Because the functional form of these equations makes interpolation difficult and also because the equations deviate somewhat from the data near the normal boiling points, the data were further treated in the following way. A large-scale plot of log P *vs.* T^{-1} was constructed for each compound. These graphs showed a mild but definite curvature. These curves were approximately fitted by four straight lines which covered successive portions in such a manner that the entire range was included. An equation of the type $\log p = A - B/T$ then represented each straight line. The range of each equation and the parameters for these equations are listed in Table III.

TABLE III

RANGES AND PARAMETERS FOR THE EQUATION $\log p = A - B/T$

Pressure range, mm.	B	A	L_v, cal./mole
	α-Pinene		
3–15	2435	8.806	11,140
15–110	2210	8.089	10,110
110–215	2130	7.871	9,747
215–760	2072	7.712	9,482
	β-Pinene		
2–23	2270	8.120	10,390
23–50	2250	8.060	10,300
50–175	2210	7.947	10,110
175–760	2100	7.663	9,610

By use of these equations the average heat of vaporization for each range was calculated from the Clapeyron equation. These values are shown in Table III.

A study of the data indicates that the normal boiling points of α-pinene and β-pinene are 155.9 ± 0.1° and 166.0 ± 0.1°, respectively.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DUKE UNIVERSITY]

Statistical Mechanics of Dilute Polymer Solutions. VI. Thermodynamic Parameters for the System Polystyrene–Cyclohexane

BY W. R. KRIGBAUM

RECEIVED JANUARY 15, 1954

Accurate osmotic pressure measurements are reported for five polystyrene fractions, ranging in molecular weight from 5 × 10^4 to 2 × 10^5, in cyclohexane at 30, 40 and 50°. Evaluation of these data yields for the thermodynamic parameters Θ = 307.6°K. and ψ_1 = 0.36. Experimental values for the factor $F(X)$ appearing in the expression for the second virial coefficient confirm the previous conclusion that the $F(X)$ function deduced theoretically is only qualitatively correct. Such defects in the theoretical $F(X)$ function should not, however, vitiate the evaluation of the thermodynamic parameters at the Θ temperature, where the molecules assume random flight configurations and $F(X) = 1$. Although the Θ value stands in good agreement with that deduced from precipitation temperature measurements, the values obtained for the entropy parameter, ψ_1, from measurement of osmotic pressure, precipitation temperature and intrinsic viscosity are not in agreement, indicating the need for further revision of the existing theories of dilute polymer solutions.

The osmotic pressure of a dilute polymer solution may be expressed in virial form, *i.e.*

$$\pi = RT[A_1c + A_2c^2 + A_3c^3 + \ldots] \qquad (1)$$

where the first coefficient, A_1, is given by $1/\bar{M}_n$. Making use of the standard procedures for treating imperfect gases, a theoretical expression for the second virial coefficient

$$A_2 = (\bar{v}^2/V_1)(1 - \Theta/T)\,\psi_1\,F(X) \qquad (2)$$

was obtained[1-3] on representing each molecule by a Gaussian distribution of segments about its center of gravity. Here $\bar{v}$ and V_1 are the partial specific volume of polymer and the molar volume of solvent, respectively, Θ is the (absolute) temperature at which the second virial coefficient vanishes, and ψ_1 is the pair interaction entropy parameter.[2]

The function $F(X)$ occurring in equation 2 expresses the dependence of the second virial coefficient upon the average configuration of the individual polymer molecules; $F(X)$ depends upon the ratio, α, of the root-mean-square distance between the ends of the polymer coil to the corresponding dimension of the random flight counterpart. At the temperature Θ for which the second coefficient vanishes, the molecules assume their random flight configurations, hence $F(X) = 1$ at this unique temperature. The expression for the second virial coefficient given by the earlier statistical treatments of polymer solutions,[4,5] which disregarded the effects of molecular configuration on the long-range intramolecular interactions, differs from equation 2 through omission of the factor $F(X)$. The results of the two treatments therefore coincide only at the Θ temperature. In general, $F(X)$ depends upon the molecular weight, temperature and the thermodynamic parameters characterizing the polymer–solvent interaction; it is this factor which imparts to the second virial coefficient a dependence upon molecular weight and molecular weight heterogeneity. The dilute solution treatment has recently been extended to apply to ternary mixtures of two chemically-dissimilar polymers and a solvent.[6]

Turning now to a comparison of theory with the experimental evidence, the osmotic measurements of Bawn, Freeman and Kamaliddin,[7] and of Frank

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(1) P. J. Flory, *J. Chem. Phys.*, **17**, 1347 (1949).

(2) P. J. Flory and W. R. Krigbaum, *ibid.*, **18**, 1086 (1950).

(3) Equation 2 gives the second coefficient corresponding to concentration expressed in g./cc. For c in the units g./100 cc., $A_2 = 10^2(\bar{v}^2/V_1)(1 - \Theta/T)\psi_1 F(X)$.

(4) M. L. Huggins, *J. Phys. Chem.*, **46**, 151 (1942); *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942).

(5) P. J. Flory, *J. Chem. Phys.*, **10**, 51 (1942); **12**, 425 (1944).

(6) W. R. Krigbaum and P. J. Flory, *ibid.*, **20**, 873 (1952).

(7) C. Bawn, R. Freeman and A. Kamaliddin, *Trans. Faraday Soc.*, **46**, 862 (1950).

and Mark,[8] for polystyrene in toluene, as well as the light scattering investigation of Outer, Carr and Zimm[9] on polystyrene in dichloroethane and in butanone, demonstrate that A_2 decreases with molecular weight in approximate accord with theory. The predicted increase in A_2 with molecular weight heterogeneity also has been qualitatively confirmed.[7,10] Accurate osmotic pressure measurements reported in a previous paper of this series,[10] covering a twenty-fold molecular weight range for polystyrene in toluene and polyisobutylene in cyclohexane, revealed that the observed molecular weight dependence of the second virial coefficient, although in qualitative agreement with theory, was definitely larger than that predicted according to equation 2. This disagreement appeared to indicate that the theoretical $F(X)$ function varied too slowly with X.

The qualitative nature of the theoretical $F(X)$ function precludes, in general, the use of equation 2 for the precise evaluation of the thermodynamic parameters, ψ_1 and Θ, from dilute solution measurements yielding the temperature dependence of A_2. Nevertheless, these parameters may be evaluated from measurements performed in the vicinity of the Θ temperature, since at that temperature $F(X)$ reduces to unity. The temperature, Θ, at which the second virial coefficient vanishes is, of course, readily determined experimentally; ψ_1 may then be deduced from the limit of $A_2/(1 - \Theta/T)$ evaluated at $T = \Theta$. In addition to the thermodynamic parameters, experimental values for the function $F(X)$ in the neighborhood of $X = 0$ also could be calculated from such measurements.

At present there exists only one set of data, the osmotic measurements for four polyisobutylene fractions in benzene at three temperatures near Θ,[11] suitable for the evaluation of the thermodynamic parameters, ψ_1 and Θ, and the experimental $F(X)$ function by this method. The $F(X)$ values deduced from these data, although exhibiting some scatter, appear to confirm the previous conclusion that the theoretical $F(X)$ function varies too slowly with X. On comparing the values for the thermodynamic parameters deduced from the second virial coefficient with those obtained for the same system by independent measurement of the precipitation temperature and the intrinsic viscosity, the Θ values were found to be in good agreement; however, a considerable disagreement in the ψ_1 values was evident. In particular, the value for the entropy parameter obtained from the osmotic data was twice that reported by Fox and Flory[12] from intrinsic viscosity, but only half that deduced from precipitation temperature measurements. The disparity observed between the ψ_1 values obtained from intrinsic viscosity and from the second virial coefficient was not surprising; the possibility that ψ_1 values obtained from intrinsic viscosity measurements might be in error by a constant factor had been foreseen.[13] However, the disagreement between the values obtained from precipitation temperature and from the second virial coefficient was quite unexpected, in view of the fact that both measurements are carried out at (or near) the Θ temperature, where earlier theories should apply.

In order to investigate the aforementioned points more thoroughly, osmotic pressure measurements are reported here for five polystyrene fractions, ranging in molecular weight from 5×10^4 to 6×10^5, in cyclohexane at temperatures of 30, 40 and 50°.

Experimental

Details of the experimental procedure have been reported previously.[11] The five polystyrene fractions employed were selected from those obtained by a multi-stage fractionation.[10] The solvent, reagent grade cyclohexane, was distilled shortly before the solutions were prepared (cor. b.p. 80.3–80.6°). Since some of these solutions exhibited phase separation at room temperature, the volumetric flasks containing the solutions were stored in the 40° bath until needed. The solutions were diluted to volume at 40°, corrections to the concentrations being applied for the volume changes at 30 and 50°. Densities of these dilute solutions were assumed to be equal to those of the solvent at the three temperatures: $\rho_{30} = 0.769$, $\rho_{40} = 0.759$ and $\rho_{50} = 0.750$ g./cc.

Results

The π/c ratios for four of the fractions are shown plotted against concentration in Fig. 1. These data exhibit negligible curvature, except those for fractions M2−2 and H1−4 at 50°. This, of course, is a consequence of the fact that the experiments were performed near the Θ temperature, where higher virial coefficients vanish. The data were fitted as before[10,11] to the equation

$$\pi/c = (\pi/c)_0 \, [1 + \Gamma_2 c + g(\Gamma_2 c)^2] \qquad (3)$$

according to the method proposed by Fox, Flory and Bueche[14]; *i.e.*, by fitting the data, plotted as log (π/c) *vs.* log c (as shown in Fig. 2), to standard curves. The calculations of Stockmayer and Casassa[15] were utilized to estimate the factor g relating the third and second coefficients for the preparation of the standard curves. Values of the molecular expansion factor, α, required for this calculation were deduced from the intrinsic viscosity data reported for polystyrene by Fox and Flory.[16] From the highest to the lowest molecular weights, g values calculated in this manner varied from −0.008 to −0.031 at 30° and from 0.039 to 0.066 at 50°. Values of the osmotic parameters for these four fractions obtained according to this procedure appear in columns 2–5 of Table I.

Dr. O. Berglund, at the Symposium on Macromolecules, XIIIth International Congress of Pure and Applied Chemistry held in Stockholm, suggested the replacement of the conventional π/c *vs.* c plot by a plot of $(\pi/c)^{1/2}$ against c. For polymers in good solvents, an average value for the factor g relating the third and second coefficients is $^1/_4$.[17] Under these circumstances, the quantity enclosed in brackets in equation 3 becomes a perfect

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[8] H. P. Frank and H. Mark, *J. Polymer Sci.*, **6**, 243 (1951).

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

[10] W. R. Krigbaum and P. J. Flory, THIS JOURNAL, **75**, 1775 (1953).

[11] W. R. Krigbaum and P. J. Flory, *ibid.*, **75**, 5254 (1953).

[12] T. G. Fox, Jr., and P. J. Flory, *ibid.*, **73**, 1909 (1951).

[13] P. J. Flory and T. G. Fox, Jr., *ibid.*, **73**, 1904 (1951).

[14] T. G. Fox, Jr., P. J. Flory and A. M. Bueche, *ibid.*, **73**, 285 (1951).

[15] W. H. Stockmayer and E. F. Casassa, *J. Chem. Phys.*, **20**, 1560 (1952).

[16] T. G. Fox, Jr., and P. J. Flory, THIS JOURNAL, **73**, 1915 (1951).

[17] W. R. Krigbaum and P. J. Flory, *J. Polymer Sci.*, **9**, 503 (1952).

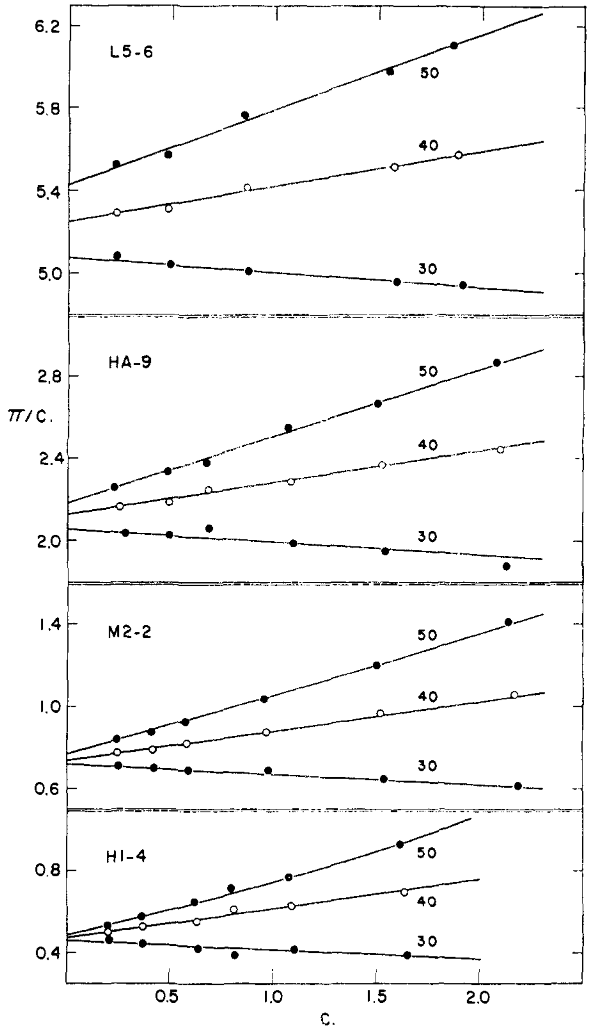

Fig. 1.—Reduced osmotic pressures plotted against concentration in g./100 cc. for four polystyrene fractions in cyclohexane at 30, 40 and 50°. The curves represent π/c ratios calculated according to equation 3 using values for the parameters fitted as described in the text.

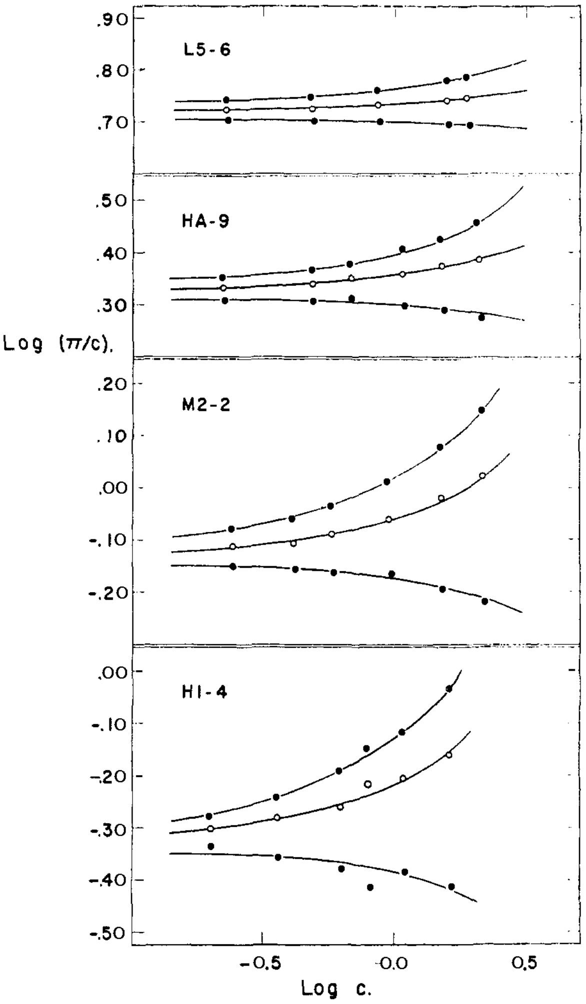

Fig. 2.—Log (π/c) plotted against log c for the polystyrene fractions shown in Fig. 1.

square, confirming the suggestion of Dr. Berglund. In order to compare these two procedures, data taken from an earlier paper in this series,[10] which covers an extended concentration range for polyisobutylene in cyclohexane and polystyrene in toluene, appear plotted as π/c vs. c, and as $(\pi/c)^{1/2}$ vs. c, in Fig. 3. The advantage of the square root plot is immediately evident; the data plotted in this way exhibit a linear dependence up to concentrations for which $(\pi/c)/(\pi/c)_0 = 3$–4, where higher terms in the virial expression begin to make a significant contribution to the osmotic pressure. As a further test of this procedure, the data of the present investigation were plotted in this manner. Values so obtained for the osmotic parameters differed only slightly from these deduced according to the procedure of Fox, Flory and Bueche, a rather surprising result in view of the fact that here g departs significantly from the value, $^1/_4$, required to produce a perfect square. The square root plot suggested by Dr. Berglund thus appears to afford the simplest procedure yet devised for the treatment of osmotic pressure data.

TABLE I

OSMOTIC PARAMETERS FOR POLYSTYRENE–CYCLOHEXANE

Fraction → $\overline{M}_n$ →		L5-6 50,500	HA-9 125,000	M2-2 359,000	H1-4 566,000	H2-8 203,000
$(\pi/c)_0$[a]	303	5.07	2.06	0.718	0.455	1.27
	313	5.25	2.13	0.734	0.472	1.31
	323	5.43	2.18	0.765	0.481	1.35[5]
10^5A_2	303	−2.76	−2.45	−1.98	−1.78	−4.55
	313	6.34	5.78	5.28	5.25	4.45
	323	13.3	11.63	10.0	9.22	9.01
$\psi_1F(X)$	303	0.365	0.338	0.306	0.310	0.398
	313	.354	.319	.280	.267	.315
	323	.319	.277	.210	.212	.237

[a] π in g./cm.^{2} and c in g./100 cc.

Thermodynamic Parameters Calculated from the Second Virial Coefficient.—Values of A_2 for the four polystyrene fractions given in columns 2–5 of Table I appear plotted against the absolute temperature in Fig. 4. According to this figure, the temperature, Θ, at which the second virial coefficient vanishes is 305.6 ± 0.4°K. The Θ values for these fractions appear to increase slightly with decreasing molecular weight; in contrast, the Θ values for the polyisobutylene–benzene system investigated previously[11] exhibited no dependence on molecular weight. The $\psi_1F(X)$ products found in Table I

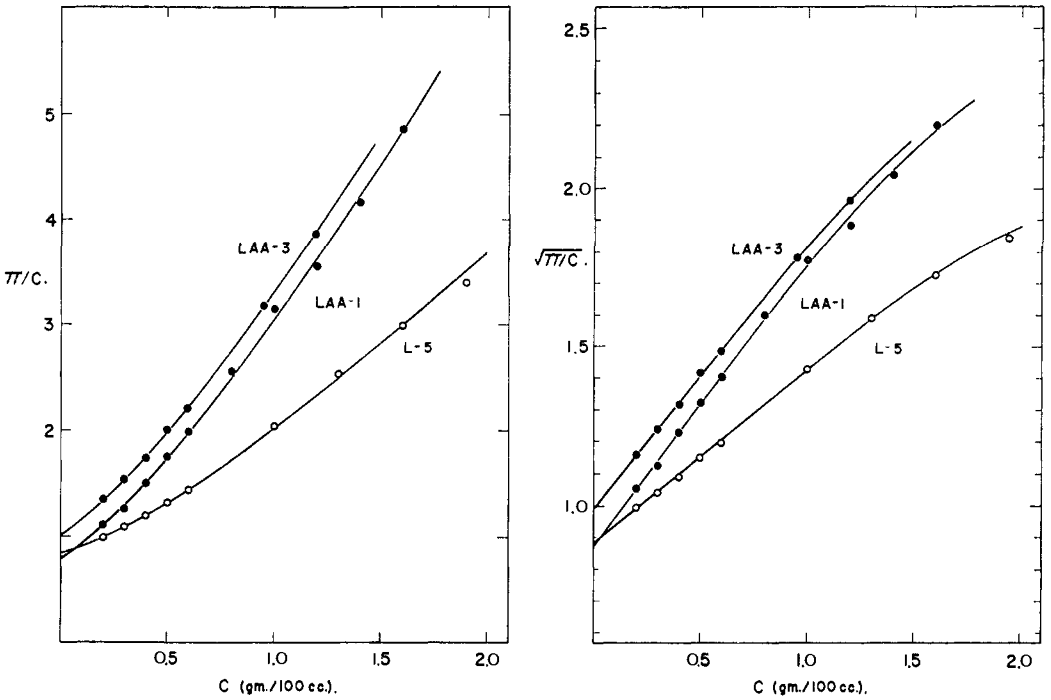

Fig. 3.—Comparison of π/c vs. c and $(\pi/c)^{1/2}$ vs. c plots for polyisobutylene fractions LAA-1 and LAA-3 in cyclohexane (filled circles) and for polystyrene fraction L-5 in toluene (open circles).[10]

were calculated from the A_2 values on assigning V_1 = 109.5, 110.9 and 112.3 cc./mole and $\bar{v}$ = 0.930, 0.935 and 0.940 cc./g. corresponding to 303, 313 and 323°K., respectively. The latter were obtained by extrapolating the volume–temperature relation for bulk polystyrene reported by Fox and Flory.[18] These $\psi_1 F(X)$ products appear plotted against the absolute temperature in Fig. 5. Since $F(X) = 1$ at $T = \Theta$, these data yield as an average value for the entropy parameter $\psi_1 = 0.33 \pm 0.03$. The individual ψ_1 values for this system also appear to increase somewhat with decreasing molecular weight, a trend which may have been present to a lesser extent in the data for the polyisobutylene–benzene system. It should be noted that the evaluation of the thermodynamic parameters from measurements near $T = \Theta$ does not depend upon the theoretical treatment of molecular configuration.

Comparison of the Θ value for polystyrene in cyclohexane deduced from the osmotic pressure measurements, Θ = 305.6°K., with the value reported from precipitation temperature measurements by Shultz and Flory,[19] Θ = 307.2°K., reveals a difference which, although small, is beyond experimental error. This disagreement was found to be due to traces of moisture which entered the polymer solutions during storage in the 40° bath. This was confirmed by measuring precipitation temperatures for fractions L5-6, HA-9, H1-4, and an additional polystyrene fraction having a molecular weight of 1.27×10^6, care being exercised to prevent the introduction of moisture. These data appear as line a in Fig. 6, where the reciprocal of the critical consolute temperature, T_c, is plotted in the conventional manner[5] against $1/\sqrt{x} + 1/2x$ (x being the ratio of the molar volumes of polymer and solvent). From the intercept of this line Θ = 307.4°K., in good agreement with the value reported by Shultz and Flory. These solutions were then stored in the 40° constant temperature bath for several days, and the precipitation temperature measurements repeated. The critical consolute temperatures of the two higher molecular weight fractions were decreased, while those of the lower molecular weight fractions were increased. These points (not shown in the figure) are represented by the dashed line marked b in Fig. 6, the intercept

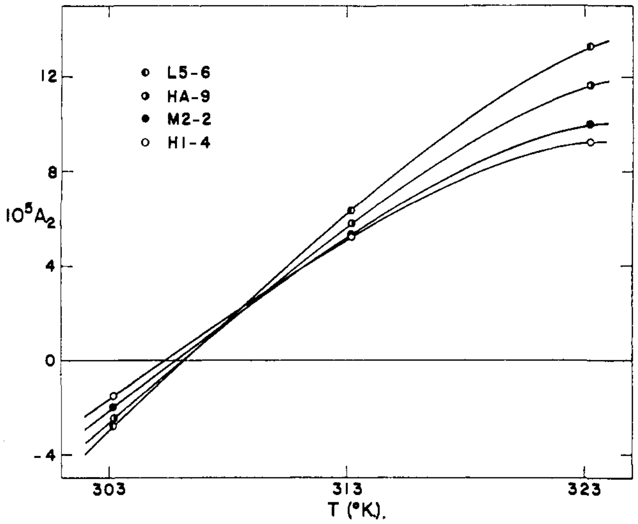

Fig. 4.—Fitted values of A_2 for four polystyrene fractions in cyclohexane plotted against the absolute temperature.

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

(19) A. R. Shultz and P. J. Flory, THIS JOURNAL, **74**, 4760 (1952).

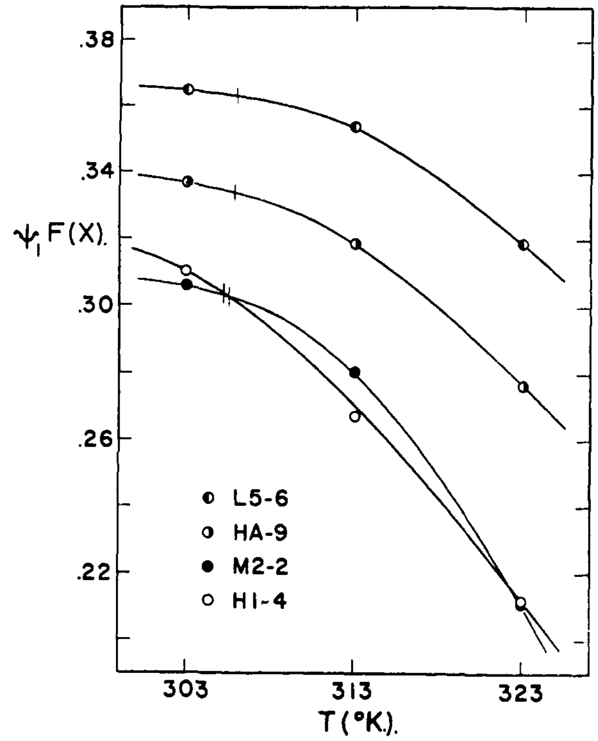

Fig. 5.—Experimental $\psi_1 F(X)$ products for polystyrene in cyclohexane plotted against the absolute temperature. The Θ temperature for each fraction is indicated by a vertical line.

of which gives Θ = 306.5°K., indicating that the ψ_1 and Θ values obtained for the first four fractions appearing in Table I will be in error to some extent due to the presence of traces of moisture.

In order to determine the magnitude of this error, further osmotic measurements were performed on the polystyrene fraction designated H2-8, using adequate precautions to prevent contamination of the solutions with water. The experimental π/c ratios for this fraction appear plotted against concentration in Fig. 7. These data were fitted as before by means of the log–log plot, yielding the values for the osmotic parameters appearing in the last column of Table I. Plots for this fraction corresponding to those shown in Figs. 4 and 5 yield Θ = 307.6°K. and $\psi_1 = 0.36^5$. Comparison with the corresponding entries in Table I for the other fractions shows that for the latter both ψ_1 and Θ were lowered slightly by contamination with moisture, although the difference in the ψ_1 values is scarcely outside the experimental error. Presumably this contamination was responsible for the slight trend of the Θ and ψ_1 values with molecular weight observed for the first four fractions investigated.

Testing the Theoretical *F(X)* Function.—According to theory,[1,2] the function $F(X)$ appearing in equation 2 is given, for small values of the argument, by

$$F(X) = 1 - X/2!2^{3/2} + X^2/3!3^{3/2} - \ldots \tag{4}$$

where

$$X = 4C_M\psi_1(1 - \Theta/T)M^{1/2}/\alpha^3 \tag{5}$$

$$C_M = (3^3/2^{5/2}\pi^{3/2})(\bar{v}^2/\mathbf{N}V_1)(\overline{r_0^2}/M)^{-3/2} \tag{6}$$

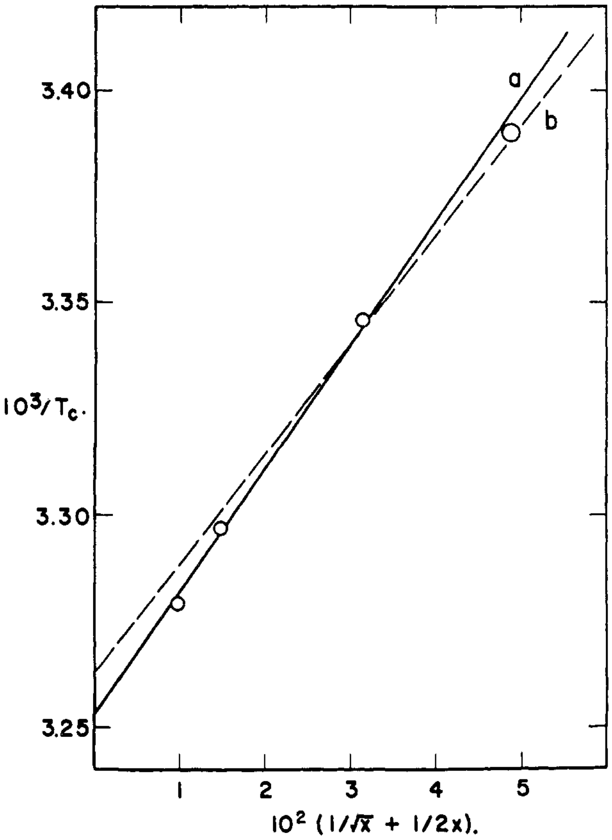

Fig. 6.—The reciprocal of the critical consolute temperature plotted against $(1/x^{1/2} + 1/2x)$ for four polystyrene fractions in dry cyclohexane (curve a), and in the presence of traces of moisture (curve b).

Here **N** is the Avogadro number, M is the molecular weight and $\overline{r_0^2}$ is the unperturbed mean-square distance between chain ends as measured under Θ conditions. The ratio $(\overline{r_0^2}/M)$ may be calculated for any polymer from the intrinsic viscosity, $[\eta]_\Theta$ measured in a Θ solvent according to the semi-

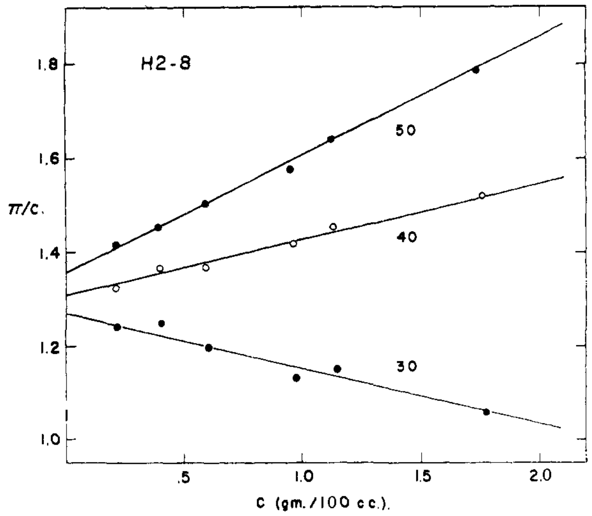

Fig. 7.—π/c ratios plotted against c for polystyrene fraction H2-8 in dry cyclohexane at 30, 40 and 50°.

empirical relation[20]

$$[\eta]_\Theta/M^{1/2} = \Phi(\overline{r_0^2}/M)^{3/2} \qquad (7)$$

The universal constant, Φ, is given, according to present estimates,[21] by 2.1×10^{21}, with $(\overline{r_0^2})^{1/2}$ expressed in cm., M in molecular weight units and $[\eta]_\Theta$ in deciliters/g. It should be noted that the ratio $\overline{r_0^2}/M$ varies with temperature, and that the value for this ratio calculated according to equation 7 corresponds to the temperature of the viscosity measurement. The molecular expansion factor α appearing in equation 5 is defined[22] as the ratio of the root-mean-square distance between chain ends in a given solvent to the corresponding unperturbed dimension at the same temperature. The factor α may be conveniently determined from the ratio of the intrinsic viscosity measured under the specific conditions to that in a Θ solvent at (about) the same temperature, making use of the relationship[13]

$$\alpha^3 = [\eta]/[\eta]_\theta \qquad (8)$$

Hence, $F(X)$ may be calculated according to theory, making use of the values of the parameters obtained with the aid of the treatment of molecular configuration and intrinsic viscosity.

Experimental $F(X)$ values are directly obtainable from the $\psi_1 F(X)$ products found at the foot of Table I, once ψ_1 has been evaluated by interpolation to $T = \Theta$. These experimental values for polystyrene in cyclohexane appear plotted against X in Fig. 8. The value of X corresponding to each point was calculated according to equation 5, using ψ_1 values taken from Table I and the intrinsic viscosity data of Fox and Flory.[16] The experimental $F(X)$ values previously reported[11] for polyisobutylene in benzene are included in Fig. 8 for comparison. The trend of the experimental points is represented by the full curve in the figure; the dashed curve gives theoretical $F(X)$ values calculated with use of equation 4 as described above. It is evident from Fig. 8 that the theoretical $F(X)$ function varies too slowly with X, a conclusion previously reached more indirectly through comparison of the theoretical and observed molecular weight dependencies of the second virial coefficient.[11] Although the qualitative nature of the theoretical $F(X)$ function precludes the evaluation of the thermodynamic interaction parameters from dilute solution measurements in good solvents, it should in no way affect the accuracy of an evaluation carried out at the Θ temperature, as pointed out above.

Comparison of the Thermodynamic Parameters with Values Obtained from Other Measurements.—In Table II the "best" values of the thermodynamic parameters for the system polystyrene–cyclohexane obtained from the osmotic measurements on fraction H2-8 are compared with those reported by Shultz and Flory[19] from precipitation temperature measurements, and by Fox and Flory[16] from intrinsic viscosity.

TABLE II

COMPARISON OF THERMODYNAMIC PARAMETERS FOR THE SYSTEM POLYSTYRENE–CYCLOHEXANE

Method of measurement	$\Theta(°K)$	ψ_1
Virial coefficient	307.6	0.36^5
Precipitation temperature[19]	307.2	1.06
Intrinsic viscosity[16]		0.13

The Θ value deduced from the osmotic measurements on fraction H2-8 stands in good agreement with that reported from precipitation temperature; however, the agreement between values for the entropy parameter deduced from the three independent measurements is not at all satisfactory. The three ψ_1 values fall in the same order as did these for the polyisobutylene–benzene system reported previously,[11] though the differences are even more marked in the present system. According to Table II, the values for the entropy parameter deduced from precipitation temperature and intrinsic viscosity differ from that obtained from the second coefficient by factors of about 3 and $^1/_3$, respectively. The corresponding factors for the polyisobutylene system were 2 and $^1/_2$. As mentioned above, a constant correction to the ψ_1 values obtained from intrinsic viscosity could easily arise from the approximations inherent in the treatment of the molecular configuration problem, but it is evident from the foregoing that correction by a constant factor will not bring the ψ_1 values deduced from viscosity into agreement with those obtained by either of the other two methods. Values taken from the literature for ψ_1 deduced according to precipitation temperature and intrinsic viscosity are collected for comparison in Table III. The last column of this table, giving the ratio of the values for the entropy parameter obtained from T_0 and

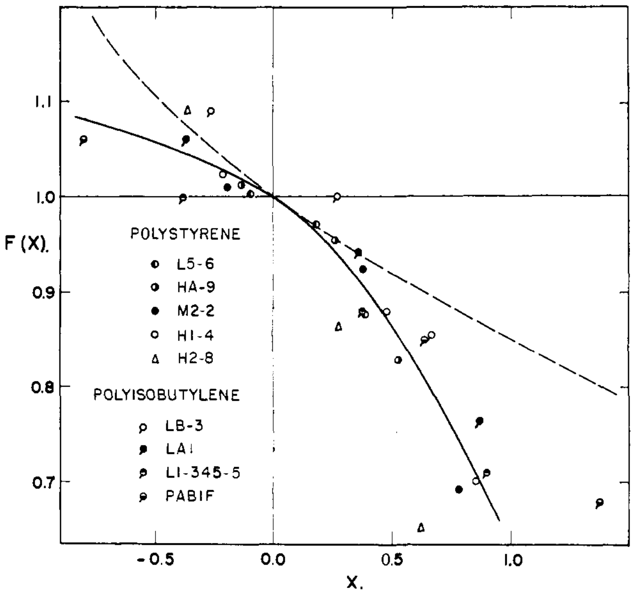

Fig. 8.—Experimental $F(X)$ values plotted against X for five polystyrene fractions in cyclohexane and for four polyisobutylene fractions in benzene.[11] The full curve represents the trend of the experimental points; the theoretical $F(X)$ function is represented by the dashed curve.

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[20] T. G. Fox and P. J. Flory, *J. Polymer Sci.*, **5**, 745 (1950); see also ref. 13.

[21] (a) S. Newman, W. R. Krigbaum, P. J. Flory and C. Laugier, in press; (b) T. G. Fox and L. Mandelkern, *J. Chem. Phys.*, **21**, 187 (1953); see also refs. 12 and 16.

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

TABLE III

COMPARISON OF ENTROPY PARAMETERS EVALUATED FROM PRECIPITATION TEMPERATURE AND INTRINSIC VISCOSITY

			ψ_1		
Polymer	Solvent	Θ (°K.)	Precipitation	Viscosity	Ratio
Polymethyl methacrylate[23]	Di-*n*-propyl ketone	305	0.61	0.23	2.6
Polyisobutylene[11]	Benzene	297.5	.65	.15	4.3
Polyisobutylene[12]	Ethylbenzene–phenyl ether (3:1)	300	.85	.17	5.0
Polydimethylsiloxane[24]	Butanone	298.2	.43	.08	5.4
Polystyrene[19]	Cyclohexane	307.2	1.06	.13	8.1
Natural rubber[25]	Heptanone-4	287.5	.80	.08^5	9.4

$[\eta]$ measurements, furnishes further evidence that this ratio is by no means constant for different polymer–solvent pairs.

The disagreement between values for the entropy parameter deduced from osmotic pressure and precipitation temperature is even more disturbing from a theoretical standpoint. The procedure involving A_2 would appear to have a slight theoretical advantage, inasmuch as the evaluation is carried out precisely at $T = \Theta$. Since the molecular expansion factor is unity at this temperature, any influence of the configuration of the polymer molecules upon the chemical potential of the solvent must vanish under these circumstances. On the other hand, Shultz and Flory have pointed out that the magnitude of the entropy parameter obtained by precipitation for polystyrene–cyclohexane stands in good agreement with that for the analogous small molecule system toluene–cyclohexane.[26] Until these differences can be resolved theoretically in favor of one of the procedures, there is no assurance that the ψ_1 values for different polymer–solvent pairs obtained by any one of these methods are even correct relative to one another.

In summary, the dilute solution treatment clearly represents a notable advance over the earlier treatments of polymer solutions. The factor $F(X)$ introduced thereby into the expression for the second virial coefficient allows, for the first time, a semiquantitative description of the observed dependencies of A_2 on molecular weight and molecular weight heterogeneity. Although these successes are encouraging, nevertheless the accurate osmotic pressure measurements reported in this series of papers indicate the necessity for further improvement on the theory. In particular, the magnitude of the important entropy parameter, ψ_1, remains in doubt pending further refinement of the existing theories.

DURHAM, N. C.

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(23) T. G. Fox, private communication.

(24) P. J. Flory, L. Mandelkern, J. B. Kinsinger and A. R. Shultz, THIS JOURNAL, **74**, 3364 (1952).

(25) H. L. Wagner and P. J. Flory, *ibid.*, **74**, 195 (1952).

(26) A. R. Shultz and P. J. Flory, abstracts of papers presented at the 124th meeting of the American Chemical Society, Chicago, Ill., Sept. 6-11 (1953).

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Macro-ions. III. The Solution Behavior of a Polymeric Ampholyte[1]

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In order to explore the effects of electrostatic attractions between acidic and basic groups upon the configuration and solution behavior of a non-rigid macro-ion, copolymers of methacrylic acid and 2-dimethylaminoethyl methacrylate, ranging in composition from 23 to 57 mole per cent. methacrylic acid, have been prepared and characterized. It has been found that ionization of the monomers exerts a marked influence on the propagation reactions in methanol, invalidating the application of the two-component copolymerization equation. A light-scattering and viscometric study of one of these copolymers (53.7% methacrylic acid), which was water soluble over the whole *p*H range, was carried out. The most interesting behavior was that at the isoionic point in the absence of salt. Here it was found that the polyampholyte molecule was contracted relative to that at higher ionic strength, that the second virial coefficient was negative and that the intensity of scattered light increased with increasing angle. This information together with theoretical considerations, shows that the extension of the molecules is decreased by the net attraction of the oppositely charged segments, and that there is a pronounced intermolecular attraction, due to the existence of both positively and negatively charged molecules at the isoionic point. The intermolecular attraction produces a distinctive type of clustering in which there is probably little interpenetration in contrast to the association of uncharged polymer molecules near the point of phase separation. Changing the *p*H away from the isoionic point destroys this type of clustering and replaces it by an ordering of the solute molecules due to mutual repulsion of like charges and characterized by large positive second virial coefficients. The behavior of similar solutions, 0.1 *M* in NaCl, was close to that of uncharged polymers but it appeared that even here there was evidence of residual electrostatic attractions between oppositely charged segments.

Polymeric ampholytes (polyampholytes) differ from polymeric acids and bases in that they possess both positively and negatively ionized groups. The unique characteristic of polyelectrolytes carrying only one type of charge is the large contribution to the molecular free energy arising from electrostatic repulsions; this is exhibited most directly by the dependence of the molecular size and the degree of ordering in solution on the charge and ionic strength. In polyampholytes, however, the electrostatic interactions can be both repulsive and attractive, the extent depending on the *p*H of the

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