Thermodynamic and hydrodynamic properties of the the systems polymer—tetrahydrofuran—water: 1. Solution properties of polystyrene

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Tetrahydrofuran (THF) is a solvent widely applied in polymer science and technology. However, because of its hygroscopic nature THF may often contain water considerably influencing the properties of the corresponding polymer solutions. In the first part of a series devoted to this problem, cloud point titrations and viscosity measurements were performed in the system polystyrene (PS)–THF–water. The limiting viscosity numbers of polystyrene considerably depended on the water content already in the domain of azeotropic composition, i.e. at about 4.5 vol.% of water. The constants of the Mark–Houwink equation, K and a were determined in pure THF and in mixtures containing up to 8.2 vol.% of water and compared with those for PS–THF found in the literature. The corresponding unperturbed dimensions were determined by various extrapolation procedures and were found to depend on solvent composition. Simultaneously, polymer-mixed solvent interaction parameters B were determined and discussed. Two theta compositions were observed: at about 7.7 vol.% of water for second virial coefficient $A_2 = 0$, and about 8.12 vol.% for $a = 0.5$. This agrees with the hypothesis of Dondos and Benoit and indicates the presence of preferential solvation in the system.

INTRODUCTION

Tetrahydrofuran (THF) is readily miscible with both polar and nonpolar liquids and dissolves many substances. Moreover, this solvent possesses both a low refractive index and viscosity, is transparent in the u.v. and visible region, and is fairly cheap. These properties make THF a popular solvent for low molecular substances and polymers. However, the solvent is very hygroscopic and absorbs moisture so that mixtures of THF and water are often used inadvertently instead of pure THF.

In this series we will discuss several effects of water present in THF on the properties of polymer solutions, starting with the system polystyrene–THF–water.

THF is a colourless liquid (b.p. 65.9°C at 760 mmHg) completely miscible with water at atmospheric pressure[1]. Thermodynamically the mixtures of THF and water are strongly non-ideal. The change of the excess free energy of mixing ΔG^E with the mixture composition is S-shaped with positive deviations in the region of low water concentration i.e. to about 40 mol.% of water[2–4]. Simultaneously, the system THF—water shows large positive deviations from Raoult's law and the excess molar volumes are negative over the whole composition range at 25°C[2,4,5]. THF forms an azeotrope with water; however, the literature data on its composition and boiling point differ considerably (*Table 1*). We adopt the mean value 5.1 wt % (4.5 vol.%) water.

It seems that the scatter of data on azeotrope composition in *Table 1* is mainly due to the lack of a precise method for water determination in THF.

In laboratory practice difficulties with moist THF are caused mainly by two facts:

(a) The boiling point of the azeotrope THF – water is very close to that of pure THF;

(b) THF rapidly absorbs moisture from air during its manipulation or storage in leaking vessels. The preferential evaporation of THF from mixtures of THF and water further increases the proportion of water in the solvent. The effects of absorption and preferential evaporation evidently depend on temperature, air humidity, time and exposed solvent surface.

Our preliminary refractometric experiments showed that the amount of water in originally dry THF reached about 2 wt.% under the following conditions: 15 g of solvent with surface 10 cm^2, relative humidity of air 50%, 22°C, time of exposure: 7 days.

Table 1 Literature data on composition of the azeotrope THF–water and its boiling point (760 mmHg, 0.1013 MPa)

Data	b.p.°C	Content of water wt.%
1 J. Matouš *et al.*[1]	–	4.5
2 R. Cigna and E. Sebastiani[2]	63.8	4.54
3 A. V. Shnitko and V. B. Kogan[5]	63.52	5.54
4 I. Yoshioka *et al.*[6]	63.4	4.5
5 J. A. Riddick[7]	63.4	6.7
6 Imperial Chem. Ind. Ltd.[8]	63	5

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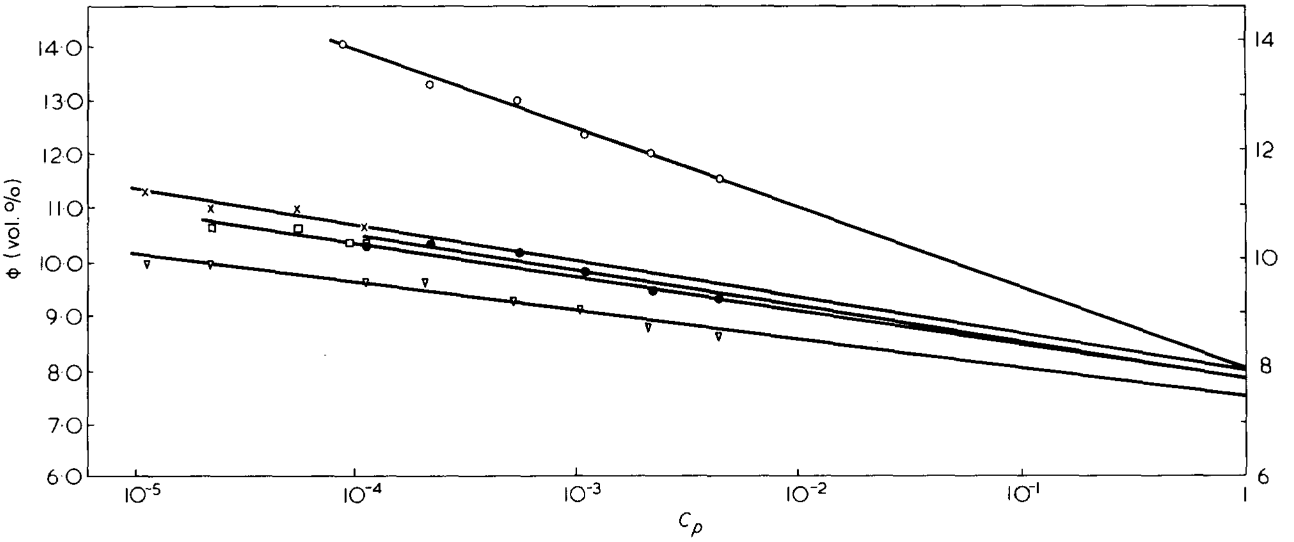

Figure 1 The dependence of volume percent of water ϕ, *versus* PS concentration c_p in the cloud point; THF, 298 K. ○, 6BPS; ×, 2.33×10^5; ●, F_1/II; □, 4.98×10^5; ▽, 1.2×10^6

EXPERIMENTAL

Solvents

Analytical grade tetrahydrofuran (VEB-Jenapharm, Laborchemie Apolda, G.D.R.) was successively stored over fresh $FeSO_4$ and KOH for several days, dried over metallic Na and then distilled. Contact of dry THF with the atmosphere was minimized and the solvent was used immediately after purification. Mixed solvents THF – water containing 7.7 and 8.2 vol.% of water before mixing were prepared by mixing appropriate amounts of an azeotropic mixture with distilled water.

Polymers

Narrow anionic polystyrenes from Pressure Chemical Co. (Pittsburgh, USA) with molecular masses $\bar{M}_w$ in the range of 3.7×10^4–2.0×10^6 and anionic polystyrene $M_{g.p.c.} = 1.2 \times 10^6$ from Centre de Recherches sur les Macromolécules, C.N.R.S. Strasbourg, France were used. In turbidimetric measurements fractions of radically polymerized PS were also applied[9]. Their g.p.c. molecular weights were 5.1×10^4 (6BPS) and 3.2×10^5 (F_1/II PS).

Turbidimetry

The theta composition of the mixture THF–water for PS at 25 ± 0.1°C was determined by cloud point titrations with an automatic turbidimeter[10]. The rate of water addition during titration was 0.1 cm^3/min. The starting volume of solution was 25 cm^3.

Viscometry

A dilution Ubbelohde viscometer modified according to Seide and Deckert[11] with a curved capillary was used. The diameter of capillary was chosen so that corrections for both the kinetic energy and the capillary curvature could be neglected.

Solutions were prepared so that their relative viscosities during measurement were between 1.1 and 1.8. Measurements were performed at 25°C. Triplicate extrapolation according to Heller[12] was used for data evaluation.

Table 2 Polystyrene viscosity data in THF–water mixtures $[\eta]$ in (cm^3/g)

	Solvent composition							
	THF		4.5		7.7		8.2	
$M \times 10^5$	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H	$[\eta]$	k_H
20.0	464	0.21	369	0.24	178	0.36	136	0.46
12.0	329	0.23	244	0.25	137	0.38	108	0.47
6.70	201	0.23	167	0.25	99	0.41	80	0.45
4.98	167	0.24	132	0.27	84	0.43	66	0.48
2.33	95	0.26	78	0.30	56	0.43	50	0.45
1.10	57	0.24	45	0.33	38.	0.45	33	0.49
0.51	32	0.28	27	0.35	25	0.49	23	0.53
0.37	25	0.29	–	–	–	–	–	–

RESULTS AND DISCUSSION

Turbidimetry

According to the original Elias' empirical method[13] the theta composition of a binary solvent –nonsolvent mixture ϕ_θ for a given polymer may be determined by extrapolation of a dependence: log of the volume fraction of nonsolvent ϕ *versus* log of polymer concentration c_p g/cm^3 in the cloud point, to the pure polymer, i.e. c_p = 1 g/cm^3.

Figure 1 shows the plot of ϕ vs. log c_p for several PS samples with the THF – water system. This modified Elias plot was theoretically substantiated[14,15]. We obtained a series of ϕ_θ values slightly increasing with decreasing PS molecular masses and ranging from 7.5 to 8.0 vol.% of water. A similar dependence of ϕ_θ on M was observed by Stasko and Elias[16] in the system narrow PS – benzene–methanol. The average value for ϕ_θ = 7.7 vol.% of water is considered in the following discussion.

Viscometry

Relation $[\eta]$ *–M.* Intrinsic viscosities $[\eta]$ were measured in four solvent systems, viz dry THF and mixtures of THF and water. The results are given in *Table 2.* The constants K and a of the corresponding Mark–Houwink equations were obtained by the least-square method:

Table 3 Mark–Houwink constants for the system PS–THF

Authors	t°C	K x 10^2 cm^3/g	*a*	Remarks
Kotera *et al.*[19]	25	2.84	0.64	
Pannell[20]	25	2.63	0.65	a,b,c,$\overline{M}$n
Ouano *et al.*[21]	30	2.89	0.65	a
Grubisic *et al.*[22a]	25	1.68	0.69	b
Grubisic *et al.*[22b]	25	1.622	0.694	a,b,d
Grubisic *et al.*[22c]	25	1.41	0.70	b
Subramaniam[23]	25	1.60	0.700	
Iwama *et al.*[24]	35	1.23	0.703	
Alliet and Pacco[25a]				
Provder and Rosen[25b]	25	1.51	0.706	a
Morris[26]	30	1.25	0.707	a
Park and Graessley[27]	25	1.25	0.713	a
Kolínský and Jančа[28]	25	1.17	0.717	a
	25	1.11	0.723	e
Kraus and Stacy[29]	25	1.251	0.717	a
Schulz and Baumann[30]	25		0.72	b
Lyngaae-Jorgensen[31]	25	1.14–1.22	0.72	a
Baijal and Kauppila[32]	25	1.09	0.723	
Smith[33]	30	1.112	0.723	a
Spatorico and Coulter[34]	25	1.11	0.725	f
Goedhart and Opschoor[35]	25	1.17	0.725	g
Lath[36]	25	1.01	0.729	a
Hattori *et al.*[37]	35	0.99	0.730	a
This paper	25	1.16	0.730	a
Ambler, McIntyre[38]	40	1.05	0.731	a
Meyerhoff[39]	25		0.74	
Williams *et al.*[40]	30	0.861	0.74	a
Boni *et al.*[41]	23	0.682	0.766	a, $\overline{M}$n
Samay[42]	25	0.609	0.768	a

a Commercial anionic polymers
b Anionic polymers
c Included data from reference 22
d Included data from reference 30
e Included data from reference 4a, 4c, 26, 30, 32 and 41
f Included only Beyer data quoted in references 34 and 30, 40
g Included data from reference 30
$\overline{M}$n Number-average molecular masses were considered

$$\text{THF} \quad [\eta] = 1.16_4 \times 10^{-2} M^{0.73_0} \tag{1}$$

$$4.5\%\ \text{of water}\ [\eta] = 1.32_1 \times 10^{-2} M^{0.70_4} \tag{2}$$

$$7.7\%\ \text{of water}\ [\eta] = 7.45_6 \times 10^{-2} M^{0.53_6} \tag{3}$$

$$8.2\%\ \text{of water}\ [\eta] = 11.9_7 \times 10^{-2} M^{0.48_5} \tag{4}$$

Surprisingly no Mark–Houwink constants for the system PS–THF are quoted in the 2nd edition of Polymer Handbook[17]. That is why we collected available literature data for this system in *Table 3* which shows considerable scatter of K and a values measured by different authors. This may be brought about e.g. by incorrect M values, (in some cases $\overline{M}_n$ instead of $\overline{M}_w$) or inappropriate (e.g. polydisperse) polymer samples. However, the majority of measurements was made with narrow anionic polystyrenes, mostly obtained from Pressure Chemical Co. On the other hand, viscometry is a simple and precise method and good agreement of the viscosity results was obtained with various polymer–solvent systems in a number of laboratories during investigation made by Division of Macromolecular Chemistry of the IUPAC[18]. That is why we believe that the presence of admixtures, e.g. stabilizers, peroxides, products of decomposition of THF but mainly water, are responsible for variation of the data in *Table 3*, especially for lower values of a. *Table 3* presents the Mark–Houwink constants for PS–THF at 23–40°C, however, no pronounced dependence of K and a constants on temperature was observed. Generally, the dependence of the viscosity on the water content in THF is expected to be different for each polymer. Thus the discrepancies in K and a for polystyrene may affect the precision of gel chromatographic results whenever universal calibration, i.e. the plot: $\log[\eta]M$ against elution volume based on PS data is used.

The dependence of $[\eta]$ on mixed solvent composition for various polymer molecular masses M is shown in *Figure 2*. As expected, the extent of both the absolute and the relative changes in $[\eta]$ with the water content increases with increasing M. $[\eta]$ seems to be almost independent of solvent composition at low water contents, and low molecular masses, but fairly steep decrease in $[\eta]$ with increasing water content can be observed already in the domain of mixtures containing ca. 2 vol.% water for $M > 2.5 \times 10^5$.

Unperturbed dimensions

The following extrapolation procedures were used for determinating unperturbed dimensions of PS in various mixtures of THF and water:

1. *Modified Stockmayer–Fixman plot*[43]

$$[\eta]/M^{1/2} = K_\theta + 0.346\,\Phi_0 BM^{1/2} \tag{5}$$

$$[\eta]/M^{1/2} = 1.05K_\theta + 0.287\,\Phi_0 BM^{1/2} \tag{6}$$

where K_θ is the constant from the Mark–Houwink equation in the theta solvent proportional to unperturbed dimensions, Φ_0 is the Flory constant equal to 2.87×10^{23} and B is the parameter characterizing the interaction of polymer and solvent. Equation 5 is valid if the data applied fit the inequality: $1 < [\eta]/K_\theta M^{1/2} < 1.6$, while equation 6 holds when the inequality: $1 < [\eta]/K_\theta M^{1/2} < 2.5$ is fulfilled.

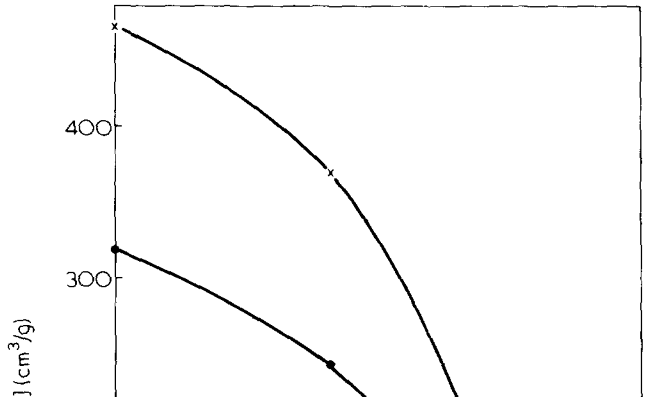

Figure 2 The change of limiting viscosity members $[\eta]$ of PS on THF – water solvent composition, for various molecular masses: +, 5.10×10^4; ▽, 1.10×10^5; □, 2.33×10^5; ○, 4.98×10^5; ▼, 6.70×10^5, ●, 1.20×10^6; x, 2.00×10^6

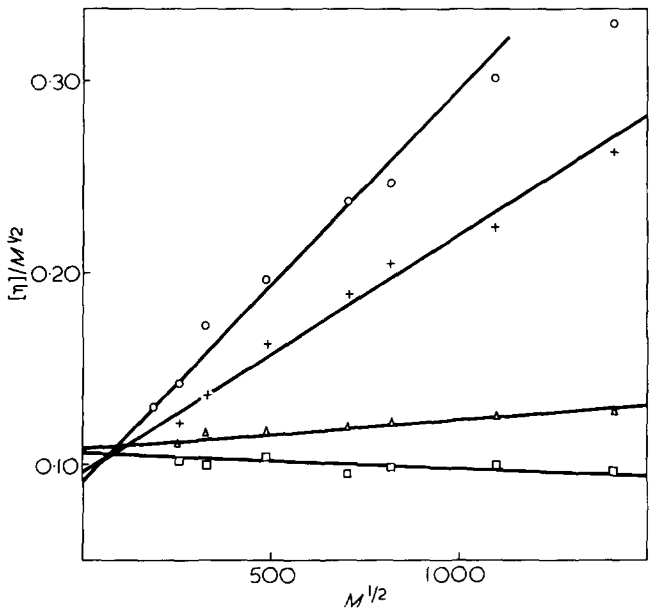

Figure 3 Modified Stockmayer–Fixman plots for PS in THF ○, and THF – water mixtures containing +, 4.5; △, 7.7 and □, 8.2 vol. % of water

In our case equation 6 was used for dry THF and for a mixture containing 4.5% of water while equation 5 could be employed for the remaining two mixtures. The application of equations 5 and 6 is represented in *Figure 3*.

2. *Berry plot*[44]

$$([\eta]/M^{1/2})^{1/2} = K_\theta^{1/2} + 0.42K_\theta^{1/2}\Phi_0 BM/[\eta] \qquad (7)$$

3. *Bohdanecký plot*[45] *modified by Cowie*[46]

$$[\eta]/M^{1/2} = \Phi_\epsilon/\Phi_0 K_\theta + 0.104\Phi_\epsilon K_\theta^{+3/10}\Phi_0^{-3/10}B^{7/10}M^{0.35} \qquad (8)$$

where

$$\Phi_\epsilon = \Phi_0(1 - 2.63\epsilon + 2.86\epsilon^2)$$

$$\epsilon = (2a - 1)/3$$

a is exponent in the Mark–Houwink equation.

All three extrapolation procedures gave practically the same values for K_θ and the results are collected in *Table 4*. It can be seen that the unperturbed dimensions of polystyrene increased with increasing content of water in the mixed solvent. The rise of the unperturbed dimensions as a consequence of the addition of nonsolvent was observed also by Elias and Etter[47] in the system PS/THF–methanol; these authors determined the value $K_\theta = 10.3 \times 10^{-2}$ for theta composition THF–methanol 71.3/28.7 vol/vol.

Dondos and Benoit[48] showed that the unperturbed dimensions of a polymer chain depended on the thermodynamic characteristics of the theta mixture used. An appropriate measure of the interaction between solvent components is the interaction parameter χ_{12} proportional to ΔG^E – the excess free energy of mixing. If $\chi_{12} > 0$, K_θ is larger, while for $\chi_{12} < 0$, K_θ is smaller than the value of unperturbed dimensions for the same polymer observed in a single θ-solvent at the same temperature. As mentioned earlier ΔG^E values of the system THF–water are positive in the region of low water concentration[1,3], resulting in an increase of K_θ in the mixed solvent in comparison with pure THF at the given temperature (*Table 4*).

Relations of K and a

Several authors[49–51] observed the following correlation between K and a from the Mark–Houwink equation

$$\log K = C - D/a \qquad (9)$$

where C and D are the constants for the given polymer. The validity of equation 9 was confirmed also for the systems PS–THF–water. We found that $C = -0.77$ and $D = 4.43$. These values differ slightly from the data published for polystyrene by Aharoni[51] who found $C = -1.14$ and $D = 3.97$. This difference can be explained by the solvent effect on unperturbed dimensions, which in our case causes the increase of these dimensions (*Table 4*).

The constant a was found to be an almost linear function of the composition of mixed solvent ϕ (in vol. %) in the vicinity of the θ point[52]. In the composition region: azeotropic mixture–theta mixture it holds

$$a = a_0 + a_1\phi \qquad (10)$$

with the constants $a_0 = 0.96$ and $a_1 = -0.57$. Equation 10 yields $a = 0.5$ for the composition of the θ-mixture for the system PS–THF–water at 25°C, with 8.12 vol.% of water, and similarly from equation 9, $K_\theta = 10.5 \times 10^{-2}$. This is in good agreement with the data obtained by extrapolation procedures (see *Table 4*).

Dondos and Benoit[53] found two theta points in several polymer–mixed solvent systems. At the first theta point (θ_{inter}) the second virial coefficient A_2 equals zero but $a > 0.5$ and at the second one (θ_{intra}) the polymer coil obeys Gaussian statistics ($a = 0.5$) but $A_2 < 0$. Dondos and Benoit[53] explained this phenomenon by preferential solvation effects which led to changes of the mixed solvent composition in the vicinity of the polymer chain. In the mixture, solvent and nonsolvent, macromolecules are usually preferentially solvated by solvent molecules. It means that the domains of polymer coils are enriched by solvent molecules compared with the bulk solvent. Thus the macromolecules may be in the perturbed state even if $A_2 = 0$. According to the above hypothesis the mixture of THF and water containing about 7.7% of water may be considered as θ_{inter} since in a number of systems at ϕ_θ the second virial coefficient measured by light scattering was zero[13]. The a value at this composition is 0.536. On the other hand, the mixture of THF and water contained 8.12% of water at $a = 0.5$ and may be considered as θ_{intra}.

However, the observed differences in theta compositions hardly exceed the experimental errors of their measurements and more precise data are needed for further discussion.

Table 4 Values K_θ obtained by graphical methods at different mixed solvent compositions

Solvent composition	$K_\theta \times 10^2$ Stockmayer–Fixman	Berry	Bohdanecký	Mean value
THF	8.57	8.32	8.35	8.41
4.5	9.14	9.00	9.21	9.12
7.7	10.8	11.2	11.1	11.0
8.2	10.6	10.6	10.7	10.6

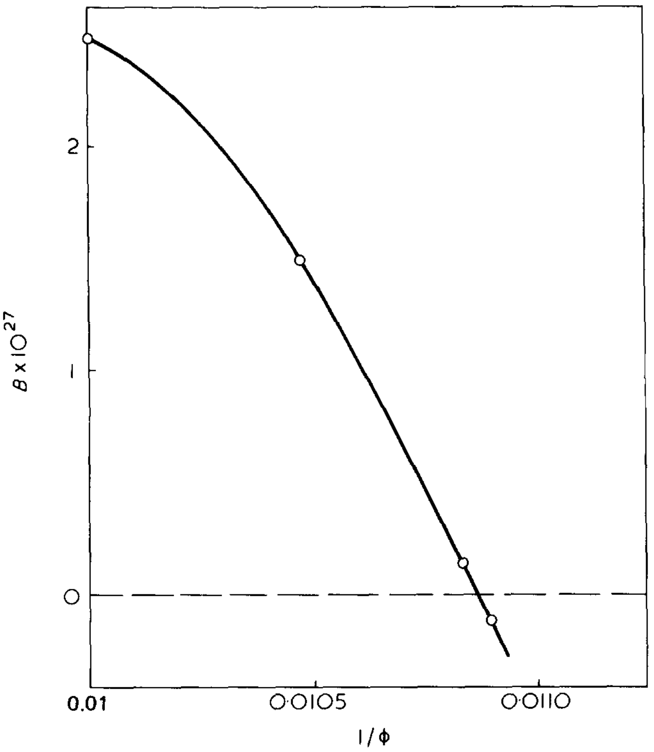

Figure 4 The dependence of interaction parameter B in the system PS–THF–water on the solvent composition (ϕ – vol.% of THF)

Interaction polymer – mixed solvent

The interaction of polystyrene with a mixed solvent THF–water can be described by the parameter B obtained from the slopes of the modified Stockmayer–Fixman plots (equations 5 and 6). *Figure 4* shows B as a function of solvent composition ϕ. The dependence can be considered linear up to azeotropic composition of the solvent in the first approximation. Since changes of temperature and composition are formally equivalent, this linear dependence of B on the composition can be used for estimating thermodynamic parameters of the system. Then it holds that

$$B = B_0(1 - \phi_\theta/\phi) \qquad (11)$$

where ϕ represents solvent composition in vol.% of THF, B_0 is proportional to the Flory parameter of the entropy of dilution and similarly $B_0\phi_\theta/\phi$ is proportional to the parameter of the enthalpy of dilution. The following values were obtained by the analysis of our experimental data according to equation 11, using the linear part in the vicinity of the θ-point: $B_0 = 4.22 \times 10^{-26}$ and $B_0\phi_\theta/\phi = 4.08 \times 10^{-26}$ for $\phi = 95$ vol.% THF. Both parameters are positive, but the entropic one exceeds the enthalpic and this situation favours dissolution of polystyrene in the mixed solvents studied. Increasing the content of THF in the mixture decreases the absolute value of the enthalpic parameter, i.e. it favours the dissolution of polymer.

Huggins constants

The slope of the dependence of η_{sp}/c, i.e. the Huggins constant k_H, is a function of the expansion coefficient α_η[54,55]

$$k_H\alpha_\eta^4 = k_H^0 + C_0(\alpha_\eta^4 - \alpha_\eta^2) \qquad (12)$$

The experimental data according to equation (12) are plotted in *Figure 5*. Expansion coefficients were calculated as $\alpha_\eta^3 = [\eta]/[\eta]_\theta$, where $[\eta]_\theta$ is the limiting viscosity number at the theta point (8.12 vol.% of water). The parameters k_H^0 and C_0 obtained from *Figure 5* are respectively 0.45 and 0.25 and are close to the values 0.46–0.55 for k_H^0, and 0.28–0.30 for C_0 published for a number of non-polar polymer–solvent systems[55].

CONCLUSIONS

On the basis of the above results and discussion we conclude that:

(i) the presence of a small amount of water does not significantly influence the thermodynamic properties of the system PS–THF. However, a pronounced decrease of the thermodynamic quality of the binary solvent for PS was observed at a water content higher than about 2 vol.%;

(ii) at water content in THF about 8 vol.% at 25°C the mixture behaves as a theta solvent for PS;

(iii) the compilation of Mark–Houwink constants for the system PS–THF from the literature (*Table 3*) showed their large scatter. This seems to be caused mainly by water and other admixtures present in THF;

(iv) unperturbed dimensions of PS in the solvent mixtures studied increased with increasing water content in the system; and

(v) analysis of the dependence of viscometric polymer–solvent parameters B on mixed solvent composition showed that the dissolution of PS in the THF–water mixture is caused by entropic effects that outweigh the unfavourable enthalpic contributions.

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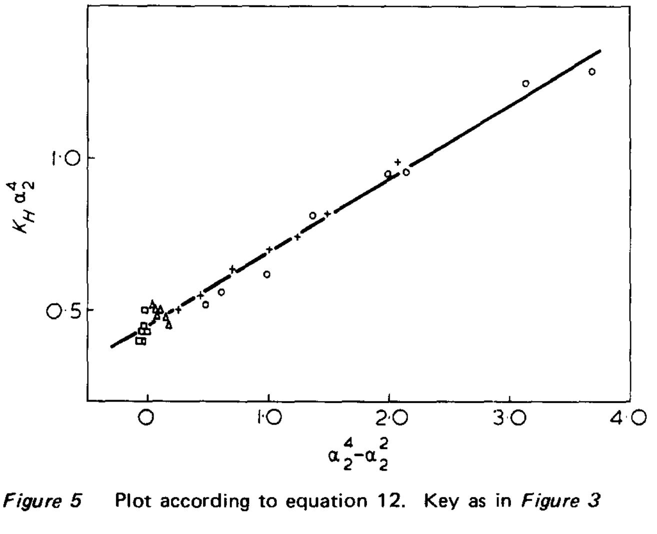

Figure 5 Plot according to equation 12. Key as in *Figure 3*

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