Viscometric behaviour of polystyrene in tetralin/cyclohexane mixtures

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For solutions of polystyrene ($M = 10^5$–10^6 g mol^{-1}), intrinsic viscosities $[\eta]$ have been measured at 34.5°C, which is the θ temperature for the polymer in cyclohexane. The solvents comprised cyclohexane in admixture with a thermodynamically good solvent, 1,2,3,4-tetrahydronaphthalene (tetralin, TET) over the whole range of solvent composition. From an assessment of several extrapolation procedures, a value of 85×10^{-3} ($\pm 1 \times 10^{-3}$) cm^3 g$^{-3/2}$ mol$^{1/2}$ was obtained for K_θ (in the relationship $[\eta] = K_\theta M^{1/2} \alpha^3$, where α is the expansion factor), thus yielding 0.681 Å g$^{-1/2}$ mol$^{1/2}$, 2.25 and 10.2 for the unperturbed dimensions, steric factor σ and characteristic ratio C_∞ respectively. The value of K_θ was independent of solvent composition despite the finite excess free energy of mixing for the solvent components alone, which has been asserted elsewhere to affect K_θ. The present results, in conjunction with previous ones relating to 98.4°C, indicate a value of -0.89×10^{-3} deg^{-1} for the temperature coefficient of the unperturbed dimensions.

Keywords Polystyrene; tetralin; cyclohexane; unperturbed dimensions; intrinsic viscosity; expansion factor

INTRODUCTION

Previous communications[1-3] have dealt with some solution properties of polystyrene (PS) in binary solvents at 98.4°C, which is the θ temperature for one of the solvent components used, 3-methyl-cyclohexanol. Because the other solvent component, 1,2,3,4-tetrahydronaphthalene (tetralin, TET), is a thermodynamically good solvent at this particular temperature, it was possible to introduce changes in overall solvent power and the chain expansion factor α by varying the composition of the mixed solvent.

In the present report we consider systems which also allow such changes to be effected[4], but which are experimentally more convenient, since 3-methyl-cyclohexanol is replaced by cyclohexane (CH) and the temperature reduced to the θ temperature for PS in CH, viz. 34.5°C. For brevity, the units of the viscosity constant K_θ are stated now as cm^3 g$^{-3/2}$ mol$^{1/2}$, but omitted hereafter.

EXPERIMENTAL

Materials

CH and TET were dried over sodium wire and distilled at atmospheric pressure. The PS samples of nominal polydispersity indices $\bar{M}_w/\bar{M}_n \leqslant 1.09$ were obtained from Polymer Laboratories Ltd, Church Stretton, Shropshire, UK. They are denoted here as PS1, PS2, PS3, PS4 and PS5, the quoted molar masses being 1.06×10^5, 2.94×10^5, 4.20×10^5, 6.40×10^5 and 9.60×10^5 g mol^{-1} respectively.

Procedures

Mixed solvents were made up volumetrically to volume fractions of CH (ϕ_{CH}) at 34.5°C of 0.20, 0.40, 0.60, 0.80 and 0.90. For these and the single solvents, densities ρ (g cm^{-3}) were measured dilatometrically to give:

at 20.0°C,
$$\rho = 0.9710 - 0.201\phi_{CH} + 7.31 \times 10^{-3}\phi_{CH}^2$$
at 34.5°C,
$$\rho = 0.9584 - 0.197\phi_{CH} + 1.68 \times 10^{-3}\phi_{CH}^2$$

Polymer solutions were prepared gravimetrically at 20°C and solution viscosity measured in an Ubbelohde dilution viscometer at 34.5°C. Concentrations of initial and subsequently diluted solutions were obtained via the density–composition relationships. Intrinsic viscosities $[\eta]$ and viscosity slope constants k were obtained via:

$$\eta_{sp}/c = [\eta] + k[\eta]^2 c \qquad (1)$$

RESULTS AND DISCUSSION

Viscosity slope constants

For the five PS samples in all the solvent media, experimental values of k are shown as data points in *Figure 1* as a function of α^3, where α^3 is given by equation (2) in which $[\eta]_\theta$ is the intrinsic viscosity of the sample measured in pure CH:

$$[\eta]/[\eta]_\theta = \alpha^3 \qquad (2)$$

The full curve represents the variation of k with α^3 according to least-squares fitting of the data. This curve is of similar form to the broken curve in *Figure 1*, which has been calculated from equation (3) due to Sakai[5]:

$$k_{calc} = 0.50 + \bar{v}_2/(2[\eta]) - 3(\alpha^2 - 1)/4\alpha^4 \qquad (3)$$

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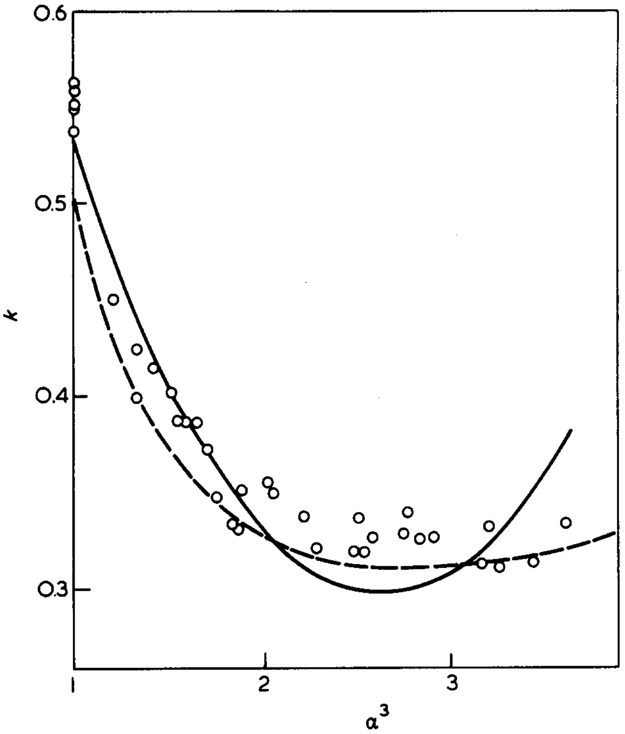

Figure 1 Variation of viscosity slope constant with solvent power, expressed as α^3. Open circles, experimental data points; full curve, according to least-squares analysis of experimental data; broken curve, slope constants calculated via equation (3)

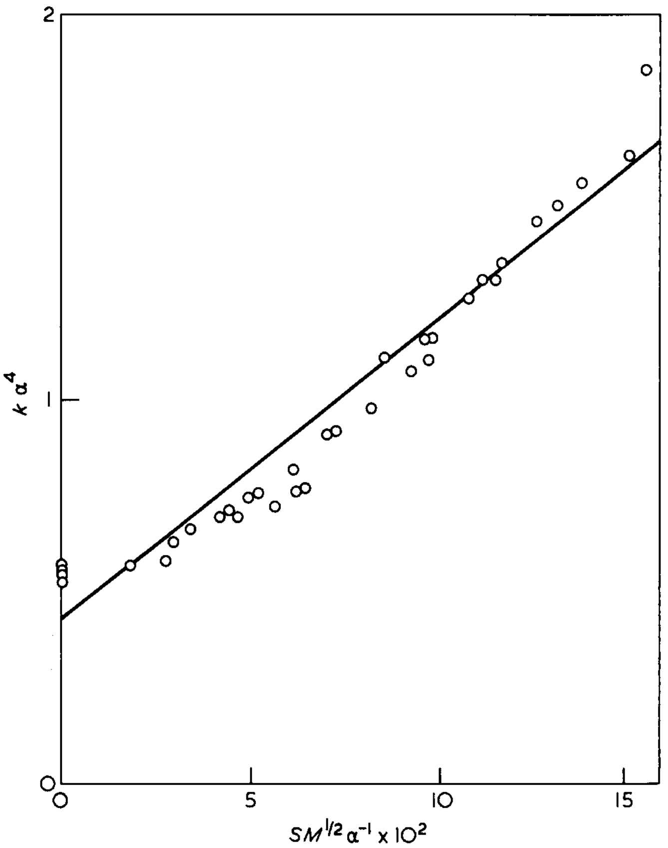

Figure 2 Plot according to equation (4)

Here $[\eta]$ has the same units as the partial specific volume of polymer in solution, $\bar{v}_2$. For the latter a literature value[6] of $0.9387\,\mathrm{cm}^3\,\mathrm{g}^{-1}$ relating to the specific volume of amorphous PS was used (see also refs 4 and 7). Equation (3) indicates that under θ conditions a unique value of 0.50 should hold for k (i.e. k_θ), which is exceeded only if $[\eta]$ is very small, i.e. at low M. In practice, the values of k_θ measured in CH were 0.54, 0.56, 0.56, 0.58 and 0.56 in order of increasing M. We have indicated previously[1] the restrictive nature of the plot due to Imai[8] in which k is correlated with α and proposed instead the following relationship:

$$k\alpha^4 = k_\theta + CSM^{1/2}\alpha^{-1} \qquad (4)$$

Here C is a factor which includes the unperturbed dimensions. Since (see later) the latter are independent of the composition of the binary solvents, C is constant. The factor S is the slope of the Stockmayer–Fixman plot[9] of $[\eta]M^{-1/2}$ *versus* $M^{1/2}$. This factor does depend on the nature of the solvent. The plot according to equation (4) is shown in *Figure 2*. Reasonably good linearity is seen to hold and the intercept represents $k_\theta = 0.43$.

Unperturbed dimensions

The values of $[\eta]$ for the five PS samples in each of the seven different solvent media are listed in *Table 1*. Mark–Houwink plots (equation (5)) are not reproduced here;

$$[\eta] = K_\mathrm{m}M^\nu \qquad (5)$$

but the derived values of the constants K_m and ν are listed also in *Table 1*.

Unperturbed dimensions are normally expressed as $(\langle r^2\rangle_0/M)^{1/2}$, where $\langle r^2\rangle_0$ is the mean square end-to-end distance in the unperturbed state. Under θ conditions, $K_\mathrm{m} = K_\theta$ and

$$K_\theta = \Phi_0(\langle r^2\rangle_0/M)^{3/2} \qquad (6)$$

where Φ_0 is the Flory constant. In CH the value of K_θ (or equivalently that of the unperturbed dimensions) is yielded directly from the Mark–Houwink plot. In the other solvents indirect methods were used to derive K_θ.

The main procedures utilize various plots involving $[\eta]$ and M and allow K_θ to be derived from the intercept, as indicated in *Table 2*, which gives also the references[9–18] to the appropriate equations. *Table 3* lists the resultant values of K_θ derived via these procedures. Procedure J differs somewhat from the others in the respect that the plot for it invokes values of K_m and ν for each of the solvents used. Consequently, only one value of K_θ is yielded, in contrast with the other methods which afford a K_θ for each solvent separately. Note also that for procedure J we have recast the complicated form of the ordinate in the original paper[18] to the simpler form[3] of $\log[2K_\mathrm{m}(1-\nu)]$.

Two other indirect procedures were used. Munk and Halbrook[19] have proposed equation (7) for calculating K_θ:

$$K_\theta = Q^{3/(4-2\nu)} \qquad (7)$$

where

$$Q = K_\mathrm{m}(\Phi_0^{(1-2\nu)/3})(N_0^{1/2}M/L)^{2\nu-1}$$

These workers postulated that there is no thermodynamic

Table 1 Intrinsic viscosities at 34.5°C for PS samples of different molecular weight* in TET/CH mixtures, and derived Mark–Houwink constants K_m and ν

Solvent		$[\eta]$ (cm^3 g^{-1})						
Designation	Composition (ϕ_{CH})	PS1	PS2	PS3	PS4	PS5	$K_m \times 10^3$ (cm^3 g^{-1})	ν
a	0.00	52.7	119	159	225	304	5.14	0.800
b	0.20	52.1	116	154	218	290	5.96	0.785
c	0.40	49.3	107	144	200	270	6.22	0.776
d	0.60	44.0	94.5	124	173	233	6.72	0.759
e	0.80	38.0	74.0	95.3	129	174	12.7	0.690
f	0.90	33.8	62.9	79.7	105	139	20.2	0.640
g	1.00	28.1	46.6	55.7	68.7	84.2	85.9	0.500

* For molecular weights of samples PS1–PS5, see the experimental section

Table 2 Extrapolation procedures used to determine K_θ via procedures A–J

Procedure	Ref.	Intercept on ordinate
A	9	K_θ
B	10	K_θ
C	11	K_θ
D	12	K_θ
E*	13	$[\Phi(\epsilon)/\Phi_0]K_\theta$
F	14	$K_\theta^{1/2}$
G	15	$K_\theta^{2/3}$
H	16	$0.786K_\theta^{4/5}$
I	17	$K_\theta^{2/3}$
J	18	$\log K_\theta$

* For formulation of the factor $\Phi(\epsilon)/\Phi_0$ see refs 3 and 13

interaction among macromolecular segments within a short section of chain with a characteristic number of segments N_0, estimated by them to be 9. The contour length parameter M/L was calculated [19] to be $4.14 \times 10^9\,\mathrm{g\,mol^{-1}\,cm^{-1}}$. These values, together with the K_m and ν for each solvent and the value of $\Phi_0 = 2.87 \times 10^{23}\,\mathrm{mol^{-1}}$ used by Munk and Halbrook, yield the values of K_θ by this procedure (indicated as procedure K in *Table 3*). We have also recast equation (7) into the following form[3]:

$$\log Q = [(4-2\nu)/3]\log K_\theta \tag{8}$$

The plot of $\log Q$ *versus* $(4-2\nu)/3$ should be linear, pass through the origin of axes and have a slope of $\log K_\theta$. The actual plot (not reproduced here) displayed considerable scatter, the value of K_θ via least-squares analysis being 74×10^{-3}, which is somewhat larger than the average of the calculated values for each solvent individually ($\sim 70 \times 10^{-3}$).

A somewhat related analysis by Munk and Gutierrez[20] yields:

$$K_\theta = [K_m(\Phi_0 l^3)^{-\varepsilon}]^{1/(1-\varepsilon)}F(\varepsilon) \tag{9}$$

where

$$F(\varepsilon) = 1 + 5.12\varepsilon + 13.3\varepsilon^2 + 38.0\varepsilon^3 - 640\varepsilon^4$$

and

$$\varepsilon = (2\nu - 1)/3$$

From the backbone carbon–carbon bond length and the average bond angle, these workers calculated the structural parameter l to be 2.45×10^{-10} cm dalton^{-1}. Using K_m and ν for each solvent, we have adopted this procedure to give the values of K_θ listed under procedure L in *Table 3*.

Graphs relating to all these methods are not given here. In general their form and the conclusions drawn from them are similar to those for the system TET/PS/3-methyl cyclohexanol at 98.4°C[3]. However, the following specific points warrant mention:

(1) Procedures A and G give constant K_θ at each ϕ_{CH}, but there is a slight downward curvature in the plots at the highest molecular weight.

(2) In procedure H the slight downward curvature occurs at low molecular weight, this deviation from linearity being less pronounced the poorer the solvent. However, although the linearity is excellent in the poor solvents, e–g, the values of K_θ in them are higher than those in the good solvents, a–d.

(3) Procedures B, C, D, F and I all give plots which intersect before the ordinate axis and hence values of K_θ

Table 3 Values of $10^3 \times K_\theta$ (in cm^3 g$^{-3/2}$ mol$^{1/2}$) derived from different procedures* for PS in mixed solvents† at 34.5°C

	Procedure											
Solvent	A	B	C	D	E	F	G	H	I	J	K	L
a	85	56	38	50	85	18	85	84	8.0	86	70	56
b	85	58	44	51	84	24	85	84	11		71	61
c	84	62	50	52	85	31	85	84	17		68	61
d	84	64	57	54	86	40	84	84	27		63	60
e	85	70	74	61	86	68	86	88	67		66	72
f	84	77	80	67	86	76	85	95	73		68	76
g	86	86	86	86	86	86	86	116	86		86	86

* For details of procedures, see references in *Table 2*

† For composition of solvents, see *Table 1*

which differ according to the solvent. In procedure C (*Figure 3*) the abscissa is $(M^{1/2} - \tilde{D}M)$, where the factor $\tilde{D}$ was assigned values of $1.2 \times 10^{-3}(v - 0.5)$ g$^{-1/2}$ mol$^{1/2}$ by Dondos and Benoit[11]. For previous systems[3] we observed upward curvature at the highest molecular weight, which was attributed to excessive reduction of $M^{1/2}$ by the factor $\tilde{D}M$ (when the exponent v within $\tilde{D}$ was greater than 0.80). However, for the present systems, v does not exceed 0.80 and hence the factor $\tilde{D}$ is not excessively large, perfect linearity being obtained.

(4) The actual plots for procedures D and E are the same. The different intercepts and K_θ values for each ϕ_{CH} in the former procedure, when corrected according to the procedure of Cowie[13], yield the constant K_θ values of procedure E.

(5) With regard to procedure L, Munk and Gutierrez[20] found that the K_θ obtained *via* equation (9) is dependent primarily on the chemical nature of the solvent. They found that aromatic solvents promoted high values of K_θ, these values remaining high provided that the content of non-aromatic solvent in the binary solvent mixture was relatively low. The systems studied by these workers were toluene/PS/CH (which contains an aromatic solvent) and ethyl acetate/PS/CH (which does not contain an aromatic solvent).

In the present work involving procedure L the values of K_θ are smaller the higher the content of aromatic solvent, TET (see *Table 3*). In fact the highest K_θ is that relating to zero content of TET, i.e. measured directly in CH. Although both TET and toluene are aromatic, the behaviour of the TET/PS/CH system agrees well with that of ethyl acetate/PS/CH but not with that of toluene/PS/CH. It would appear, therefore, that the postulated influence of solvent aromaticity is not relevant. Furthermore, the procedure is not wholly reliable, since it affords values of K_θ, which are significantly different from the correct, directly measured one (i.e. in CH).

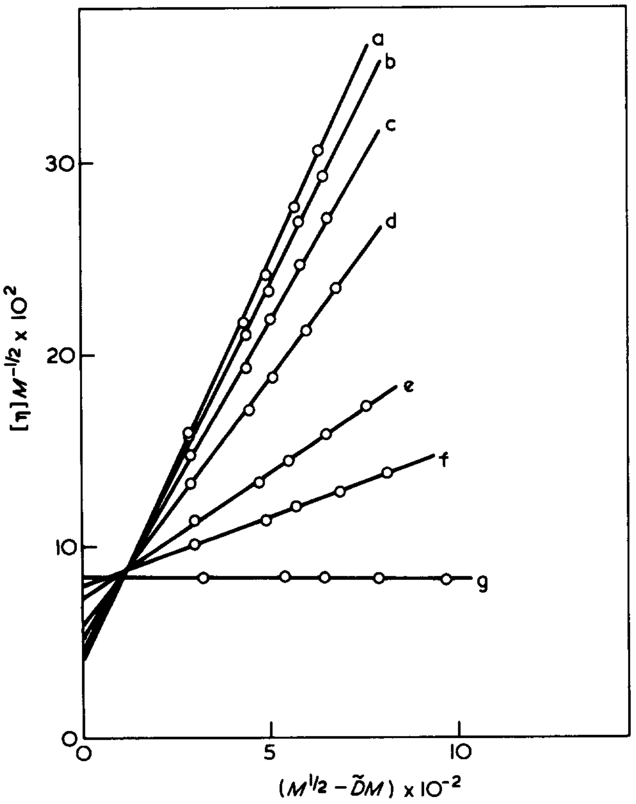

Figure 3 Extrapolation to determine K_θ via procedure C. For composition of solvents a–g, see *Table 1*

(6) As indicated before, procedure K affords values of K_θ which vary according to the solvent composition and are smaller than the correct value except for the value calculated for PS in CH.

Steric factors

Subject to an uncertainty of $\pm 1 \times 10^{-3}$ the present results indicate that $K_\theta = 85 \times 10^{-3}$ at 34.5°C. To obtain the unperturbed dimensions *via* this value and equation (6) necessitates the use of Φ_0. Commonly adopted values of 2.5×10^{23} and 2.87×10^{23} mol^{-1} for Φ_0 yield $(\langle r^2 \rangle_0/M)^{1/2} = 0.699$ Å g$^{-1/2}$ mol$^{1/2}$ and 0.668 Å g$^{-1/2}$ mol$^{1/2}$ respectively. Our experimental value[21] of $\Phi_0 = 2.71 \times 10^{23}$ mol^{-1} gives unperturbed dimensions of 0.681 Å g$^{-1/2}$ mol$^{1/2}$.

The chain steric factor σ is defined by:

$$\sigma = (\langle r^2 \rangle_0/M)^{1/2} / (\langle r^2 \rangle_{0f}/M)^{1/2} \tag{10}$$

Use of the value[22] 0.302 Å g$^{-1/2}$ mol$^{1/2}$ for the unperturbed dimensions of a freely rotating chain, $(\langle r^2 \rangle_{0f}/M)^{1/2}$, yields $\sigma = 2.25$. Chain flexibility can be expressed also in terms of the characteristic ratio C_∞:

$$C_\infty = (\langle r^2 \rangle_0/M)(M_0/2l_c^2) \tag{11}$$

In equation (11), M_0 is the molecular weight of the segment (= 104 g mol^{-1}) and l_c is the carbon–carbon bond length (= 1.54 Å). The resultant value of C_∞ is 10.2.

Literature values

We consider next literature values for PS solutions at about the same temperature (34°–35°C) as that used here.

From quoted values (Inagaki *et al.*[16]) of $[\eta]_\theta$ in CH for PS samples of $M = 0.22 \times 10^6$, 1.8×10^6 and 7.1×10^6, the corresponding K_θ values can be calculated to be 85 $\times 10^{-3}$, 87×10^{-3} and 80×10^{-3} respectively. From the quoted $[\eta]_\theta$ in CH for $M = 0.88 \times 10^6$ g mol^{-1} (Shultz and Flory[23]) the calculated K_θ is 82×10^{-3}. Krigbaum *et al.*[24] obtained values of K_θ within the range $(84–89) \times 10^{-3}$ from the viscosity of fractions of PS of different M in CH. These authors asserted their findings to represent remarkable constancy and that the slight increase in K_θ at very low M was within the overall experimental error. From an analysis of intrinsic viscosities in CH over a range of M, values of $K_\theta \times 10^3 = 79$, 78, 83, 85, 85 and 84 have been reported by Fox and Flory[25], Dondos and Benoit[26], Munk *et al.*[27], Berry[14], Zilliox *et al.*[28] and Bazuaye and Huglin[29]. A range of 84–89 with an overall mean of 87.7 was obtained by Fukuda *et al.*[30]

With regard to binary solvents the following values of $K_\theta \times 10^3$ have been reported at compositions corresponding to θ conditions: 82 (in dioxan/methanol[31]), 72 (in dioxan/isopropanol[31]), 71 (in benzene/isopropanol[31]), 83 (in carbon tetrachloride/n-heptane[31]), 94 (in benzene/cyclohexane[26]) and 74 (in 1-chlorodecane/3-methylcyclohexanol[29]). Other reported values in mixed solvents[19,31,32] relate to lower temperatures (20° and 25°C) and are not listed here.

Flory[22,33] has quoted $\sigma = 2.35 - 2.44$ and $C_\infty = 10$. Dondos and Benoit[26] report a slightly lower range of 2.2–2.34 for σ in single and mixed solvents.

Effective length of monomer unit

The effective hydrodynamic radius (R) of a polymer coil, which is swollen but impermeable to the rest of the solvent, has been expressed by Peterlin[34] as:

$$R = 1.1\{[\eta]M/(1-v)\}^{1/3} \tag{12}$$

(where R is in Å and $[\eta]$ in $\mathrm{cm^3\,g^{-1}}$). The Kirkwood–Riseman[35] theory gives equation (13) where Z is the degree of polymerization and b is the effective length of the monomer unit:

$$R = Z^{1/2}b \tag{13}$$

Using equations (12) and (13), values of b were calculated for each M and each ϕ_{CH}. Detailed results are not tabulated here, but the overall trend was as follows: (1) for a particular M an increase in solvent power leads to an increase in b; (2) for a particular ϕ_{CH} there is an increase in b with increasing M, this increase being most significant in good solvents (i.e. large v and small ϕ_{CH}); (3) in pure CH the value of b remains constant ($=6.2$ Å) at all molecular weights.

Diffusion and sedimentation experiments of Klenin and Ptitsyn[36] afforded values of b for PS in different single solvents for which $v = 0.50$, 0.66 and 0.74. The general changes of b with M and with solvent power were the same as observed here, although the value of b in the (unnamed) θ solvent was somewhat lower (5.5 Å). Apart from b under θ conditions the non-constancy of b is clearly attributable to neglect of excluded volume effects.

CONCLUSIONS

Despite a few reports[26,32,37] indicating a definite dependence of K_θ on the composition of binary solvents, the present work reinforces the growing body of evidence to the contrary. The value of K_θ measured directly in CH is certainly very close to most published values. Mixtures of CH and TET exhibit positive values for the excess free energy of mixing ΔG_{E}, the maximum ΔG_{E} being[21] $\sim 0.22\,\mathrm{kJ\,mol^{-1}}$ at $\phi_{\mathrm{CH}} = 0.50$. The influence of a finite (positive or negative) ΔG_{E} on K_θ has been proposed by Dondos and Benoit[26,32], e.g. for PS in a 50/30 (vol) mixture of benzene/CH, $K_\theta = 94 \times 10^{-3}$ and for these solvents a maximum ΔG_{E} of $\sim 0.30\,\mathrm{kJ\,mol^{-1}}$ obtains at this composition. This system and the present one both contain non-polar solvents, thus precluding any very pronounced specific solvent effects. Consequently, it appears that the proposal of Dondos and Benoit is not of universal application.

The present K_θ in conjunction with that previously found[3] for the higher temperature of 98.4°C gives a value of $-0.89 \times 10^{-3}\,\mathrm{deg^{-1}}$ for the temperature coefficient of the unperturbed dimensions, $\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$. The sign of this dependence is in accord with the conformational energy calculations of Flory *et al.*[38]

In view of the constancy of K_θ (and hence the unperturbed dimensions) at the particular temperature used here it was possible to apply equation (4). The linearity encompassing a variety of different molecular weights and solvent powers supports the application of this expression as a means of obtaining k_θ.

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