Attempts at a mathematical description of this function were published by several authors, e.g. Yamakawa[52], Rao[53], Sakai[38] and Bohdanecký[21,54]. The last author derived the following equation, taking into account thermodynamic as well as hydrodynamic aspects:

$$k'=k'^{\theta}-3K_1[\eta]^{-1} \tag{3}$$

where

$$3K_1[\eta]^{-1}=10.2(\alpha_s^2-1)H(\alpha_s)$$

The calculated k' value will thus be dependent on the form of the $H(\alpha_s)$ function chosen.

For the application of this relationship it is necessary to know the values of k'^{θ} and $[\eta]^{\theta}$. Direct determination of these quantities is often difficult because of the polydispersity of commercial polymers; they can, however, be determined indirectly. The k'^{θ} value can be obtained from a graph of the function $k'\alpha_\eta^4$ *versus* $(\alpha_\eta^4-\alpha_\eta^2)$, resulting from the relationship derived by Imai[40]:

$$k'=k'^{\theta}\alpha_\eta^{-4}+C_0 z\alpha_\eta^{-5} \tag{4}$$

by putting $C_1 z=\alpha_\eta^5-\alpha_\eta^3$.

The value $[\eta]^{\theta}$ can be calculated from the Mark–Houwink–Sakurada (MHS) equation, if $\bar{M}_w$ and K^{θ} are known. If K^{θ} is not available in the literature, which is often the case for copolymers, it must be determined laboriously and again with a certain error resulting from the procedure used.

In associating systems the situation will be still more complicated. Effects of association of macromolecules in solution on the value of the Huggins constant were studied in more detail by Wolff *et al.*[32] and Šebenda and Králíček[33]. Theoretical analysis of dimerization and multimerization led Wolff *et al.* to the assumption that k' is the sum of a 'natural' k'' value and an 'additional' k_a value:

$$k'=k''+k_a \tag{5}$$

According to Šebenda and Králíček k' is also the sum of two contributions. The first one, corresponding to Wolff's 'natural' value, depends on the character of the polymeric chain and is given by the total action of forces between monomeric units, on the one hand, and between monomeric units and solvent molecules, on the other. The second contribution, analogous to the k_a value, depends on interactions of other groups, mainly ionic and end groups, which associate easily. This second contribution depends on the concentration of the above groups and their distribution in the volume, and thus also on the molecular weight of the polymer. The k_a value can therefore be considered as a contribution expressing the extent of association in a given polymer–solvent system. For non-associating systems we thus obtain:

$$k_a = 0 \quad \text{and} \quad k' = k'' = k_{\text{nass}}$$

and in associating systems:

$$k' = k_{\text{nass}} + k_a = k_{\text{ass}}$$

It can thus be assumed that the curves of k' *versus* α_η^3 for associating systems will be similar to the ones for non-associating systems, only steeper. If a sufficiently accurate and generally valid formulation of the function k' *versus* α_η^3 were available for non-associating systems, the goodness of a solvent and the presence and importance of associates could be quantitatively determined by comparison of experimental and calculated (at a given expansion factor) values of the Huggins constant.

Although this method is doubtless theoretically well justified, it is to be noted, however, that the expansion coefficient is dependent on the excluded volume and, with increasing molecular weight, this dependence becomes more pronounced. It is thus doubtful whether there exists a generally valid relationship between k' and α_η^3 for non-associating systems. Moreover, for the calculation of the expansion factor it is necessary to know the θ values, and their determination for polydisperse polymers is usually difficult. As will be shown below, it is therefore more convenient to take as independent variable the value K'_{HE} from Heller's viscosity equation:

$$0.5\left[\left(\frac{\eta-\eta_0}{\eta_0 C}\right)^{-1}+\left(\frac{1}{C}\ln\frac{\eta}{\eta_0}\right)^{-1}\right]=\frac{1}{[\eta]_{\text{HE}}}-K'_{\text{HE}}C \qquad (6)$$

where $K'_{\text{HE}} = k_{\text{HE}} - 0.25$.

The Huggins constant can be calculated from the Martin–Staudinger–Heuer relationship

$$\ln\left(\frac{\eta-\eta_0}{\eta_0 C}\right)=\ln[\eta]_{\text{MSH}}+k_{\text{MSH}}[\eta]_{\text{MSH}}C \qquad (7)$$

According to the theoretical conclusions of Sakai[30], k_{MSH} is in very good agreement with k' determined in poor solvents and it is equally applicable for good solvents.

EXPERIMENTAL

Polymers

Aliphatic polyurethanes were synthesized at our Institute in two series. In both cases prepolymers were prepared by the reaction of polycaprolactone (series A, $\bar{M}_n = 830$; series B, $\bar{M}_n = 2000$) with isophorone diisocyanate and, in the final phase, extended with ethylenediamine. Each series consisted of four samples with different molecular weights (see *Table 1*). Solid polymers for measurement were obtained by evaporation of solvents at 50°C.

Table 1 Molecular weights of polyurethanes investigated

Polymer	$\bar{M}_w$ ($\times 10^{-4}$)	Polymer	$\bar{M}_w$ ($\times 10^{-4}$)
A1	7.3	B1	8.9
A2	7.5	B2	9.0
A3	2.8	B3	4.5
A4	10.0	B4	19.9

Polystyrene ($\bar{M}_\eta = 2 \times 10^5$), prepared by radical polymerization, was supplied by n.p. Kaučuk, Kralupy.

Solvents

All solvents, with the exception of diacetone alcohol, were dried for at least 24 h over CaO and then distilled (column length, 20 cm; diameter, 2.5 cm; packing, glass rings).

Measurement of viscosities

Viscosities were measured in Ubbelohde viscometers with diameters of capillaries varying according to the viscosities of solvents. Hagenbach's correction[31] was applied in the calculations. Measurements were performed at 25°C and at θ temperatures. The initial concentrations of solutions of polyurethanes were approximately 1 g/100 cm^3, and for polystyrene 0.8 g/100 cm^3. Before metering into the viscometer, all liquids were filtered through sintered glass S2.

RESULTS AND DISCUSSION

Approximation of viscosity data to equations (6) and (7) by the least-squares method enabled calculation of k_{MSH}, $[\eta]_{\text{MSH}}$ and K'_{HE}. Several polystyrene-based systems were measured also at the θ temperature. The variance of the

Table 2 Experimental viscometric values for polystyrene

Solvent	$[\eta]_{\text{MSH}}$ (dl g^{-1})	k_{MSH}	K'_{HE}
Tetrahydrofuran (THF)	0.810	0.238	−0.005
Benzene	0.801	0.287	0.019
Chloroform	0.789	0.309	0.052
Toluene	0.758	0.301	0.047
Tetrachloromethane	0.787	0.321	0.062
Cyclohexanone	0.734	0.269	0.022
Dichloromethane	0.727	0.296	0.043
Trichloroethylene	0.719	0.426	0.151
Dioxane	0.687	0.343	0.081
Xylene	0.687	0.271	0.023
1,2-Dichloroethane	0.656	0.323	0.065
THF–water (91.4:8.6)	0.512	0.320	0.065
Butyl acetate	0.494	0.381	0.116
Ethyl methyl ketone	0.455	0.442	0.169
Ethyl acetate	0.432	0.458	0.182
Methyl isobutyl ketone	0.377	0.526	0.243
Cyclohexanone–acetone (20:80)[a,b]	0.294	0.665	0.362
Toluene–methanol (76.9:23.1) 34°C[a,b]	0.369	0.568	0.274
30°C[a]	0.360	0.527	0.242
Cyclohexane 34°C[a,b]	0.310	0.606	0.314
28°C[a]	0.284	0.550	0.268
27°C[a]	0.247	0.605	0.323
Methyl acetate 35°C[a]	0.281	0.625	0.329
Diisobutyl ketone 34°C[a]	0.286	0.634	0.341

[a] θ state

[b] Temperature for given solvents taken from literature data

Table 3 Experimental viscometric values for series A polyurethanes

	$[\eta]_{MSH}$ (dl g^{-1})				k_{MSH}				K'_{HE}			
Solvent	A1	A2	A3	A4	A1	A2	A3	A4	A1	A2	A3	A4
Toluene–isopropanol (10:90)[a]	–	–	0.206	–	–	–	0.644	–	–	–	0.347	–
(12:88) 24.5°C[a]	–	–	–	0.352	–	–	–	0.593	–	–	–	0.287
(15:85)	0.286	–	–	0.414	0.662	–	–	0.601	0.347	–	–	0.283
(19:81)	0.432	–	–	–	0.576	–	–	–	0.265	–	–	–
(20:80)	0.433	–	–	–	0.547	–	–	–	0.239	–	–	–
(25:75)	0.489	–	–	–	0.475	–	–	–	0.183	–	–	–
(30:70)	0.565	–	–	0.593	0.424	–	–	0.475	0.144	–	–	0.181
(40:60)	0.648	–	–	–	0.348	–	–	–	0.078	–	–	–
(50:50)	0.714	–	–	0.800	0.361	–	–	0.372	0.089	–	–	0.095
(60:40)	0.737	–	–	–	0.366	–	–	–	0.093	–	–	–
(70:30)	0.756	–	0.435	0.820	0.343	–	0.399	0.383	0.076	–	0.134	0.104
(75:25)	0.757	–	–	–	0.349	–	–	–	0.078	–	–	–
(80:20)	0.708	–	–	–	0.384	–	–	–	0.102	–	–	–
(85:15)	0.651	–	–	–	0.435	–	–	–	0.144	–	–	–
(90:10)	0.536	–	–	0.591	0.606	–	–	0.665	0.256	–	–	0.300
(94:6)	–	–	–	0.401	–	–	–	1.348	–	–	–	0.727
(95:5)	0.301	–	–	–	1.701	–	–	–	0.964	–	–	–
Ethylene glycol monomethyl ether	–	0.555	–	–	–	0.382	–	–	–	0.111	–	–
Ethylene glycol monoethyl ether	–	0.509	0.339	0.628	–	0.476	0.422	0.406	–	0.181	0.151	0.125
Diacetone alcohol	0.635	–	–	–	0.351	–	–	–	0.086	–	–	–
Dimethylformamide	0.696	0.706	–	–	0.370	0.316	–	–	0.095	0.057	–	–
Dimethylsulphoxide	0.568	0.564	–	–	0.410	0.418	–	–	0.130	0.138	–	–
Cyclohexanone	0.340	0.294	–	–	1.422	2.097	–	–	0.736	1.179	–	–
Dioxane	0.326	0.373	0.316	0.535	1.704	1.352	0.662	0.685	0.949	0.753	0.344	0.314
Tetrahydrofuran	0.309	0.215	0.225	0.341	2.087	3.420	1.812	2.032	1.124	1.914	1.170	1.074
Dichloromethane	0.270	0.278	0.194	0.312	3.281	3.340	3.363	3.091	1.571	1.460	1.954	1.385

[a] θ state

Table 4 Experimental viscometric values for series B polyurethanes

	$[\eta]_{MSH}$ (dl g^{-1})				k_{MSH}				K'_{HE}			
Solvent	B1	B2	B3	B4	B1	B2	B3	B4	B1	B2	B3	B4
Toluene–isopropanol (20:80)[a]	–	–	0.280	–	–	–	0.559	–	–	–	0.269	–
(22:78)[a]	–	–	–	0.435	–	–	–	0.756	–	–	–	0.385
(25:75)	0.367	0.360	–	0.534	0.606	0.496	–	0.678	0.294	0.210	–	0.319
(30:70)	0.449	–	–	0.717	0.503	–	–	0.500	0.205	–	–	0.184
(40:60)	0.567	–	–	–	0.406	–	–	–	0.128	–	–	–
(50:50)	0.673	–	–	1.056	0.361	–	–	0.358	0.091	–	–	0.080
(60:40)	0.747	–	–	–	0.355	–	–	–	0.086	–	–	–
(70:30)	0.797	–	0.528	1.219	0.342	–	0.357	0.323	0.075	–	0.096	0.055
(75:25)	0.790	0.654	–	–	0.326	0.361	–	–	0.063	0.092	–	–
(80:20)	0.805	–	–	–	0.345	–	–	–	0.077	–	–	–
(85:15)	0.764	–	–	–	0.360	–	–	–	0.087	–	–	–
(90:10)	0.711	–	–	0.672	0.417	–	–	1.029	0.124	–	–	0.421
(95:5)	0.602	–	–	–	0.602	–	–	–	0.256	–	–	–
(97.5:2.5)	0.408	0.394	–	–	1.535	1.110	–	–	0.717	0.619	–	–
Toluene–isopropanol–water (25:65.8:9.2)	–	0.472	–	–	–	0.363	–	–	–	0.097	–	–
Ethylene glycol monomethyl ether	–	0.508	–	–	–	0.415	–	–	–	0.136	–	–
Ethylene glycol monoethyl ether	–	0.469	0.354	0.680	–	0.465	0.419	0.475	–	0.173	0.148	0.175
Diacetone alcohol	0.653	–	–	–	0.281	–	–	–	0.029	–	–	–
Dimethylformamide	0.675	0.706	–	–	0.364	0.354	–	–	0.093	0.084	–	–
Dioxane	0.678	0.610	0.443	1.185	0.463	0.678	0.512	0.481	0.155	0.309	0.213	0.148
Dimethylsulphoxide	0.424	0.491	–	–	0.583	0.557	–	–	0.251	0.242	–	–
Cyclohexanone	0.570	0.597	–	–	0.587	0.589	–	–	0.246	0.251	–	–
Tetrahydrofuran	0.606	0.641	0.404	0.835	0.621	0.588	0.746	0.843	0.268	0.247	0.387	0.308
Dichloromethane	0.576	0.622	0.408	0.783	1.219	1.177	1.297	1.457	0.544	0.529	0.690	0.500
1,2-Dichloroethane	0.462	0.483	–	–	1.685	1.730	–	–	0.743	0.744	–	–

[a] θ state

$[\eta]^{\theta}_{MSH}$ values was, however, such that we considered it preferable to put, in the calculation of α_{η}^{3}, the value $[\eta]^{\theta}$ obtained from the MHS equation with $M_{\eta} = 2 \times 10^5$ and $K^{\theta} = 8 \times 10^{-4}$ dl g^{-1}. The $[\eta]^{\theta}_{MSH}$ values of polyurethanes A3, A4, B3 and B4 were measured, and those of other samples calculated approximately using $K^{\theta}_{A} = 1.2 \times 10^{-3}$ dl g^{-1} and $K^{\theta}_{B} = 1.1 \times 10^{-3}$ dl g^{-1}. These values are summarized in *Tables 2–4*, and the functions k_{MSH} *versus* α_{η}^{3} of individual samples are plotted in *Figures 1–3*.

It can be observed that the experimental points for polystyrene are approximated by a single convex curve, decreasing with increasing value of the expansion factor, while the experimental points for the polyurethanes suggest the existence of two curves. Systems with two-component toluene–isopropanol solvents (generally with isopropanol as the major component) and with some one-component solvents behave much like polystyrene (open circles); in the second group are systems with two-component solvents, containing a high proportion of toluene and those with the remaining one-component solvents (full circles). Because polystyrene is considered as a non-associating polymer, it can be assumed that the first group contains non-associating and the second associating systems.

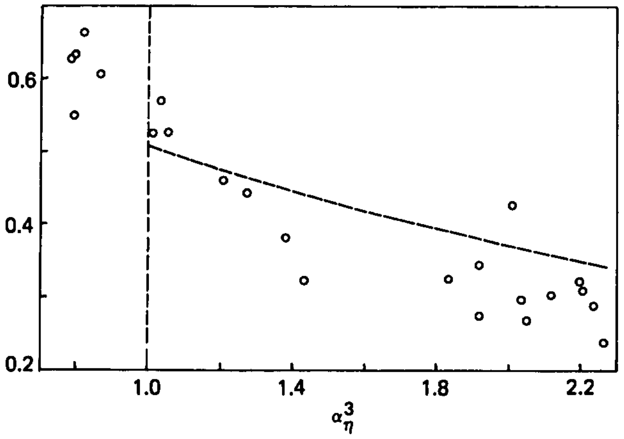

Figure 1 Dependence of the Huggins constant on the expansion factor for polystyrene. The broken curve is the theoretical curve according to Bohdanecký

As pointed out before, for quantitative evaluation of polymer–solvent systems it is necessary to know the relationship k' *versus* α_η^3. Therefore the equation used by Bohdanecký (equation (3)) was applied. Calculated curves are plotted as broken curves in *Figures 1–3*. The k_{MSH} values were calculated using the Stockmayer function $H(\alpha_s^3)$, putting $\alpha_\eta^3=\alpha_s^{2.4}$; the k^θ_{MSH} values were calculated by the least-squares method from the function $k_{MSH}\alpha_\eta^4$ *versus* $(\alpha_\eta^4-\alpha_\eta^2)$ plotted for individual polymers in *Figures 4* and *5*. The value $k^\theta_{MSH}=0.51$ obtained for polystyrene is in good agreement with the value of 0.5 given for example by Bohdanecký. The k^θ_{MSH} values for polyurethanes are summarized in *Table 5*. Because their variance was rather high, k^θ_{MSH} values for both series of samples were calculated by using all experimental results; the mean k^θ_{MSH} value of the A series was 0.66, and that of the B series 0.64.

As can be seen from *Figures 1–3*, experimental points are not satisfactorily approximated by the calculated

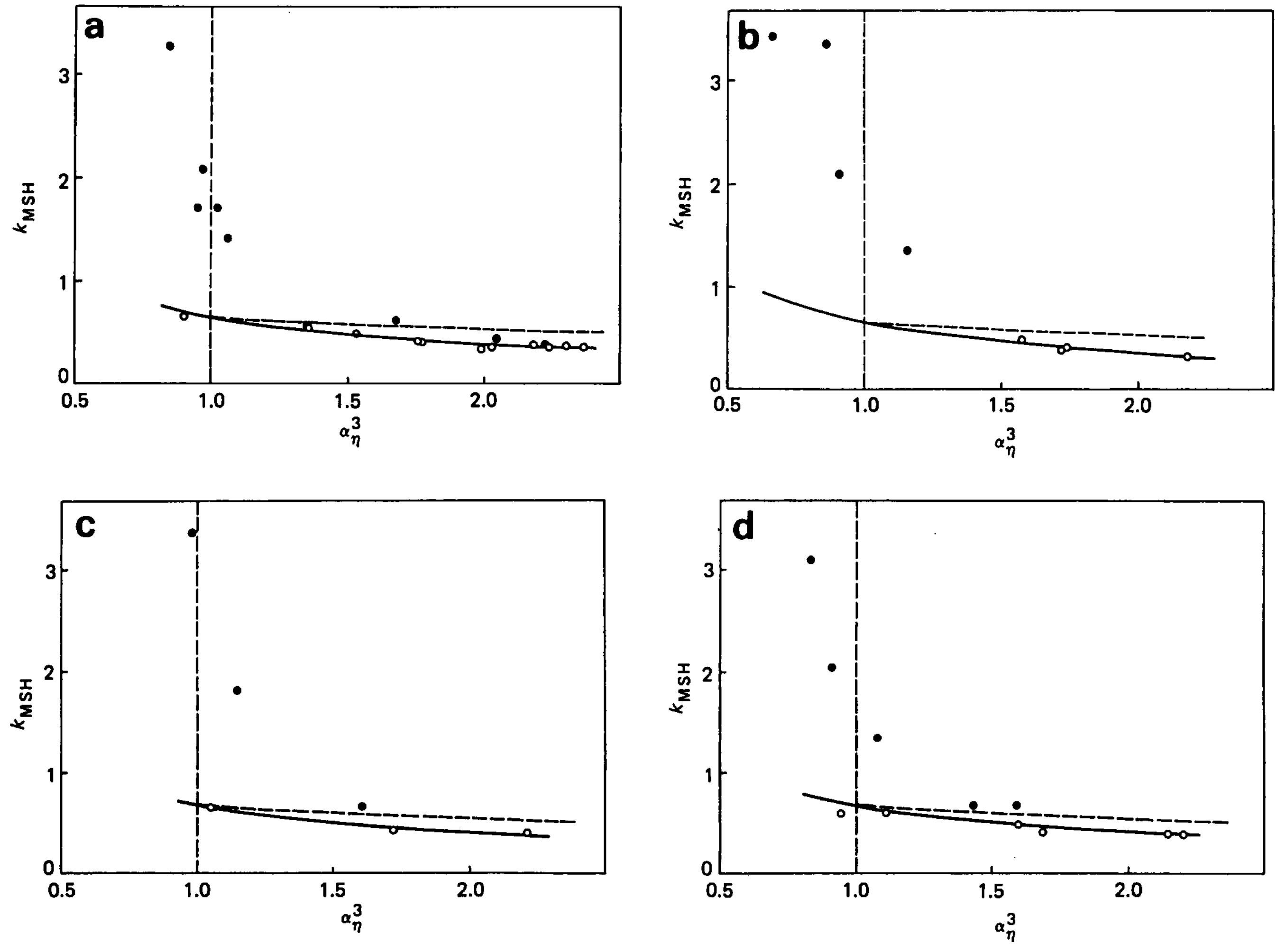

Figure 2 Dependence of the Huggins constant on the expansion factor for series A polyurethanes: (a) sample A1; (b) sample A2; (c) sample A3; (d) sample A4. The open circles are for non-associating systems, the full circles for associating systems, and the broken curves are theoretical curves according to Bohdanecký

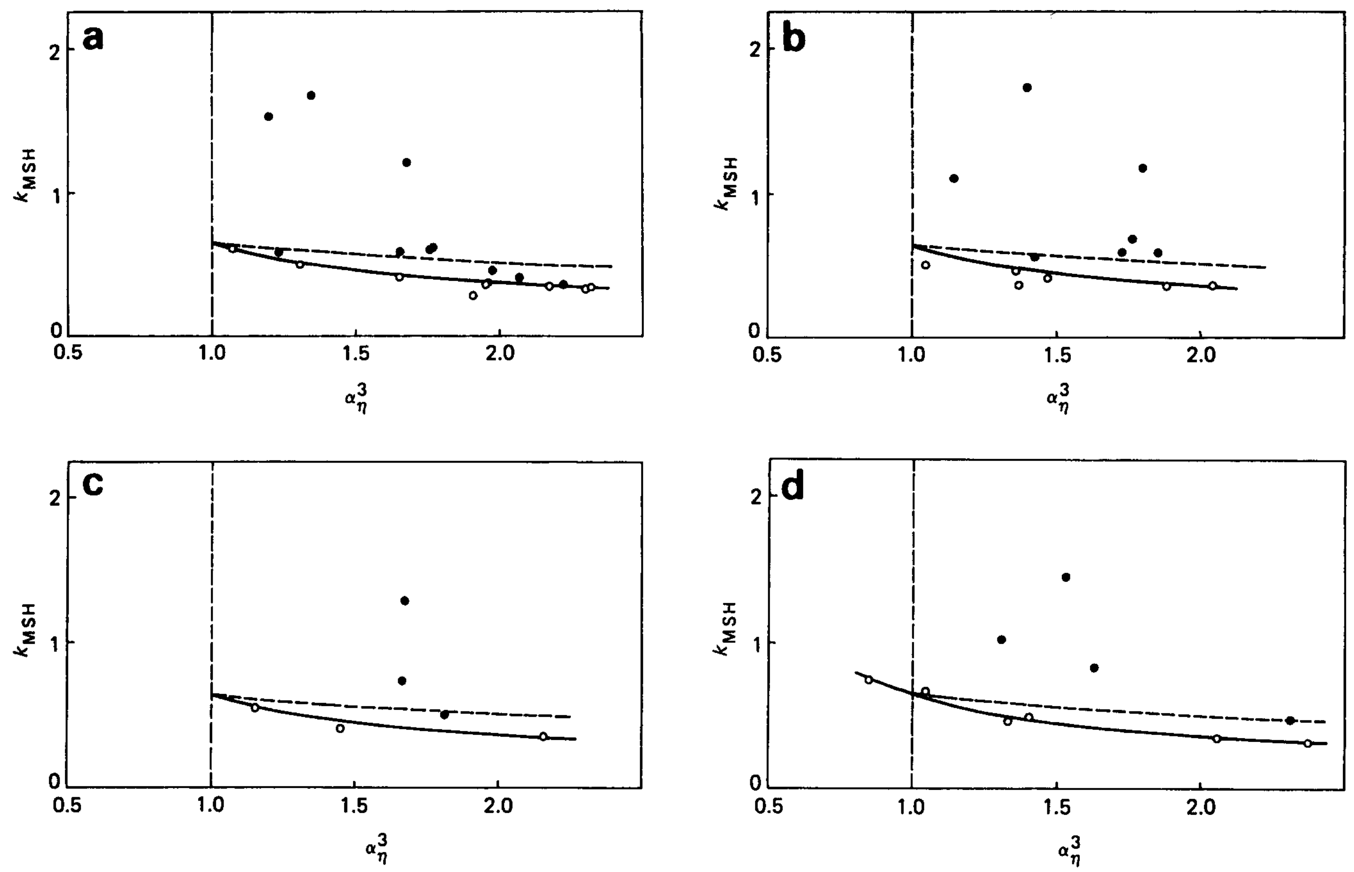

Figure 3 Dependence of the Huggins constant on the expansion factor for series B polyurethanes: (a) sample B1; (b) sample B2; (c) sample B3; (d) sample B4. Circles and broken curves as in *Figure 2*

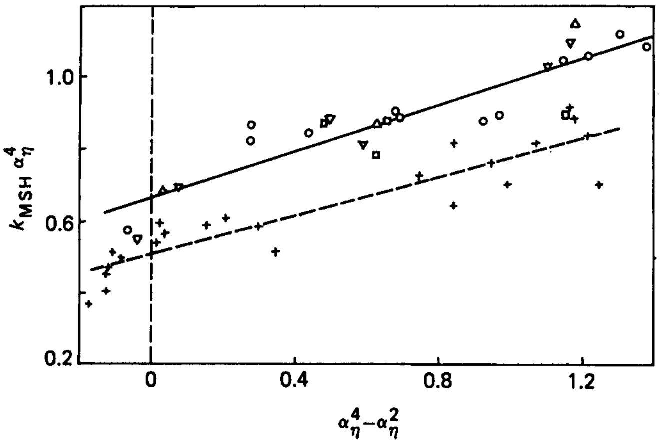

Figure 4 Plot of Imai relationship for series A polyurethanes: (○) sample A1; (□) sample A2; (△) sample A3; (▽) sample A4; (+) polystyrene; (-----) curve for polystyrene

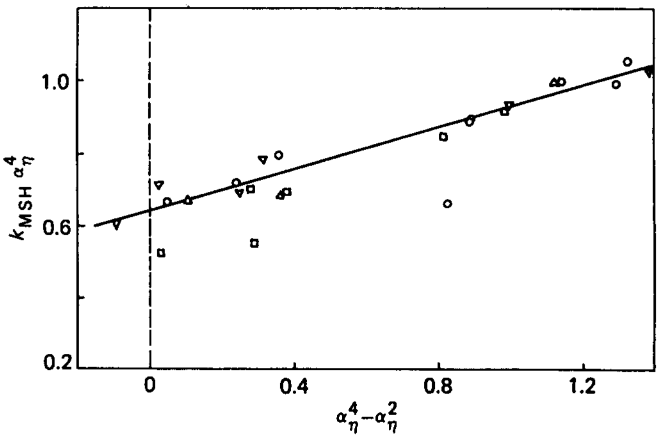

Figure 5 Plot of Imai relationship for series B polyurethanes: (○) sample B1; (□) sample B2; (△) sample B3; (▽) sample B4

curves, as with increasing expansion factor the decrease of experimental points is steeper. The equation proposed by Bohdanecký is thus not suitable for numerical evaluation of the extent of association. If sufficient data were available for non-associating systems to plot a curve and read the difference, graphical determination could be considered. Such experimental curves are plotted as full curves in *Figures 2* and *3*. Values of k_{MSHa} obtained by this method are given in *Table 5*.

Therefore it is difficult or almost impossible to use this method for a simple decision as to whether a given polymer–solvent system is or is not associating, particularly in the interval of k_{MSH} between 0.25 and 0.7, or to obtain a more accurate numerical evaluation of the association rate in obviously associating systems.

We have therefore attempted to choose another independent variable, namely the slope of Heller's equation. This value does not contain the intrinsic viscosity and is thus independent of the accurate concentration value of dilute solutions to be measured.

In *Figures 6–8* are plotted the k_{MSH} values of individual samples as a function of K'_{HE}. Experimental points for polystyrene can be approximated by a straight line, and those for polyurethanes again provide (like in the case of

Table 5 Values of $k^{\theta}_{\mathrm{MSH}}$, k_{MSHa} and k'_{MSHa} of associating systems for series A and B polyurethanes. Values of k_{MSHa} were determined from graphs, and values of k'_{MSHa} were calculated from equation (10) (with $b=1.21$)

Polymer	Solvent	$k^{\theta}_{\mathrm{MSH}}$	k_{MSHa}	k'_{MSHa}	Polymer	Solvent	$k^{\theta}_{\mathrm{MSH}}$	k_{MSHa}	k'_{MSHa}
A1	Toluene–isopropanol (80:20)		0.02	0.01	B1	Dimethylsulphoxide		0.05	0.03
	(85:15)		0.06	0.02		Toluene–isopropanol (90:10)		0.06	0.02
	(90:10)		0.17	0.05		Dioxane		0.09	0.02
	Cyclohexanone		0.80	0.28		Cyclohexanone		0.16	0.04
	Toluene–isopropanol (95:5)	0.69	1.03	0.28		Toluene–isopropanol (95:5)	0.64	0.19	0.04
	Dioxane		1.07	0.30		Tetrahydrofuran		0.22	0.05
	Tetrahydrofuran		1.42	0.48		Dichloromethane		0.80	0.31
	Dichloromethane		2.53	1.13		Toluene–isopropanal (97.5:2.5)		0.99	0.42
						2,2-Dichloroethane		1.20	0.54
A2	Dioxane		0.70	0.19	B2	Dimethylsulphoxide		0.09	0.02
	Cyclohexanone		1.39	0.42		Cyclohexanone		0.19	0.04
	Tetrahydrofuran	0.81	2.52	0.85		Tetrahydrofuran	0.52	0.21	0.04
	Dichloromethane		2.61	1.32		Dioxane		0.28	0.05
						Toluene–isopropanol (97.5:2.5)		0.55	0.11
						Dichloromethane		0.79	0.29
						1,2-Dichloroethane		1.26	0.58
A3	Dioxane		0.20	−0.01	B3	Dioxane		0.12	0.00
	Tetrahydrofuran	0.65	1.22	0.14		Tetrahydrofuran	0.61	0.33	0.15
	Dichloromethane		2.70	0.75		Dichloromethane		0.88	0.22
A4	Dioxane		0.17	0.06	B4	Dioxane		0.16	0.05
	Toluene–isopropanol (90:10)		0.20	0.06		Tetrahydrofuran		0.42	0.22
	(94:6)	0.62	0.72	0.22		Toluene–isopropanol (90:10)	0.67	0.53	0.27
	Tetrahydrofuran		1.33	0.48		Dichloromethane		1.01	0.60
	Dichloromethane		2.34	1.16					

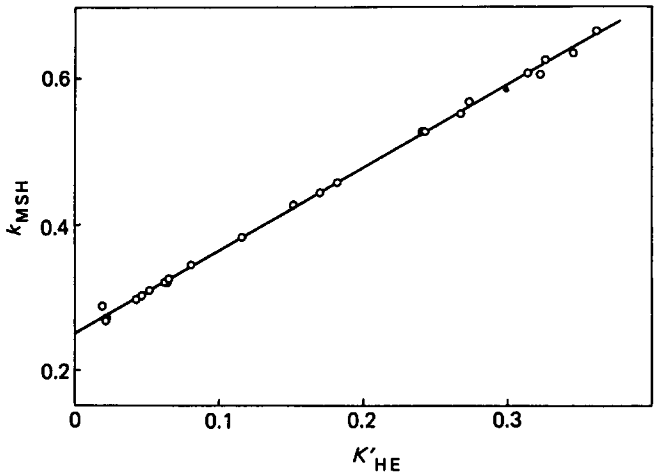

Figure 6 Dependence of the Huggins constant on the slope of the Heller relationship for polystyrene

Table 6 Values of constants a, b and c for the polymers investigated. Values of constants c in last two columns were calculated from equation (10) with $b=1.21$ and 1.14

Polymer		a	b	c	c^a	c^b
Polystyrene		0.249	0.136			
Polyurethane	A1	0.254	1.198	0.42	0.41	0.48
	A2	0.241	1.290	0.31	0.36	0.41
	A3	0.248	1.143	0.21	0.17	0.21
	A4	0.259	1.185	0.53	0.52	0.59
	B1	0.249	1.223	0.86	0.88	1.02
	B2	0.253	1.183	0.79	0.75	0.89
	B3	0.246	1.166	0.47	0.36	0.50
	B4	0.251	1.321	1.81	2.10	2.28

[a] Values calculated with $b=1.21$
[b] Values calculated with $b=1.14$

k_{MSH} *versus* α_{η}^{3}) two types of curves: straight lines (analogous to polystyrene) for non-associating systems (open circles) and convex curves for associating systems (full circles). The common starting point of the two functions is $K'_{\mathrm{HE}}=0$.

Linear relationships between k_{MSH} and K'_{HE} can be described by the equation:

$$y'=a'+b'x$$

where $y'=k_{\mathrm{MSHnass}}$, $x=K'_{\mathrm{HE}}$ and a', b' are constants, which can be calculated for each system by the least-squares method.

Experimental points characterizing the associating systems can be satisfactorily approximated by the quadratic function:

$$y=a+by+cx^2$$

where $y=k_{\mathrm{MSHass}}$ and a, b and c are constants.

Because the two curves have a common point on the y axis and the linear function is a tangent to the quadratic function at the point $x=0$, we can put

$$a=a'$$

$$b=b'$$

$$c=\frac{\bar{y}-a-b\bar{x}}{\bar{x}^2}$$

Values of the constants a, b and c are given for all polymers in *Table 6*.

Comparison of constants a and b for individual polyurethane samples suggests that they are not molecular-weight-dependent; the b value of the B4 sample, with a relatively high molecular weight, is,

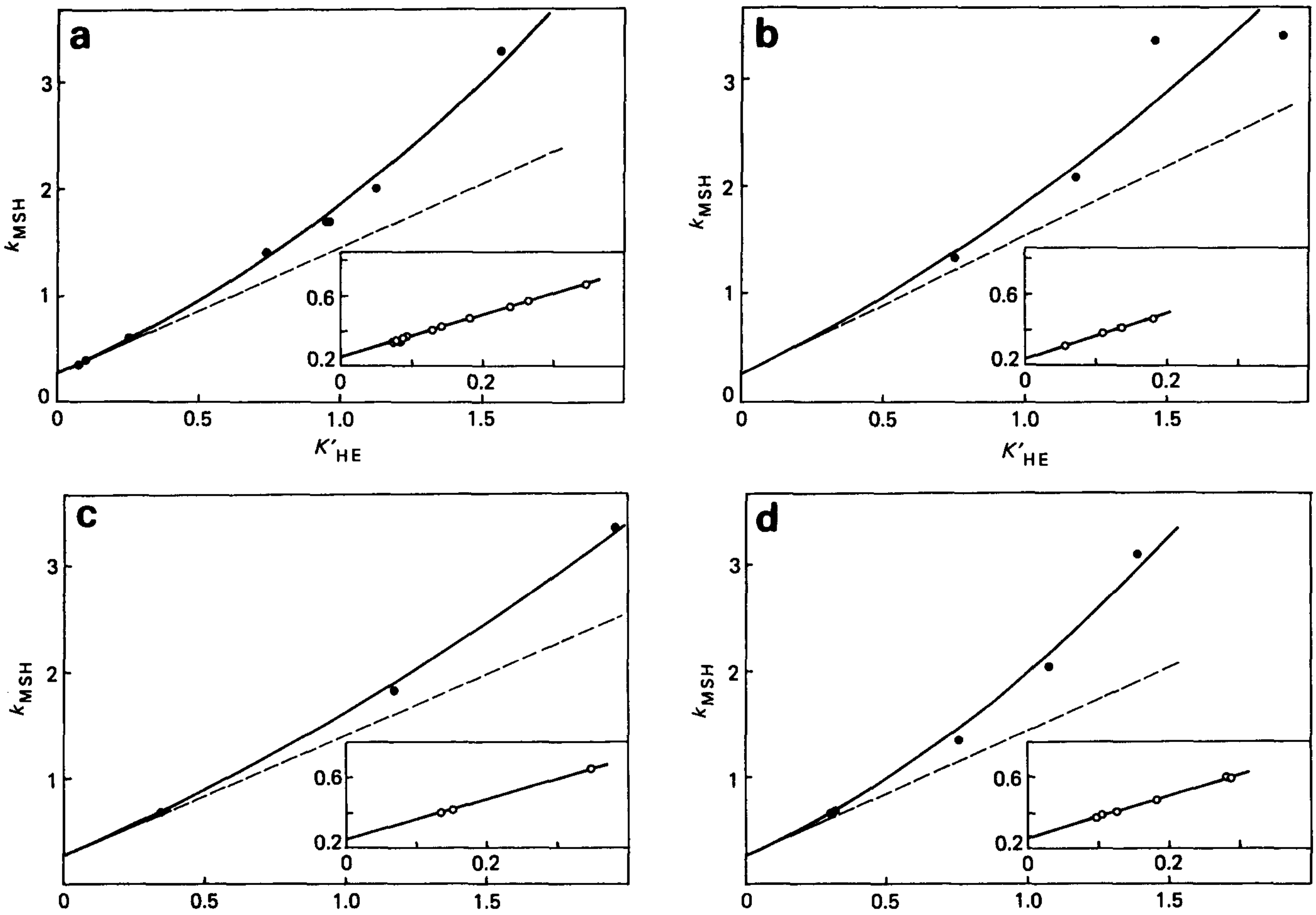

Figure 7 Dependence of the Huggins constant on the slope of the Heller relationship for series A polyurethanes: (a) sample A1; (b) sample A2; (c) sample A3; (d) sample A4. The open circles are for non-associating systems (enlarged insert), the full circles for associating systems. Curves of non-associating systems beyond the true region are plotted on the main figures as broken curves

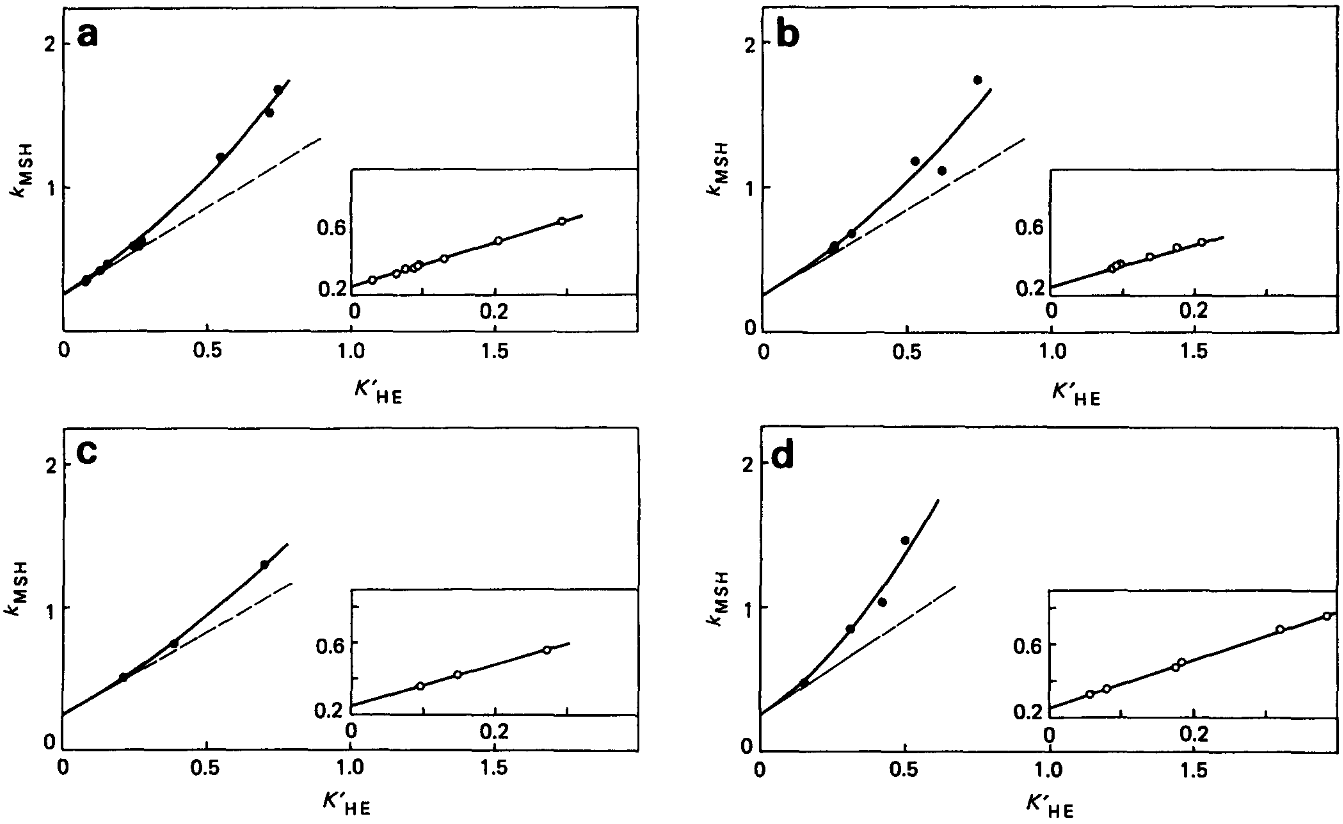

Figure 8 Dependence of the Huggins constant on the slope of the Heller relationship for series B polyurethanes: (a) sample B1; (b) sample B2; (c) sample B3; (d) sample B4. Comments on plots as in *Figure 7*

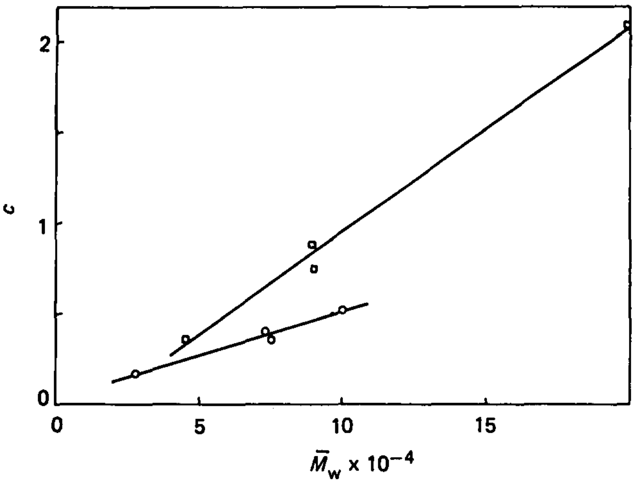

Figure 9 Dependence of the constant c on the molecular weight of polyurethanes: (○) series A polyurethanes; (□) series B polyurethanes

however, slightly higher. The mean value $\bar{a}$ for polyurethanes, 0.25, is in agreement with the respective value for polystyrene. The mean value $\bar{b}$ for polyurethanes is 1.214 (without the B4 sample, the mean value would be 1.198), which is slightly higher in comparison with that for polystyrene. This difference could be caused by effects such as mechanical 'entanglement' of chains (eventually increased by chain branching), formed easily during the preparation of polyurethanes. With increasing molecular weight, the effect of entanglement could become more pronounced, and this is a possible explanation for the higher value found for the B4 sample. For polymers with not very low molecular weight, this difference is, however, negligible, if we consider the contribution of the third term to the k_{MSHass} value.

The c values seem to be directly proportional to the molecular weight. In *Figure 9* are plotted the c values as a function of molecular weight for both series of polyurethanes. Experimental points give two straight lines. This suggests that the c value depends on both the total molecular weight of the polymer and the molecular weight of polyol, and thus on the relative length of soft segments. If we consider the value of the constant c to be a measure of the ability of a polymer to associate in its solutions, it can be expected that, with increasing molecular weight of the entire polymeric chain and especially of the polyol, associate formation will become easier.

This is, however, not in agreement with the results commonly presented for hydrolytic polyamides, probably due to different mechanisms of associate formation. In polyamides, associates are formed mostly by ionic end groups, while in polyurethanes they are formed by hydrogen bonding of hard segments. Then in systems with poor solvation of these segments (e.g. solutions in two-component solvents such as toluene–isopropanol with high proportion of toluene), intra- and intermolecular contacts are preferred. With increasing molecular weight, the probability of mutual contacts between macromolecules will be even higher; this effect will become still more pronounced with increasing molecular weight of polyols, due to better flexibility of polymeric chains. In the case of polyamides, with decreasing molecular weight the relative frequency of end groups, and thus the ability to associate, is increased.

The above results suggest that the dependence of k_{MSH} on the slope of Heller's equation for all non-associating systems of linear polymers can be described by a generalized equation:

$$k_{\mathrm{MSHnass}} = 0.25 + 1.14K'_{\mathrm{HE}} \qquad (8)$$

and for associating systems by the equation:

$$k_{\mathrm{MSHass}} = 0.25 + 1.14K'_{\mathrm{HE}} + cK'^{2}_{\mathrm{HE}} \qquad (9)$$

or

$$k_{\mathrm{MSHass}} = k_{\mathrm{MSHnass}} + cK'^{2}_{\mathrm{HE}} \qquad (10)$$

The product cK'^{2}_{HE} (or k'_{MSHa}) thus expresses the extent of association and the constant c the ability of a polymer to associate in a suitable solvent.

Calculated values of k'_{MSHa} are given in *Table 5*. Comparison with k_{MSHa} values shows good agreement as to expressing the extent of association, even if at higher K'_{HE} the numerical values of k'_{MSHa} are markedly lower than the k_{MSHa} values.

CONCLUSIONS

A method has been proposed for the evaluation of 'goodness' of the solvent in a given polymer solution from the Huggins constant, which is obtained from the dependence of k_{MSH} on the slope of Heller's equation. The method is based on the observation that the Martin–Staudinger–Heuer relationship, and particularly the value of the Huggins constant calculated, is more sensitive to the presence of supermolecular structures than is Heller's equation. The method is not time-consuming, requires only simple equipment and, in spite of being a kind of empirical artefact (i.e. dependence of k_{MSH} on k_{HE}), enables a relatively easy decision as to whether a system is or is not associating. Simultaneously the goodness of the solvent can be evaluated by the k_{MSH} value. In the case of associating systems the method enables a quantitative estimation of the degree of association from the k'_{MSHa} value as well as the ability of a given polymer to form supermolecular structures in suitable solvents from the c value.

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