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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

Intrinsic Viscosity Relationships for Polystyrene[1]

BY T. G FOX, JR.,[2] AND P. J. FLORY

Intrinsic viscosities of polystyrene fractions ($M = 7.0 \times 10^4$ to 1.27×10^6) have been determined in various solvents at several temperatures. Critical miscibility temperatures Θ in the limit of infinite molecular weight were found to be 307 and 343°K. for polystyrene in cyclohexane and in ethylcyclohexane, respectively. From intrinsic viscosities measured in these solvents at temperatures equal to their respective Θ's, K in the equation $[\eta] = KM^{1/2}\alpha^3$ was found to be about 8.0×10^{-4} at 34° and about 7.3×10^{-4} at 70°. Present data, as well as other data from the literature, are well represented by the above equation in conjunction with the relationship $\alpha^5 - \alpha^3 = 2\psi_1 C_M(1 - \Theta/T)M^{1/2}$ where α is the factor representing the linear expansion of the polymer coil due to interactions. The entropy of dilution parameter ψ_1 has been found to be about 0.1 for the solvents with cyclic structures; ψ_1 for methyl ethyl ketone is about 0.01. The universal viscosity constant Φ in the relationship $K = \Phi(\overline{r_0^2}/M)^{3/2}$ has been calculated to be 2.1×10^{21} on the basis of data of Outer, Carr and Zimm on molecular dimensions of polystyrene in solution as deduced from the dissymmetry of scattered light. The root-mean-square distance $\sqrt{\overline{r_0^2}}$ separating the ends of a polystyrene chain in the absence of interactions of the polymer segments with their environment, apart from hindrances to free rotation, is calculated to be 730 Å. at 25° for a polystyrene of $M = 10^6$; the calculated distance for free rotation is 302 Å. In benzene, a good solvent, at 25°, $\alpha \cong 1.5$ and the root-mean-square distance between the ends of the chain is *ca.* 1100 Å. The polystyrene molecule appears to be more extended than is one of polyisobutylene having the same number of chain atoms.

Introduction

The results of the application of the theory of intramolecular interactions in dissolved polymer molecules to the interpretation of their intrinsic viscosities are summerized in the equations[3,4]

$$[\eta] = KM^{1/2}\alpha^3 \tag{1}$$

$$\alpha^5 - \alpha^3 = 2\,\psi_1 C_M(1 - \Theta/T)M^{1/2} \tag{2}$$

$$K = \Phi(\overline{r_0^2}/M)^{3/2} \tag{3}$$

$$\begin{aligned} C_M &= 27(2^{5/2}/\pi^{3/2}\mathrm{N})(\bar{v}^2/\mathrm{v}_1)(M/\overline{r_0^2})^{3/2} \\ &= 1.4 \times 10^{-24}\,(\bar{v}^2/\mathrm{v}_1)(\Phi/K) \end{aligned} \tag{4}$$

The various quantities appearing in these equations are defined in preceding papers.[4,5]

Equations (1) and (2) have been subjected to rigorous test in their application to precisely measured intrinsic viscosities of polyisobutylenes[6,7] over wide ranges in molecular weight and temperature and in a number of different solvents. The adequacy of these relationships has been confirmed and the various parameters have been evaluated. The present paper is concerned with the similar treatment of intrinsic viscosities of polystyrene, and with the deduction from such data of the ratio $\overline{r_0^2}/M$ characterizing the configuration of the chain, and the determination of the thermodynamic parameters Θ and ψ_1 for polystyrene in several solvents. Experimental data on the dependence of intrinsic viscosities of polystyrenes on molecular weight[8] and on solvent and temperature[9,10] have been reported by several investigators, and more recently the mean-square extension $\overline{r^2}$ of polystyrene chains has been obtained in various solvents through measurements on the angular dissymmetry of light scattered by dilute solutions.[10,11] For the successful application of equations (1) and (2), however, intrinsic viscosities at the temperature $T = \Theta$ are virtually required for reliable evaluation of K; this constitutes the first step in the determination of all other quantities appearing in the above equations. Such measurements have been carried out in the present investigation. With their aid, previously reported intrinsic viscosity data (and some additional results reported here) and results of chain dimension measurements are interpreted in the light of the relationships presented above.

Experimental

Materials.—Four polystyrenes were prepared by bulk polymerizations of styrene at 60° in the presence of benzoyl peroxide according to the method described elsewhere.[12] Details of the polymerizations are summarized in Table I. The polymers were fractionated by the addition of methanol to their dilute (1 to 2 g./100 cc.) solutions in methyl ethyl ketone at 30°.[12] Seven of the fractions were selected for the work reported here. The percentage of the corresponding whole polymer represented by each of these fractions, together with their viscosity-average molecular weights $\bar{M}$ are listed in Table I. The latter were calculated from the intrinsic viscosities in benzene using the relationship[8]

$$\log \bar{M}_v = (\log [\eta] + 4.013)/0.74 \tag{5}$$

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[1] This investigation was carried out at Cornell University in connection with the Government Research Program on Synthetic Rubber under contract with the Office of Rubber Reserve, Reconstruction Finance Corporation.

[2] Rohm and Haas Company, Inc., Philadelphia, Penna.

[3] P. J. Flory, *J. Chem. Phys.*, **17**, 303 (1949).

[4] P. J. Flory and T. G Fox, Jr., THIS JOURNAL, **73**, 1904 (1951).

[5] See also in this connection, P. J. Flory and W. R. Krigbaum, *J. Chem. Phys.*, **18**, 1086 (1950).

[6] T. G Fox, Jr., and P. J. Flory, *J. Phys. Colloid Chem.*, **53**, 197 (1949).

[7] T. G Fox, Jr., and P. J. Flory, THIS JOURNAL, **73**, 1909 (1951).

[8] R. H. Ewart and H. C. Tingey, Abstracts of papers presented at the 111th Meeting of the American Chemical Society, Atlantic City, N. J., April 14-18 (1947).

[9] L. H. Cragg and J. E. Simkins, *Can. J. Research*, **B27**, 961 (1949).

[10] F. D. Kunst, *Rec. trav. chim.*, **69**, 125 (1950).

[11] P. Outer, C. I. Carr and B. H. Zimm, *J. Chem. Phys.*, **18**, 830 (1950).

[12] T. G Fox, Jr., and P. J. Flory, THIS JOURNAL, **70**, 2384 (1948).

The solvents employed were of high purity and were freshly distilled before use.

Table I

Polystyrenes Used for Fractionation

Designation	Mole % peroxide	Mole % dodecyl mercaptan	Extent of reaction, %	$\overline{M}_v$
18A	0.006	0	14	800,000
14A[a]	0.04	0	26	350,000
11A[a]	0.5	0	22	150,000
3D[a]	1.0	0.055	28	45,000

Polystyrene Fractions Used in These Studies

Designation	Whole polymer. %	$\overline{M}_v$
18AF1B[b]	9	1,270,000
14AF1	12	540,000
18AF5	8	360,000
3DF2′	14	92,000
11AF4	13	89,000
3DF3′	19.5	70,000
3DF8	9	43,600

[a] The preparation and fractionation of polystyrenes 3D, 14A and 11A were described previously.[12] [b] This fraction was prepared by a refractionation of polystyrene fraction 18AF1.

Intrinsic Viscosity Determinations.—The solution viscosities were measured with a Ubbelohde No. 1 viscometer employing techniques which have been described in detail elsewhere.[7] Since the effect of the rate of shear on the observed specific viscosity η_{sp} should be small for polymers having intrinsic viscosities in the range of those used here, *i.e.*, for $[\eta] < 3$,[13] correction to zero rate of shear was not applied.

Determination of the Precipitation Temperatures.—Precipitation temperatures T_p were determined for solutions of polystyrene fractions by observing the temperatures at which the stirred solutions became turbid on slow cooling. The maximum temperature T_c for the co-existence of two phases was obtained within ±0.3° for each fraction in the chosen solvent from measurements at several concentrations in the vicinity of the theoretical critical volume fraction of polymer: $v_2(\text{crit.}) = 1/x^{1/2}$,[14] where $x = M\bar{v}/v_1$, *i.e.*, the ratio of the molar volumes for the polymer and solvent, respectively.

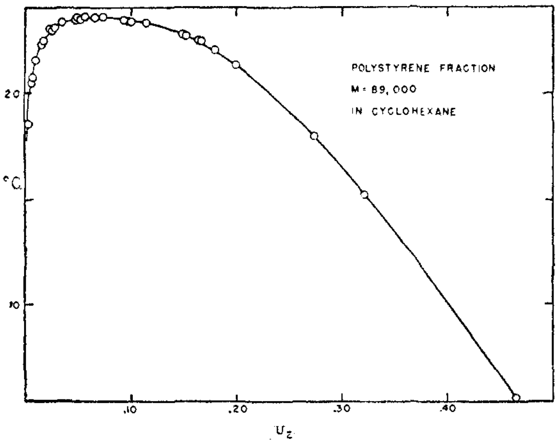

Fig. 1.—Precipitation temperature for polystyrene fraction M = 89,000 in cyclohexane against concentration expressed as volume fraction v_2 of polymer.

Results

Precipitation temperatures T_p for solutions of the polystyrene fraction of molecular weight 89,000 in cyclohexane are plotted in Fig. 1 against the volume fraction v_2 of polymer; the curve exhibits a maximum at a low value of v_2 as predicted by theory (see above). Values of T_c for cyclohexane and ethylcyclohexane plotted against $M^{-1/2}$ in Fig. 2 are represented by relationships of the form[7,14]

$$T_c = \Theta(1 - b/M^{1/2}) \qquad (6)$$

where Θ is the value of T_c at $M = \infty$; b, which according to the simple lattice theory of polymer solutions equals $2\sqrt{v_1/\bar{v}}$,[14] is treated as an empirical constant.[7] The intercepts give Θ's of 307 and 343°K. (34° and 70°), respectively, for cyclohexane and ethylcyclohexane.

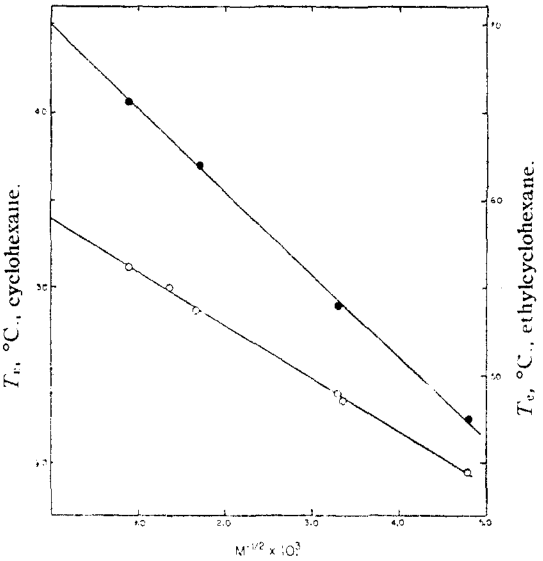

Fig. 2.—Critical miscibility temperature T_c *vs.* $M^{-1/2}$ for various polystyrene fractions in cyclohexane (lower line, left ordinate side) and in ethylcyclohexane (upper line, right ordinate scale).

Solution viscosities were measured at various concentrations on several polystyrene fractions in cyclohexane, ethylcyclohexane, toluene and benzene. The values of η_{sp}/c obtained in cyclohexane at 34° and in ethylcyclohexane at 70° are plotted against c in Fig. 3. The data are represented by straight lines corresponding to the equation[15]

$$\eta_{sp}/c = [\eta] + k[\eta]^2c \qquad (7)$$

where k is a constant for the polymer–solvent system at a given temperature. In the few cases where η_{sp}/c was determined at a single concentration only, corrections to $c = 0$ were made by means of equation (5) using the value of k established for other fractions in the same solvent at the same temperature. While no attempt was made to determine k accurately, the intrinsic viscosities determined by the extrapolations of η_{sp}/c to c =

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(13) T. G Fox, Jr., J. C. Fox and P. J. Flory, This Journal, **73**, 1901 (1951).

(14) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942).

(15) M. L. Huggins, This Journal, **64**, 2716 (1942).

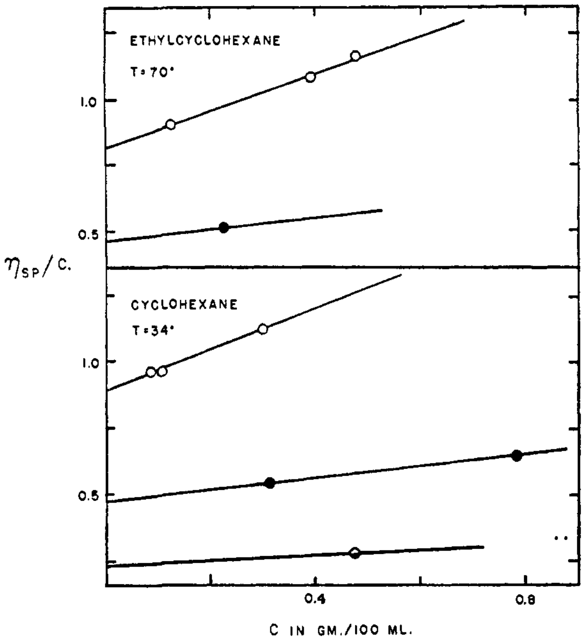

Fig. 3.—Viscosity–concentration data plotted as η_{sp}/c *vs.* c for polystyrene fractions in cyclohexane or ethylcyclohexane at 34 and 70°, respectively: O, M = 1,270,000; ●, M = 360,000; ⊖, M = 92,000.

0 are sufficiently precise (± 4%) for the present purpose. In benzene, where the value of k is known accurately, the precision is ± 1%. The results are summarized in Table II; values of [η] calculated by equations (1) and (2) using the parameters obtained in the following sections are included also.

TABLE II

INTRINSIC VISCOSITIES FOR POLYSTYRENE FRACTIONS IN VARIOUS SOLVENTS

Solvent	T, °C.	k (approx.)	[η] Obsd.	[η] Calcd.
18AF1B, M = 1,270,000				
Cyclohexane	34	1.0	0.89	0.90
	45	0.9	1.14	1.17
	55	0.45	1.43	1.41
Ethylcyclohexane	70	1.0	0.82	..
Benzene	30	0.38	3.20	3.18
	45	.38	3.17	3.14
	55	.38	3.13	3.12
Toluene	30	.38	2.92	2.72
14AF1, M = 540,000				
Benzene	30	0.38	1.68	1.71
Toluene	30	.38	1.48	1.48
18AF5, M = 360,000				
Cyclohexane	34	1.0	0.47	0.48
	45	0.9	.56	.56
	55	.45	.66	.66
Ethylcyclohexane	70	..	0.46	..
Benzene	30	0.38	1.26	1.28
Toluene	30	.38	1.21	1.11
3DF2′, M = 92,000				
Cyclohexane	34	..	0.23	0.24
	45	..	.25	.26
	55	..	.28	.29
Benzene	30	0.38	.455	.495
3DF3′, M = 70,000				
Benzene	30	0.38	0.38	0.41
Toluene	30	.38	.36	.37

Comparison of the intrinsic viscosities for the polystyrene fractions in toluene with the corresponding values in benzene leads, on the basis of equation (5), to the following intrinsic viscosity-molecular weight relationship for polystyrene in toluene at 30°.

$$\log \bar{M}_v = (\log [\eta] + 4.01/0.73) \quad (8)$$

For molecular weights of the order of 10^5 to 10^6 this equation is in close agreement with a similar relationship reported recently by Outer, *et al.*[11]

Calculations and Discussion

Evaluation of K.—As shown previously,[4,7] $K = [\eta]_{T=\Theta}/M^{1/2}$. Values of K computed from intrinsic viscosities of various fractions in cyclohexane and in ethylcyclohexane at temperatures equal to the Θ's for these two solvents are given in Table III. No dependence of K on molecular weight is indicated within the experimental error. The "best values" for $K \times 10^4$ at 34° and at 70° are 7.9 and 7.3, respectively.

TABLE III

CALCULATED VALUES OF K FOR POLYSTYRENE

Solvent	T, °C.	Mol. wt. of polymer fractn.	[η]	$K \times 10^4$
Cyclohexane	34	1,270,000	0.89	7.9
Cyclohexane	34	360,000	.47	7.8
Cyclohexane	34	92,000	.23	7.6
Ethylcyclohexane	70	1,270,000	.82	7.3
Ethylcyclohexane	70	360,000	.46	7.7

K at room temperature may be estimated from the recent data of Outer, *et al.*,[11] on intrinsic viscosity–molecular weight relationships for polystyrene in various solvents by the procedure previously outlined.[4] In Fig. 4 their results at 22 or 25° in methyl ethyl ketone, dichloroethane and in toluene are plotted in a manner suggested by

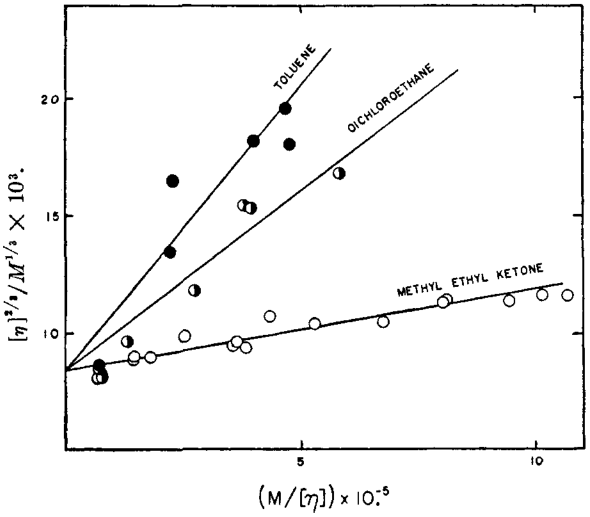

Fig. 4.—A plot of $[\eta]^{2/3}/M^{1/3}$ *vs.* $M/[\eta]$ from the data of Outer, *et al.*,[11] for polystyrene fractions in methyl ethyl ketone (O), in dichloroethane (◑), and in toluene (●) at 22 or 25°.

elimination of α from equations (1) and (2)[4]; although the experimental data show considerable scatter, they may, in conformity with theory, be represented by straight lines with a common intercept on the ordinate axis. The value of K corresponding to this intercept is 7.7×10^{-4} in good agreement with the results given above. It may be concluded that K for polystyrene at room temperature is about 8×10^{-4} and that it probably decreases slightly with increasing temperature.

Calculation of Φ.—Outer, Carr and Zimm[11] report molecular weights and mean-square end-to-end distances $\overline{r^2}$ for a number of polystyrene fractions, as determined from light scattering measurements in various solvents at several temperatures, together with the intrinsic viscosities in the same solvents. From these data Φ may be calculated, for according to equations (1) and (3)

$$\Phi = [\eta]M/\alpha^3(\overline{r_0^2})^{3/2} = [\eta]M/(\overline{r^2})^{3/2}$$

The data and calculated Φ's for several polystyrene fractions in six solvents and solvent mixtures are given in Table IV. There are no systematic variations in the computed values of Φ, except in the mixed solvents where Φ increases as the concentration of cyclohexane is increased. Averaging all of the results yields $\Phi = 2.0 \times 10^{21}$; excluding the data in the mixed solvents, the average is 2.2×10^{21}.

Table IV

Calculation of Φ for Polystyrene from the Data of Outer, Carr and Zimm

Polymer	T, °C.	$M \times 10^{-3}$	$[\eta]$	$\overline{r^2}^{1/2}$, Å.	Calcd. $\Phi \times 10^{-21}$
Methyl Ethyl Ketone					
A-1	22	1760	1.65	1070	2.37
B-2	22	1620	1.61	1015	2.49
B-2	67	1620	1.50	980	2.58
A-2	22	1320	1.40	900	2.53
(2-1-49)-2	25	980	1.21	840	2.00
A-3	22	940	1.17	750	2.61
A-6	22	520	0.77	545	2.47
(2-1-49)-1	25	318	0.60	475	1.78
A-7	22	230	0.53	400	1.90
Dichloroethane					
F-2	22	1780	2.60	1410	1.65
B-2	22	1620	2.78	1335	1.89
B-2	67	1620	2.83	1295	2.11
F-1	22	562	1.42	760	1.82
A-6	22	520	1.38	680	2.28
Toluene					
B-2	22	1620	3.45	1290	2.60
	67	1620	3.42	1280	2.64
Dichloroethane–Cyclohexane (65:35)					
B-2	22	1620	3.20	1580	1.31
	67	1620	3.50	1530	1.36
Dichloroethane–Cyclohexane (35:65)					
B-2	22	1620	2.80	1380	1.72
	67	1620	2.90	1360	1.86
Dichloroethane–Cyclohexane (6:94)					
B-2	22	1620	1.30	1000	2.11
	67	1620	2.25	1170	2.28

Debye and Bueche have reported[16] $(\overline{r^2})^{1/2} = 1110$ Å. for a polystyrene of $M = 10^6$ in benzene; using $[\eta] = 2.67$ as calculated by equation (5), this corresponds to $\Phi = 2.0 \times 10^{21}$. The average value of Φ calculated from the data of Kunst[10] for polystyrene in benzene and in mixtures of benzene with ethanol or heptane agrees with this value for Φ. However, there is some doubt as to the correct molecular weight of his polystyrene fraction since the value (6.5×10^5) calculated by equation (5) from the intrinsic viscosity in benzene is considerably lower than the molecular weight (1.1×10^6) determined by Kunst from light scattering measurements. On the other hand, Kunst's data on polyisobutylene solutions[10] suggest 2.1×10^{21} for Φ,[7] if the value of M for his polyisobutylene is calculated from its intrinsic viscosity in *n*-heptane.[7] Considering all presently available data the best value of Φ appears to be 2.1×10^{21}. A more satisfactory determination of Φ must await further accurate angular dissymmetry light scattering results in conjunction with intrinsic viscosities.

Dimensions of the Polystyrene Chain.—Assuming $\Phi = 2.1 \times 10^{21}$, values of $\overline{r_0^2}/M$ at 34 and 70° calculated from equation (3) and from the indicated values of K at these temperatures are 5.25×10^{17} and 4.94×10^{17}, respectively. To illustrate the significance of these figures, they correspond to root-mean-square end-to-end distances $\sqrt{\overline{r_0^2}}$ at $M = 10^6$ of 725 and 703 Å., respectively, in the absence of distortion arising from interactions of the segments with their environment (*i. e.*, interactions of the segments with solvent molecules and with other remotely connected segments). The root-mean-square distance calculated assuming free rotation (bond length 1.54 Å. and angle of 109.5°) is 302 Å. Thus, $\sqrt{\overline{r_0^2}}$ is about 2.35 times the free rotation value, compared with a ratio of 2.0 for polyisobutylene.[7] Similarly, the number of chain atoms per segment of the equivalent freely jointed chain is about eleven compared with eight for polyisobutylene.[7] The polystyrene chain is more highly extended than the latter; in both cases increasing the temperature has the effect of preferentially overcoming the barrier to free rotation in the direction of decreasing $\overline{r_0^2}$.

The actual dimensions of the coiled polymer chain in a given solvent will, of course, depend on the thermodynamic interactions with that solvent. For example, the value of $\sqrt{\overline{r^2}}$ for polystyrene of $M = 10^6$ in any one of several "good" solvents at room temperature has been reported[16] to be about 1100 Å. Thus the thermodynamic interactions in these cases increase the linear dimensions of the coiled polymer chain about 50%, *i.e.*, $\alpha \cong 1.5$.

Estimation of Thermodynamic Parameters.—Θ and $\psi_1 C_M$ have been calculated, using the procedure recommended previously,[4] for various solvent–polystyrene systems on which intrinsic viscosities have been measured at several temperatures. Assuming K to vary linearly with T with

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[16] P. Debye and A. M. Bueche, *J. Chem. Phys.*, **16**, 573 (1948).

the temperature coefficient indicated by the values assigned above for 34 and 70°, α's were calculated from the given intrinsic viscosities using equation (1). Then, $(K_T/K_{25})(\alpha^5 - \alpha^3)/M^{1/2}$ was plotted *vs.* $1/T$, where K_T and K_{25} are the values of K at T and at 25°. From the intercepts and slopes of such plots (see equations (2), (3) and (4)), $\psi_1 C_M$ and Θ were calculated in each case. Results are summarized in Table V. The molecular weights determined by Outer, *et al.*,[11] from light scattering measurements were employed in calculation of these quantities from their data; these molecular weights agree closely with the values calculated by equation (8) from the intrinsic viscosities in toluene which they report. The molecular weights reported by Cragg and Simkins[9] are from 10 to 35% higher than the values calculated from the intrinsic viscosities of their samples in toluene (see Table VI). In view of the close agreement between the intrinsic viscosity-molecular weight relationships reported by Ewart and Tingey[8] and by Zimm and co-workers,[11] we consider the molecular weights calculated from the intrinsic viscosities to be the more reliable. Hence, they have been used in the calculations of Θ and $\psi_1 C_M$ (Table V) from the viscosity data of Cragg and Simkins (see also Table VI) in preference to the osmotic molecular weights reported by them.

TABLE V

PRELIMINARY VALUES FOR THE THERMODYNAMIC INTERACTION PARAMETERS AT 25° FOR POLYSTYRENE IN VARIOUS SOLVENTS

Solvent[a]	Θ, °K.	100 $\psi_1 C_M$ at 25°	$\psi_1 C_M v_1$ at 25°	ψ_1	κ_1
Cyclohexane	307	0.35	0.38	0.13	0.13
Toluene[9,11]	160	.30	.32	.11	.06
Benzene	100	.29	.26	.09	.03
Dichloroethane[11]	190	.23	.18	.06	.038
Methyl ethyl ketone[11]	0	.02	.018	.006	0

[a] The parameters for cyclohexane and for benzene are derived from the results given in Table II of this paper. Others are derived from the data of the references given.

Intrinsic viscosities calculated from equations (1) and (2) using Θ and $\psi_1 C_M$ values from Table V and the above values of K (assumed to vary linearly with temperature) are given in the last column of Table II and in Table VI. Agreement with observed intrinsic viscosities is generally good. Discrepancies which appear can be shown to arise in part, at least, from random errors in the values reported for the intrinsic viscosities and molecular weights.

The value of 3.0 for $C_M v_1$ at 25° was calculated using equation (4) from $\overline{r_0^2}/M$ extrapolated to this temperature. The specific volume $\bar{v}$ of the polystyrene at 25° was taken to be 0.92 as calculated from the specific volume and expansion coefficient above the second order transition.[17] The values for ψ_1 given in the fifth column of Table V were computed from $\psi_1 C_M v_1$ in the preceding column and the above estimate of $C_M v_1$. The heat of mixing parameters κ_1 were calculated from the relationship $\kappa_1 = \psi_1 \Theta / T$. Absolute values of both

TABLE VI

PREVIOUSLY REPORTED INTRINSIC VISCOSITIES COMPARED WITH THOSE CALCULATED FROM THE PARAMETERS OF TABLE V

Solvent	Polymer designation	$M \times 10^{-3}$	T, °C.	[η] Obsd.	[η] Calcd.
Toluene[9]	F-3	975[a]	25	2.30	2.29
			35	2.29	2.29
			45	2.28	2.29
			55	2.29	2.28
			65	2.28	2.28
Toluene[9]	F-21	456[a]	25	1.32	1.32
			35	1.32	1.32
			45	1.32	1.31
			55	1.32	1.31
			65	1.30	1.31
Toluene[9]	F-35	144[a]	25	0.57	0.60
			35	.57	.60
			45	.56	.59
			55	.56	.59
			65	.57	.59
Toluene[9]	Unfractionated	604[a]	25	1.62	1.60
			35	1.62	1.60
			45	1.60	1.60
			55	1.59	1.60
			65	1.60	1.59
Toluene[11]	B-2	1620	22	3.45	3.25
	B-2	1620	67	3.42	3.25
	A-2	1320	22	2.78	2.80
	A-3	940	22	2.35	2.20
	A-7	230	22	1.01	0.83
	150-2	123	22	0.55	0.54
	J-1	3.3	25	0.047	0.056
Dichloroethane[11]	B-2	1620	22	2.78	2.62
	B-2	1620	67	2.83	2.66
	E-2	1780	22	2.60	2.79
	F-1	562	22	1.42	1.27
	A-6	520	22	1.38	1.19
	150-2	123	22	0.45	0.46
	C-1	16.1	22	.12	.13
	J-1	3.3	25	.045	.054
	D-1	3.08	22	.041	.051
Methyl ethyl ketone[11]	B-2	1620	22	1.61	1.59
	B-2	1620	67	1.50	1.47
	A-1	1760	22	1.65	1.69
	A-2	1320	22	1.40	1.40
	(2-1-49)-2	980	25	1.21	1.17
	A-3	940	22	1.17	1.14
	A-6	520	22	0.77	0.79
	(2-1-49)-1	318	25	.60	.58
	A-7	230	22	.53	.49
	150-2	123	22	.32	.34
	G-1	117	25	.32	.33
	(2-1-49)-3	114	25	.32	.32
	G-3	62	25	.24	.23
	H-1	23.7	25	.13	.14
	C-1	16.1	22	.11	.11
	H-3	14.6	25	.10	.11
	J-1	3.3	25	.043	.048
	D-1	3.08	22	.042	.047
	J-3	2.46	22	.036	.042
Benzene[13]	..	653[b]	25	1.95	1.96
			60	1.81	1.90

[a] The molecular weights of these polystyrenes were computed by equation (8) from their intrinsic viscosities in toluene at 30°. [b] The molecular weight of this polystyrene fraction was computed by equation (5) from the intrinsic viscosity given for benzene at 25°.

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(17) T. G Fox, Jr., and P. J. Flory, *J. Appl. Phys.*, **21**, 581 (1950).

ψ_1 and κ_1 given in Table V are subject to the uncertainty in C_M as evaluated from equation (4).[4]

In view of the inadequacy of our results on the dependence of K and of C_M on temperature, the uncertain accuracy of the intrinsic viscosities from the various sources of the data above, and the failure to correct to zero rate of shear (which may be important for the higher intrinsic viscosities), the ψ_1's and κ_1's given in Table V should be considered as provisional values only. Estimated uncertainties in ψ_1 and κ_1 are about 50%, aside from the absolute error which arises from the value of C_M. Likewise, the Θ's given may be incorrect by as much as ±50°, except in the case of the poor solvent, cyclohexane, where it is known within ±1°.

Notwithstanding the uncertainties in the results, definite conclusions are clearly indicated by the data of Table V. Thus the ψ_1's for the solvents possessing cyclic structures agree with each other within the experimental error and are in approximate agreement with the value of 0.15 obtained for polyisobutylene in the same solvents.[7] On the other hand, ψ_1's for methyl ethyl ketone and dichloroethane are lower, as were the ψ_1's for polyisobutylene in acyclic solvents. The κ_1 values are in qualitative agreement with predictions based on the cohesive energy densities of these solvents,[18] provided that the cohesive energy density of polystyrene is assumed to be equal to that for methyl ethyl ketone.

The low values found for the parameters for methyl ethyl ketone are in qualitative agreement with the osmotic results of Schick, Doty and Zimm.[19] They concluded, however, that the heat of dilution, though very small, is negative while the entropy of dilution is about zero, whereas our measurements lead to the conclusion that the heat is zero and the entropy, though unusually small, is nevertheless positive. Thus, methyl ethyl ketone appears to be a thermally neutral solvent for polystyrene; the small negative temperature coefficient of the intrinsic viscosity in this solvent we attribute to the decrease in K with temperature. It is a "configurationally poor" solvent as evidenced by the low magnitude of the intrinsic viscosity, which leads to the conclusion that ψ_1 is very low. Also in support of the low value of ψ_1 (in conjunction with a negligibly small heat of dilution) is the low value (0.58) found[11] for the exponent a in the empirical relationship $[\eta] = K'\bar{M}_v^a$ for this polymer-solvent combination.

Recent results of Bawn, Freeman and Kamaliddin[20] on vapor pressures of more concentrated solutions of polystyrene in toluene and methyl ethyl ketone show that the contrasting behavior of these solvents persists at high concentrations. Although neither shows a perceptible heat of mixing (*i. e.*, the activity is very nearly independent of temperature), the activity of methyl ethyl ketone is substantially greater than is that of toluene at the same concentration.

In order to arrive at more precise values for the parameters occurring in equations (1) and (2), the change in K with temperature should be established with greater certainty and viscosities should be determined over wide temperature ranges in each solvent. These latter determinations preferably should be made on polystyrene fractions of high molecular weight where corrections to zero shear rate doubtless will be required. The reliability of the absolute magnitudes of ψ_1 and κ_1 obtained in this manner depends on the validity of C_M as given by theory. This may be ascertained from independent determinations of ψ_1 and κ_1 through thermodynamic measurements on very dilute solutions.

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[18] M. Magat, *J. Chim. Phys.*, **46**, 23 (1949).

[19] M. J. Schick, P. Doty and B. H. Zimm, THIS JOURNAL, **72**, 530 (1950).

[20] C. E. H. Bawn, R. F. J. Freeman and A. R. Kamaliddin, *Trans. Faraday Soc.*, **46**, 677 (1950).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

The Racemization of Alkyl Hydrogen Sulfates in Sulfuric Acid[1]

BY N. C. DENO AND MELVIN S. NEWMAN

The racemization of *d-s*-butyl and *d*-pinacolyl hydrogen sulfates has been measured in several concentrations of sulfuric acid. The experimental results are best explained by an ionization (carbonium ion) mechanism.

The sulfation of *d*-2-butanol has been shown to yield mainly *d-s*-butyl hydrogen sulfate, which undergoes racemization in the sulfuric acid medium.[2] In order to obtain more evidence on the mechanism of this racemization, we have studied the behavior of *d-s*-butyl hydrogen sulfate in 45, 55 and 65% sulfuric acid solutions.

Three types of kinetic experiments were conducted at 25°. (A) Lithium *d-s*-butyl sulfate was added to excess 45% sulfuric acid, and the optical rotation of the solution was measured at intervals. (B) Barium *d-s*-butyl sulfate was added to excess 45, 55 or 65% sulfuric acid and shaken well to effect the conversion to barium sulfate and *s*-butyl hydrogen sulfate. The acid sulfate was then isolated as the barium salt and the specific rotation and per cent. recovery were determined. (C) Lithium *d-s*-butyl sulfate was dissolved in 58% acid and recovered. The optical activity in the recovered salt was determined. It must be emphasized that owing to experimental difficulties all three

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[2] N. C. Deno and M. S. Newman, THIS JOURNAL, **72**, 3852 (1950).