HIGH POLYMER SOLUTIONS

PART 8.—THE VAPOUR PRESSURE OF SOLUTIONS OF POLY*ISO*BUTENE IN TOLUENE AND CYCLOHEXANE

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Measurements are reported of the vapour pressure of solutions of poly*iso*butene fractions in toluene and cyclohexane at 25, 40 and 60° C. The heat of dilution in cyclohexane was very small but in toluene $\Delta H_1/\phi_2^2$ increased with increase in ϕ_2. The value of the μ in the free energy equation

$$\Delta \overline{G}_1 = RT[\ln (1 - \phi_2) + (1 - 1/n)\phi_2 + \mu\phi_2^2]$$

increased with ϕ_2 and this supports the viewpoint that μ must be regarded as a free-energy parameter containing an entropy contribution μ_s together with a heat of mixing term.

The present investigation forms part of a series of studies on the vapour pressures of solutions of high polymers. In previous papers [1] results were reported on the vapour pressures of polystyrene in a series of polar and non-polar solvents. These measurements have now been extended to solutions of poly*iso*butene in toluene and cyclohexane in order to provide a further check on, and a better understanding of the theoretical relationships for the free energies of polymer solutions.

EXPERIMENTAL

The method of measurement and experimental procedures were precisely as described in previous papers.[1]

POLY*iso*BUTENE.—Polymer fractions of molecular weight 45,000 and 100,000 prepared as described [2] in part 6 were used. The solvents were very carefully purified by chemical

methods, followed by repeated fractional distillations. The measured vapour pressures and densities agreed very closely with the best values in the literature.

DENSITIES.—The measured densities of cyclohexane at 25, 40 and 65° C respectively were 0·7728, 0·7607 and 0·7360, and for benzene at 25 and 60° C, 0·8689 and 0·8292 g cm⁻³. The densities of the polymer at 25, 40 and 65° C were 0·9437, 0·9251 and 0·9010 g cm⁻³ respectively.

RESULTS

The results are shown in fig. 1 as a plot of the activity a_1 against weight fraction of the solvent W_1 and the data are summarized in tables 1 and 2.
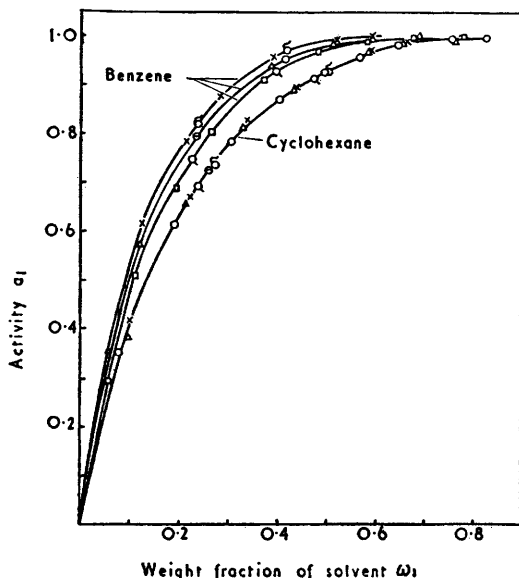

FIG. 1.—Variation of activity with weight fraction in benzene and cyclohexane at three temperatures: 25° C, ⊘ and ×; 40°, △ and ⊖; 65°, □ or ○ and ○. The symbols refer to increasing and decreasing concentration respectively.

With benzene the activity was found to be dependent on the temperature, and an average value of the partial molar heat of dilution was evaluated between the temperatures studied by use of the relationship

$$H_1 = R \frac{T_1 T_2}{T_2 - T_1} [(\ln a_1)_{T_1} - (\ln a_1)_{T_2}].$$

The values of $\Delta H_1/\phi_2^2$ in the range $W_1 = 0·1$ to $W_1 = 0·5$ are summarized in table 3. As with other polymers for which reliable data are available $\Delta H_1/\phi_2^2$ increases with ϕ_2. The vapour pressure results for cyclohexane solutions showed no differences at 25, 40 and 65° C. The maximum scatter of the measurements from the curve of fig. 1 was 2 % and hence it may be assumed that the heat of dilution for this system is very small.

DISCUSSION

As pointed out in the previous paper the theoretical expression for the partial molal free energy,

$$\Delta \overline{G}_1 = RT[\ln (1 - \phi_2) + (1 - 1/n)\phi_2 + \mu\phi_2^2],$$

affords a good working approximation for polymer solutions. The validity of this expression may be judged in part by the constancy of the parameter μ over a

wide concentration range. Except for the rubber + benzene system for which μ is remarkably constant, measurements on other polymers suggest that μ is
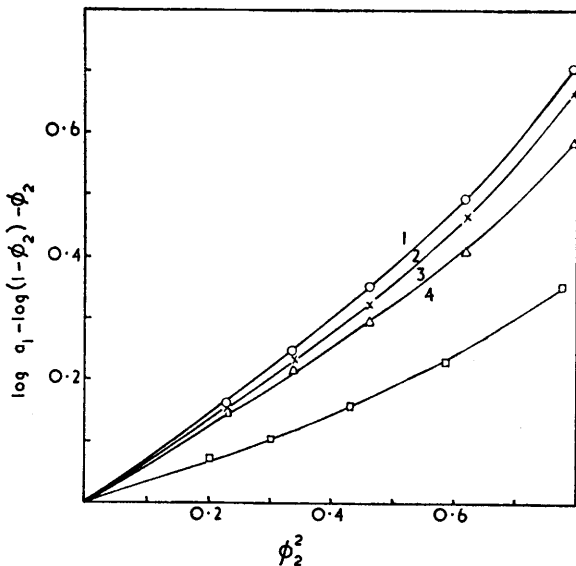

FIG. 2.—Plot of the Huggins-Flory equation, curves 1, 2 3, for benzene 25, 40 and 65° C ; curve 4 for cyclohexane.

TABLE 1.—VAPOUR PRESSURE DATA FOR CYCLOHEXANE SOLUTIONS OF POLY*iso*BUTYLENE FRACTION OF MOL. WT. 100,000

temp. ° C	W_1 increasing		W_1 decreasing	
	wt. fraction of solvent (W_1)	activity of solvent (a_1)	wt. fraction of solvent (W_1)	activity of solvent (a_1)
25	0·100	0·419	0·504	0·928
	0·224	0·670	0·273	0·738
	0·338	0·830	—	—
	0·439	0·895	—	—
	0·592	0·972	—	
	0·663	0·990	—	—
	0·767	0·994	—	—
	0·827	1·00	—	—
40	0·094	0·378	0·500	0·924
	0·216	0·657	0·257	0·724
	0·331	0·813	—	—
	0·433	0·892	—	—
	0·589	0·968	—	—
	0·660	0·986	—	—
	0·764	0·986	—	—
	0·826	1·00	—	—
65	0·082	0·351	0·476	0·913
	0·192	0·611	0·239	0·961
	0·311	0·784	—	—
	0·406	0·871	—	—
	0·571	0·960	—	—
	0·649	0·982	—	—
	0·762	0·993	—	—
	0·824	1·00	—	—

concentration dependent and this may be very marked for solutions of hydrocarbon polymers in polar solvents. The above relationship was tested by plotting $\ln a_1 - \ln (1 - \phi_2^2) - (1 - 1/n)\phi_2$ against ϕ_2^2 and the results shown in fig. 2 indicate clearly an upward curvature at three temperatures for benzene and also
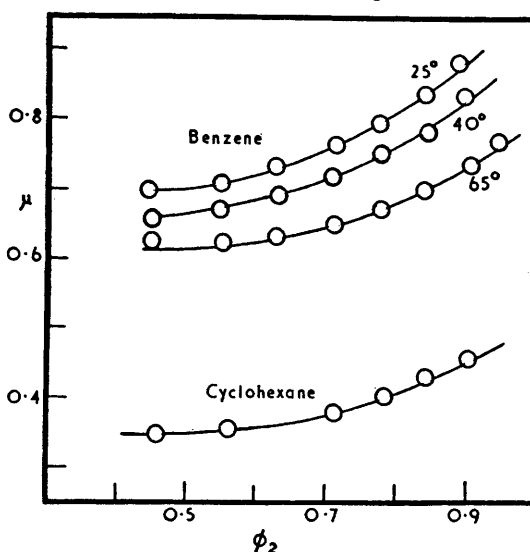

FIG. 3.—Variation of μ with volume fraction of polymer in benzene and cyclohexane.

TABLE 2.—VAPOUR PRESSURE DATA FOR BENZENE SOLUTIONS OF POLYisoBUTYLENE FRACTION OF MOL. WT. 45,000

temp. ° C	W_1 increasing		W_1 decreasing	
	wt. fraction of solvent (W_1)	activity of solvent (a_1)	wt. fraction of solvent (W_1)	activity of solvent (a_1)
25	0·124	0·616	0·423	0·972
	0·214	0·786	0·241	0·823
	0·286	0·878	—	—
	0·393	0·959	—	—
	0·518	0·992	—	—
	0·595	1·00	—	—
40	0·053	0·353	0·418	0·954
	0·121	0·575	0·238	0·799
	0·210	0·753	—	—
	0·282	0·852	—	—
	0·389	0·940	—	—
	0·516	0·983	—	—
	0·594	0·996	—	—
	0·687	1·00	—	—
65	0·053	0·293	0·401	0·930
	0·109	0·511	0·225	0·724
	0·195	0·690	—	—
	0·265	0·802	—	—
	0·373	0·911	—	—
	0·484	0·969	—	—
	0·585	0·989	—	—
	0·682	0·997	—	—
	0·778	1·00	—	—

for cyclohexane. The value of μ calculated from the plotted data of fig. 2 varies with concentration in a non-linear manner as shown in fig. 3. These results are in agreement with the viewpoint expressed in the previous paper, and for hydro-carbon polymers in non-polymer solvents the parameter μ contains heat and entropy components. It is evident that the refined theoretical interpretation of μ as a free-energy parameter is soundly based although as yet no theoretical evaluation of the entropy component μ_s is possible.
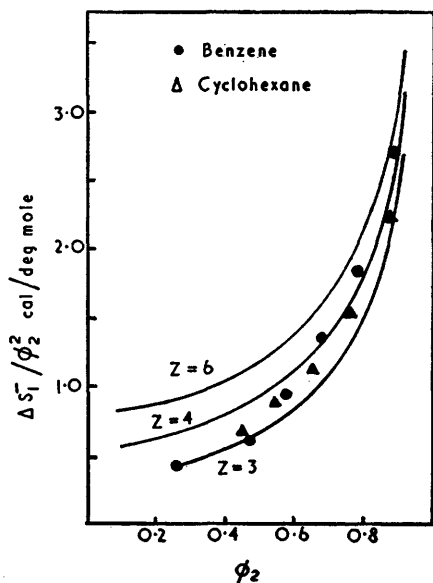

FIG. 4.

ENTROPY OF DILUTION

Several independent theoretical relationships have been derived for the entropy of mixing [3] and these all approximate to a common result as $z \to \infty$. Thus, Miller has shown that for athermal solutions $\Delta \overline{S_1}$ is given by

$$\Delta \overline{S_1} = R \ln (1 - \phi_2) - \frac{z}{2}\left[1 - \frac{z}{2}\ln\left\{1 - \frac{2}{z}\left(1 - \frac{1}{n}\right)\phi_2\right\}\right].$$

TABLE 3.—HEATS OF DILUTION OF POLY*iso*BUTYLENE + BENZENE

W_1	ΔH_1 cal/mole	$\Delta H_1/\phi_2^2$ cal/mole
0·1	281·6	353·2
0·2	183·1	295·9
0·3	125·6	269·3
0·4	74·5	221·3
0·5	37·5	162·9

Assuming that this equation may apply to the case with a finite heat of mixing the calculated values of $\Delta \overline{S_1}/\phi_2^2$ for $z = 3$, 4 and 6 together with the experimental values are shown in fig. 4. The latter were calculated from the following equations :

$$T\Delta \overline{S_1} = \Delta \overline{H_1} - \Delta \overline{G_1},$$

$$\frac{\Delta \overline{S_1}}{\phi_2^2} = \frac{1}{T}\frac{\Delta \overline{H_1}}{\phi_2^2} - \frac{R \ln a_1}{\phi_2^2}.$$

The agreement between theory and experiment appears satisfactory for $\phi_2 > 0\cdot6$ but at higher dilutions noticeable deviations from theory occur.

[1] Bawn, Freeman and Kamaliddin, *Trans. Faraday Soc.*, 1950, **46**, 677. Bawn and Wajid, *Trans. Faraday Soc.*, 1956, **52**, 1658.

[2] Bawn, Hill and Wajid, *Trans. Faraday Soc.*, 1956, **52**, 1651.

[3] (*a*) Flory, *J. Chem. Physics*, 1941, **9**, 660; 1942, **10**, 51. (*b*) Huggins, *Ann. N.Y. Acad. Sci.*, 1943, **44**, 431; *Ind. Eng. Chem.*, 1943, **35**, 216. (*c*) Miller, *Proc. Camb. Phil. Soc.*, 1942, **38**, 109; 1943, **39**, 54, 131. (*d*) Guggenheim, *Proc. Roy. Soc. A*, 1944, **183**, 203; *Trans. Faraday Soc.*, 1948, **44**, 1007.