Equilibrium Sorption Data for Polyisobutylene–Hydrocarbon Systems

By S. Prager, E. Bagley and F. A. Long

Equilibrium sorption isotherms have been determined at three temperatures, for polyisobutylene with the hydrocarbons propane, n-butane, isobutane, n-pentane, isopentane and neopentane. Two of these, n-pentane and isopentane, are solvents for the polyisobutylene; the rest are swelling agents. The data fit the Flory–Huggins equation and the calculated values of the interaction parameter, χ_1, are essentially constant and greater than 0.5 for all six systems even though for the two solvents the value of χ_1 must ultimately drop below 0.5 at high solvent concentrations. For one of the solvents, n-pentane, the isotherm has been extended to a p/p_0 value of 0.993, corresponding to a volume fraction of solvent of 0.61, with no observable decrease in the χ_1 value.

Since the publication of the original papers by Flory[1] and Huggins[2] on the thermodynamics of high polymer solutions, the theory presented by these authors has been the subject of considerable investigation both from the theoretical and the experimental side. The original treatments assumed that specific interactions between polymer segments and solvent molecules, if present at all, were sufficiently small so that the randomness of polymer–solvent mixing remained unaffected, and that furthermore only an enthalpy change was involved in the formation of a polymer–solvent contact. The resulting relation between the activity (a_1) of the solvent and the composition of the mixture is given by Flory as

$$\ln a_1 = \ln v_1 + \left(1 - \frac{1}{x}\right) v_2 + \chi_1 v_2^2 \qquad (1)$$

where v_1 and v_2 are, respectively, the volume fractions of solvent and polymer, x the number of segments per polymer chain, and χ_1 (which we are using in place of the original symbol μ) a parameter characteristic of a given polymer–solvent pair at a fixed temperature. Huggins,[2] Miller,[3] Orr[4] and Guggenheim[5] have by means of somewhat more rigorous treatments obtained expressions for a_1 which include the coördination number (z) of the polymer–solvent lattice as an additional parameter and Orr[4] has pointed out that equation (1) corresponds to $z = \infty$. Systems where polymer–diluent interactions are strong enough to cause deviations from random mixing have been treated by Orr,[4] Dole[6] and Guggenheim.[7] The last author has introduced an entropy as well as an enthalpy of contact formation so that, even when random mixing prevails, the entropy of dilution is not that calculated from the original Flory–Huggins theory. However equation (1) remains valid with a somewhat different interpretation of the parameter χ_1

$$\chi_1 = -(\bar{S}_1/R) + (\bar{H}_1/RT) \qquad (2)$$

where $\bar{S}_1$ and $\bar{H}_1$ are, respectively, the changes in entropy (other than configurational) and enthalpy involved when a mole of diluent is mixed with an infinite amount of polymer; in Flory's earlier interpretation of χ_1, $\bar{S}_1$ was assumed to be zero. More

recently, Flory and Krigbaum[8] have discussed the deviations from equation (1) which arise in dilute polymer solutions owing to the fact that the polymer segments are no longer uniformly distributed.

On the experimental side Gee and Orr[9] have applied equation (1) to benzene–rubber mixtures and have found that the χ_1 value is independent of concentration. Measurements on polysilicone–benzene mixtures[10] show an increase of χ_1 with v_2, as is also the case with the system methyl ethyl ketone–polystyrene,[11] while χ_1 decreases with increasing polymer concentration in polystyrene–toluene mixtures.[11] As a matter of fact, the constancy of χ_1 for the rubber–benzene system seems to be due to a somewhat fortuitous cancellation of variations in $\bar{S}_1$ and $\bar{H}_1$.[9] Baughan[12] has determined χ_1 for a wide variety of mixtures of polystyrene with both polar and non-polar diluents at relatively high values of v_2. Among systems for which osmotic data at high dilution were available, he found good agreement between χ_1 values in the two concentration ranges for benzene and toluene, and significant differences for carbon tetrachloride and dioxane; furthermore, three liquids for which χ_1 at high values of v_2 was greater than 0.5 (dioxane, diethyl ketone, and butyl acetate) turned out to be solvents, which, from equation (1) means that χ_1 must decrease below that value at higher diluent concentrations. Shultz and Flory[13] have found that χ_1 for the systems polyisobutylene–diisobutyl ketone and polystyrene–cyclohexane increases with increasing diluent concentrations.

The present investigation deals with six polyisobutylene–hydrocarbon systems, for which the chemical similarity of the diluent to the polymer and the non-polar nature of both may be expected to lead to small interactions between the two, and which should therefore be especially suitable for application of the Flory–Huggins theory. In addition, the fact that polyisobutylene at room temperature is far above its second-order transition makes the observation of hysteresis phenomena such as those mentioned by Baughan[12] rather unlikely.

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(2) M. L. Huggins, ibid., 9, 440 (1941); Ann. N. Y. Acad. Sci., 43, 1 (1942).
(3) A. R. Miller, Proc. Camb. Phil. Soc., 38, 109 (1942).
(4) W. J. C. Orr, Trans. Faraday Soc., 40, 320 (1944).
(5) E. A. Guggenheim, Proc. Roy. Soc. (London), 183A, 203 (1944).
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(11) C. E. H. Bawn, R. F. J. Freeman and A. R. Kamaliddin, ibid., 46, 677 (1950).
(12) E. C. Baughan, ibid., 44, 495 (1948).
(13) A. R. Shultz and P. J. Flory, This Journal, 74, 4760 (1952).

Experimental

The procedure for measuring the composition of the polymer–diluent mixture in equilibrium with a given pressure of diluent vapor has been given in detail elsewhere.[14] A film of polyisobutylene (viscosity average molecular weight ca. 10^6) was suspended from a calibrated quartz spring in an atmosphere of hydrocarbon vapor at a pressure, p. After equilibrium had been reached, the weight of diluent sorbed was calculated from the elongation of the spring as observed with a traveling microscope. Runs were made in this manner on propane at 35° and on n-butane, isobutane, n-pentane, isopentane and neopentane at 25, 35 and 46.5°.

In addition, experiments were conducted to classify the hydrocarbons as either solvents or swelling agents for polyisobutylene. A small sample of polymer was sealed up in a thick-walled tube with a large excess of diluent, and allowed to stand at room temperature for several weeks. The solvents gave homogeneous solutions within a few days whereas the swelling agents gave two phase systems which stayed unchanged indefinitely.

Calculations.—To a first approximation a_1 may be set equal to the relative vapor pressure p/p_0 of the diluent, p_0 being the vapor pressure when $v_1 = 1$. Values of p_0 for the hydrocarbons studied were found by linear interpolation of log p vs. $1/T$ plots constructed from data in the catalogs of the Phillips Petroleum Company. The approximate activities were then corrected for deviations of the vapor from the perfect gas law using the equation

$$\ln a_1 - \ln p/p_0 = \frac{p_0 - p}{RT}\left(\frac{\alpha}{RT} - \beta\right) \qquad (3)$$

where α and β are the two van der Waals constants. To calculate χ_1, the $1/x$ term in equation (1) was neglected, giving

$$\chi_1 = \frac{\ln(a_1/v_1) - v_2}{v_2^2} \qquad (4)$$

The volume fractions were readily obtained from the known densities of the pure components,[15,16] assuming no volume change on mixing

$$v_1 = 1 - v_2 = \frac{1}{(\rho_1/\rho_2 c) + 1} \qquad (5)$$

where c is weight penetrant sorbed per unit weight

TABLE I

EQUILIBRIUM SORPTION OF SWELLING AGENTS BY POLYISOBUTYLENE

p (mm.)	c (g./g.)	a_1	v_1	χ_1
Propane: 35°, p_0 = 9050, ρ_1 = 0.490				
496	0.0061	0.0538	0.0113	0.58
941	.0116	.1018	.0212	.62
1452	.0183	.1569	.0330	.63
1446	.0185	.1569	.0333	.62
			$\bar{\chi}_1 =$	.61
n-Butane: 25°, p_0 = 1848, ρ_1 = 0.573				
255	0.0185	0.1436	0.0289	0.67
280	.0215	.1581	.0334	.63
503	.0405	.2814	.0611	.67
506	.0419	.2834	.0631	.64
658	.0558	.3668	.0823	.68
729	.0661	.4054	.0961	.66
734	.0669	.4083	.0971	.65
			$\bar{\chi}_1 =$	.66

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(15) T. G. Fox, Jr., and P. J. Flory, *J. Phys. Colloid Chem.*, **55**, 221 (1951).

(16) G. Egloff, "Physical Constants of Hydrocarbons," Reinhold Publ. Corp., New York, N. Y., 1939.

n-Butane: 35°, p_0 = 2487, ρ_1 = 0.562				
242	0.0126	0.1022	0.0201	.67
492	.0281	.2064	.0438	.65
503	.0288	.2116	.0448	.65
662	.0355	.2776	.0546	.76
712	.0424	.2981	.0646	.68
719	.0434	.3012	.0661	.67
736	.0438	.3084	.0666	.69
763	.0466	.3196	.0705	.67
786	.0475	.3288	.0719	.69
994	.0653	.4142	.0962	.68
1243	.0905	.5148	.1284	.68
1448	.1161	.5963	.1590	.68
			$\bar{\chi}_1 =$	.67
n-Butane: 46.5°, p_0 = 3417, ρ_1 = 0.549				
289	0.0113	0.0909	0.0183	0.64
507	.0203	.1576	.0325	.65
747	.0325	.2320	.0510	.63
			$\bar{\chi}_1 =$	.64
Isobutane: 25°, p_0 = 2664, ρ_1 = 0.554				
721	0.0345	0.2829	0.0543	0.79
788	.0389	.3085	.0608	.78
839	.0426	.3280	.0661	.77
941	.0473	.3667	.0730	.80
1018	.0542	.3962	.0827	.77
1104	.0595	.4285	.0900	.79
1227	.0723	.4759	.1074	.75
			$\bar{\chi}_1 =$	.78
Isobutane: 35°, p_0 = 3545, ρ_1 = 0.542				
210	0.0069	0.0632	0.0116	0.72
488	.0171	.1469	.0281	.72
712	.0260	.2130	.0421	.72
767	.0281	.2287	.0453	.73
980	.0373	.2909	.0593	.73
1246	.0509	.3679	.0792	.73
1460	.0622	.4300	.0951	.74
			$\bar{\chi}_1 =$	.73
Isobutane: 46.5°, p_0 = 4738, ρ_1 = 0.528				
270	0.0069	0.0620	0.0117	0.70
513	.0135	.1170	.0227	.69
512	.0127	.1170	.0214	.75
770	.0219	.1757	.0363	.66
940	.0245	.2127	.0405	.76
1175	.0317	.2653	.0517	.76
			$\bar{\chi}_1 =$	.72
Neopentane: 25°, p_0 = 1275, ρ_1 = 0.613				
258	0.0256	0.2067	0.0370	0.82
493	.0547	.3924	.0759	.84
727	.0958	.5755	.1257	.85
			$\bar{\chi}_1 =$	.84
Neopentane: 35°, p_0 = 1736, ρ_1 = 0.613				
489	0.0373	0.2878	0.0528	0.83
703	.0595	.4118	.0815	.83
1052	.1104	.6127	.1415	.82
1242	.1515	.7197	.1843	.82
			$\bar{\chi}_1 =$	.825
Neopentane: 46.5°, p_0 = 2402, ρ_1 = 0.613				
329	0.0160	0.1413	0.0232	0.87
959	.0580	.4077	.0791	.85
1188	.0780	.5041	.1036	.85
			$\bar{\chi}_1 =$	.86

of polymer and ρ_1 and ρ_2 are the densities of solvent and polymer, respectively.

Results and Discussion

Values of the interaction parameter, χ_1, and the data for its calculation are given in Table I for the swelling agents, propane, n-butane, isobutane, neopentane, and in Table II for the two solvents, n-pentane and isopentane. The densities of poly-

TABLE II

EQUILIBRIUM SORPTION OF SOLVENTS BY POLYISOBUTYLENE

p (mm.)	c (g./g.)	a_1	v_1	χ_1
n-Pentane: 25°, p_0 = 514.8, ρ_1 = 0.620
83	0.0244	0.1634	0.0350	0.62
113	.0324	.2230	.0459	.69
114	.0324	.2240	.0459	.69
152	.0434	.2986	.0605	.74
153	.0493	.3007	.0682	.64
			$\bar{\chi}_1$ =	.68
n-Pentane: 35°, p_0 = 730.7, ρ_1 = 0.610
32	0.0061	0.0450	0.0091	0.62
55	.0103	.0766	.0152	.65
59	.0109	.0817	.0161	.66
102	.0211	.1428	.0307	.60
104	.0213	.1448	.0310	.61
105	.0215	.1469	.0312	.62
153	.0319	.2128	.0456	.64
200	.0478	.2786	.0669	.57
203	.0450	.2827	.0632	.64
207	.0474	.2877	.0664	.61
306	.0787	.4246	.1055	.62
385	.1136	.5327	.1454	.61
388	.1123	.5368	.1442	.62
388	.1102	.5368	.1418	.64
388	.1130	.5368	.1449	.62
389	.1135	.5378	.1453	.62
492	.1797	.6781	.2122	.59
495	.1774	.6820	.2102	.62
497	.1752	.6850	.2081	.64
598	.2855	.8214	.2996	.63
600	.2975	.8244	.3083	.61
692	.7605	.9481	.5326	.50
697	.6265	.9550	.4842	.61
697	.6468	.9550	.4922	.60
698	.6091	.9570	.4774	.63
724	1.0561	.9912	.6129	.63
			$\bar{\chi}_1$ =	.62
n-Pentane: 46.5°, p_0 = 1058.3, ρ_1 = 0.598
104	0.0138	0.1007	0.0205	0.64
153	.0212	.1489	.0312	.63
189	.0262	.1836	.0382	.66
230	.0333	.2223	.0481	.64
290	.0438	.2802	.0623	.64
			$\bar{\chi}_1$ =	.64
Isopentane: 25°, p_0 = 686.5, ρ_1 = 0.615
77	0.0156	0.1142	0.0228	0.66
80	.0178	.1193	.0260	.58
111	.0236	.1650	.0342	.65
112	.0242	.1660	.0350	.64
127	.0280	.1883	.0403	.63
144	.0290	.2137	.0402	.77
159	.0350	.2359	.0499	.67
199	.0460	.2956	.0655	.66
			$\bar{\chi}_1$ =	.65
Isopentane: 35°, p_0 = 963.0, ρ_1 = 0.604
58	0.0081	0.0616	0.0121	0.66
106	.0156	.1128	.0231	.64
116	.0168	.1231	.0248	.66
121	.0179	.1292	.0264	.65
203	.0322	.2158	.0465	.64
222	.0353	.2362	.0508	.65
324	.0570	.3425	.0795	.64
333	.0596	.3526	.0828	.63
333	.0587	.3526	.0816	.65
422	.0808	.4451	.1060	.65
666	.1795	.6981	.2136	.64
			$\bar{\chi}_1$ =	.65
Isopentane: 46.5°, p_0 = 1376, ρ_1 = 0.592
87	0.0081	0.0663	0.0123	0.71
103	.0097	.0777	.0147	.70
147	.0147	.1107	.0220	.67
189	.0194	.1426	.0289	.66
301	.0329	.2256	.0480	.66
			$\bar{\chi}_1$ =	.68

isobutylene used for calculation of volume fractions were 0.921, 0.915 and 0.908 g./cc. at the temperatures 25, 35 and 46.5°, respectively. Figure 1 gives typical plots (for isobutane) of p/p_0 versus concentration at the three temperatures. The very slight variation of the equilibrium isotherm with temperature is evidence that the energy of interaction between polymer and hydrocarbon is small. Both Fig. 1 and the tables of data show that the reproducibility of the experiments is good. Experiments not listed, wherein equilibrium was approached from both higher and lower diluent concentrations, revealed no detectable hysteresis.

For the interaction of all six hydrocarbons with polyisobutylene the values of χ_1 at a fixed temperature are essentially independent of concentration. The χ_1 values at 35° range from 0.61 for propane to 0.83 for neopentane indicating that χ_1 increases with increased branching of the hydrocarbons. For the two solvents n-pentane and isopentane the χ_1 values are close to 0.65 at all three temperatures. However, equation (1) demands that at high values of v_1 the value of χ_1 for solvents must decrease to below 0.5. In an attempt to observe this expected decrease, the sorption isotherm of n-pentane was extended to a p/p_0 value of 0.993, corresponding to a volume fraction of n-pentane of 0.613, but no appreciable drop in χ_1 was found. If χ_1 were to remain constant at the observed value of 0.62 for this system, p/p_0 would reach unity at v_1 = 0.7. Therefore χ_1 must start to decrease somewhere between v_1 = 0.6 and v_1 = 0.7. Unfortunately this range could not be covered with our apparatus.

The variation of χ_1 with temperature is small for all five systems, in fact comparable to the observed fluctuations at a single temperature. Furthermore there is no consistent trend of χ_1 with temperature. This result clearly shows that ΔH_1 of eq. (2) is small. However the precision of the experiments is not enough to enable us to determine the separate contributions to χ_1 of the heat and entropy terms.

In looking for an explanation for the concentration dependence of χ_1 which must arise at high

concentrations of the solvents, two possibilities can be discarded at once: deviations from random mixing due to large polymer–penetrant interaction, and non-uniform distribution of polymer segments at large v_1, as discussed by Flory and Krigbaum.[8] The former cannot be important for χ_1 less than unity (free energy of contact formation less than kT), while the latter would produce a change in χ_1 only at values of v_1 much higher than 0.7. As pointed out by Flory and Krigbaum[17] the assumption, fundamental in the derivation of equation (1), of a concentration independent lattice structure for the polymer–penetrant mixture, is probably not always valid. In general, therefore, one may expect the coördination number z to vary with composition, which will, of course, lead to a more complex formula than equation (1). In this connection it might be useful to examine the assumption, made in calculating v_1, that there is no volume change on mixing polymer and penetrant; if the lattice does indeed depend on the penetrant concentration, one might find some difference between the partial molar volumes in the mixture and the molar volumes of the pure components.

The authors wish to express their gratitude to

(17) P. J. Flory and W. R. Krigbaum, "Ann. Review of Physical Chemistry," Vol. 2, Annual Reviews, Inc., Stanford, Cal., 1951, p. 383.
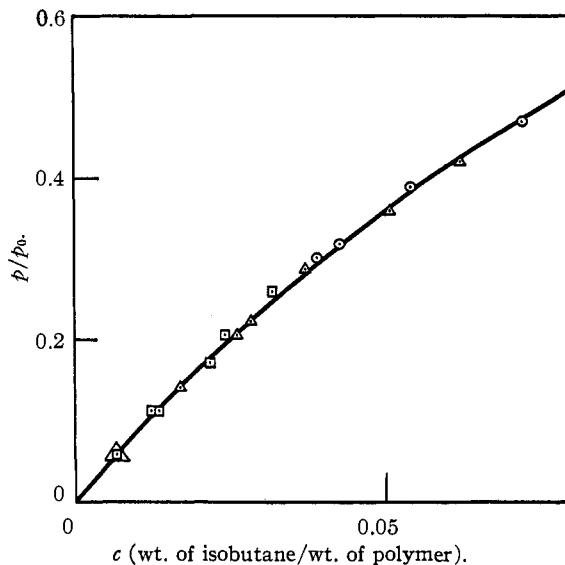

Fig. 1.—Sorption isotherms for isobutane with polyisobutylene: $\bigcirc$, 25°; $\triangle$, 35°; $\square$, 45°.

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ITHACA, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF TEXAS TECHNOLOGICAL COLLEGE]

Electric Moments of Some Methyl Ketones[1]

BY GEORGE K. ESTOK AND JOHN H. SIKES

Electric moments have been determined in benzene and dioxane solutions for four aliphatic unsaturated methyl ketones. The observed moments are interpreted in terms of resonance, methyl hyperconjugation, preferred configurations and solvent effects. Steric effects appear to favor the s-cis configuration when no hydrogen is present on the beta carbon. Moments for ethyl methyl ketone and isopropyl methyl ketone were also determined.

The influence of alpha-methyl group hyperconjugation in reducing the electric moments of certain unsaturated aldehydes and nitriles through the generation of hyperconjugated resonance structures in opposition to the primary moments has been discussed by Smyth.[2]

The influence of solvent on contribution of polar resonance structures in the case of anilines substituted in the para positions by electron withdrawing groups has been reported for dioxane solutions, which yielded higher apparent moments than benzene solutions.[3] Increased contributions from polar structures in dioxane were attributed to stabilization by hydrogen bonding, i.e., OC_4H_8O

$$\cdots\ H_2\overset{+}{N}{=}C_6H_4{=}C{=}N^{-}.$$

The compounds chosen for this investigation were mostly unsaturated methyl ketones with methyl groups in several positions subject to hyperconjugation. Determinations were made in benzene and dioxane solutions to observe the influences

(1) Presented at the 8th Southwest Regional Meeting of the American Chemical Society, Little Rock, Arkansas, December 4–6, 1952.

(2) R. E. Burk and O. Grummitt, Editors, "Chemical Architecture," Interscience Publishers, Inc., New York, N. Y., 1948, pp. 23–51.

(3) C. Curran and G. K. Estok, THIS JOURNAL, 72, 4575 (1950).

of resonance, methyl hyperconjugation, favored configurations, and solvents.

Experimental

Preparation and Purification of Compounds.—Boiling points reported for compounds have been corrected to 760 mm.

Mesityl oxide, an Eastman Kodak Co. White Label product was carefully fractionated through a metal helix packed column at reduced pressure; b.p. 129°, n^{25}D 1.4438, d^{25}_4 0.8597.

Methylmesityl oxide (3,4-dimethyl-3-penten-2-one) was obtained at an earlier date by careful fractionation from the several products obtained by the acetylation of trimethylethylene with acetic anhydride in the presence of anhydrous zinc chloride.[4] The compound was purified again by careful fractionation at reduced pressure just prior to use; b.p. 149°, n^{25}D 1.4500, d^{25}_4 0.8704.

Isopropenyl methyl ketone was prepared by deaminating the product formed by the reaction of ethyl methyl ketone, formaldehyde and dimethylamine hydrochloride, as reported by Hagemeyer[5]; b.p. 98°, n^{25}D 1.4212.

3,4-Dimethyl-4-penten-2-one was obtained as one of the products from the same reaction which produced methylmesityl oxide, and was similarly purified; b.p. 131°, n^{25}D 1.4230, d^{25}_4 0.8406.

Ethyl methyl ketone, b.p. 79.5°, n^{25}D 1.3774, d^{25}_4 0.8023, and **isopropyl methyl ketone**, b.p. 94°, n^{25}D 1.3860, d^{25}_4

(4) G. Estok, M.S. Thesis, The Pennsylvania State College, 1947.

(5) H. J. Hagemeyer, Jr., THIS JOURNAL, 71, 1119 (1949).