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ESTIMATION OF SOLUBILITY PARAMETERS FOR POLY(VINYL ACETATE) BY INVERSE GAS CHROMATOGRAPHY

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SUMMARY

Infinite dilution weight fraction activity coefficients, $(a_1/w_1)^\infty$, partial molar heats of mixing, $\Delta\bar{H}_1^\infty$, and Flory–Huggins interaction parameters, χ , were determined for 11 hydrocarbons in poly(vinyl acetate) (120–150°C) by the gas chromatographic method. Hildebrand–Scatchard solubility theory was combined with Flory theory in order to estimate infinite dilution solubility parameters (δ_2^∞) for the polymer at 135°C (8.5 ± 0.4) and 25°C (10.2 ± 0.5), respectively.

INTRODUCTION

The solubility parameter concept has found extensive application in various polymer–solvent systems. Hildebrand–Scatchard solution theory defines the solubility parameter, δ [(cal/cm³)^{1/2}] for any compound as the square root of the cohesive energy density

$$\delta = (\Delta E_v/V)^{1/2} \quad (1)$$

where ΔE_v is the molar energy of vaporization and V is the molar volume of the compound, both referred to the same temperature¹.

Since high-molecular-weight polymers have no appreciable vapor pressure and an ill-defined molar volume, there is presently no direct experimental determination of the solubility parameter for a polymer. This value has been generally deduced from measurements of swelling, solubility, viscosity, or calculated from an approximate theory. Although useful, these methods are often tedious and time consuming.

DiPaola-Baranyi and Guillet² have demonstrated that the gas chromatographic technique could readily give consistent estimates of polymer solubility parameters at infinite dilution of the probe (δ_2^∞). Thermodynamic interaction parameters (weight fraction activity coefficients at infinite dilution, $(a_1/w_1)^\infty$, partial molar heats

of mixing, $\Delta\bar{H}_1^\infty$, partial molar free energies of mixing, $\Delta\bar{G}_1^\infty$, and Flory-Huggins interaction parameters, χ) were evaluated for 13 hydrocarbons in polystyrene (178–208°C) and 19 hydrocarbons in poly(methyl acrylate) (88–112°C).

In contrast to the poor correlation shown by the heat of mixing data with solubility theory¹,

$$\Delta\bar{H}_1^\infty = V_1(\delta_1 - \delta_2)^2 \quad (2)$$

the free energy parameters ($\Delta\bar{G}_1^\infty$, χ) gave much better agreement with theory. V_1 and δ_1 refer to the molar volume and solubility parameter of the probe.

The χ parameter gave the most self-consistent and reasonable estimates of solubility parameters for both polymers: 7.6 ± 0.2 for polystyrene (193°C), and 8.7 ± 0.3 for poly(methyl acrylate) (100°C). Flory theory was combined with Hildebrand-Scatchard solubility theory in order to calculate polymer solubility parameters δ_2 from χ^{3-8} .

$$\chi = (V_1/RT)(\delta_1 - \delta_2)^2 \quad (3)$$

where χ has free energy characteristics, *i.e.*,

$$\chi = \chi_H + \chi_S \quad (4)$$

Values of δ_2^∞ for the polymers were also estimated at 25°C, from χ values obtained by extrapolation of the high-temperature data. This procedure resulted in good agreement with literature values of δ_2 obtained by conventional methods.

The successful application of this technique to another synthetic polymer, poly(vinyl acetate), is reported.

EXPERIMENTAL

All materials (reagent grade) were obtained from standard laboratory supply sources, and were used without further purification. Poly(vinyl acetate) B1000 ($\bar{M}_n = 86,000$), was a product of Wacker Chemicals (Munich, G.F.R.).

The column was prepared in the usual manner. Poly(vinyl acetate) was dissolved in benzene and then deposited on Chromosorb G AW DMCS (70–80 mesh) by slow evaporation of the solvent. After vacuum drying for *ca.* 48 h with slight heating, the coated support (10.00% loading) was packed into a copper column (44 in. \times 0.25 in. O.D.). The weight of polymer in the column was 1.3148 g.

Retention data were obtained on a Hewlett-Packard 5840A gas chromatograph. Details of the experimental procedure are given in previous publications^{1,2}.

Data reduction

Specific retention volumes, V_g , were computed from the relation⁹

$$V_g = (t_R F/w_L) J_2^2 (760/P_o) \quad (5)$$

where t_R is the net retention time, F is the flow-rate at 273.16°K (760 mm Hg), w_L is the mass of polymer in the column and J_2^3 is given by the relation¹⁰

$$J_2^3 = (3/2)\{[(P_i/P_o)^2 - 1]/[(P_i/P_o)^3 - 1]\} \quad (6)$$

where P_i and P_o are the inlet and outlet pressures.

Solute vapor pressures were computed from the Antoine equation

$$\log p_1^0 = A - B/(t + C) \quad (7)$$

where p_1^0 is the solute vapor pressure in mm Hg, t is the temperature (°C) and A , B , C are constants taken from standard sources¹¹.

Solute densities were obtained from various sources, including the compilations of Orwoll and Flory¹², International Critical Tables¹³ and Timmermans¹⁴. If density data for a solute were not available in the required temperature range, then data from lower temperatures were extrapolated to the required range.

Second virial coefficients, B_{11} , were computed from

$$B_{11}/V_c = 0.430 - 0.886 (T_c/T) - 0.694 (T_c/T)^2 - 0.0375 (n - 1) (T_c/T)^{4.5} \quad (8)$$

where \bar{V}_c and T_c are the critical volume and temperature, T is the temperature (°K) and n is the number of carbon atoms of the n -alkane¹⁵.

For the other hydrocarbons investigated, an effective number of carbon atoms, n_A , was estimated, and replaced n in eqn. 8. n_A takes on the value of n of the n -alkane having the same value for the vapor pressure parameter A , in

$$\ln(P_c/p) = A(T_c - T)/T \quad (9)$$

where P_c and T_c are the critical pressure (mm Hg) and temperature (°K), respectively, and p is the saturation vapor pressure (mm Hg) of the solute at temperature T (°K)¹⁶.

Weight fraction activity coefficients at infinite dilution were then calculated from the following relationship¹⁷:

$$\ln(a_1/w_1)^\infty = \ln(273.16R/p_1^0 V_g M_1) - p_1^0 (B_{11} - V_1)/RT \quad (10)$$

where V_1 and M_1 are the molar volume and molecular weight of the probe molecule, and R is the gas constant. Chi parameters were calculated using the following equation^{18,19}:

$$\chi = \ln(273.16Rv_2/p_1^0 V_g V_1) - 1 - p_1^0 (B_{11} - V_1)/RT \quad (11)$$

where v_2 is the specific volume of the polymer²⁰.

RESULTS AND DISCUSSION

Experimental retention volumes, derived activity coefficients (weight fraction) and χ parameters for several hydrocarbons in poly(vinyl acetate) at $T > T_g$ (120–

150°C) are tabulated and are available upon request (ca. 7–12 experimental points per solute).

Tables I and II list activity coefficients and χ parameters for the various solutes at selected temperatures. In all cases, activity coefficients and χ parameters decrease with increasing temperature, suggesting that the solubility of the hydrocarbons in the polymer increases accordingly. The largest activity coefficients and χ parameters are observed for the *n*-alkanes.

TABLE I

WEIGHT FRACTION ACTIVITY COEFFICIENTS, $(a_1/w_1)^\infty$, OF SELECTED SOLUTE-POLY(VINYL ACETATE) SYSTEMS AT SEVERAL TEMPERATURES

The reliability of the present $(a_1/w_1)^\infty$ values, based on repeated measurements, is within 1–2%.

Solute	Temperature (°C)		
	125	135	145
<i>n</i> -Nonane	37.15	34.15	31.78
<i>n</i> -Decane	41.32	38.04	35.13
<i>n</i> -Undecane	46.62	42.51	38.99
<i>n</i> -Dodecane	53.47	48.37	43.98
3,3,4,4-Tetramethylhexane	24.08	22.43	20.81
Cyclohexane	16.90	15.93	—
<i>n</i> -Butylcyclohexane	27.92	25.73	24.22
<i>cis</i> -Decalin	19.17	17.67	16.54
Benzene	5.71	5.73	5.72
<i>n</i> -Butylbenzene	10.03	9.68	9.43
Tetralin	7.76	7.52	7.30

TABLE II

 χ PARAMETERS OF SELECTED SOLUTE-POLY(VINYL ACETATE) SYSTEMS AT SEVERAL TEMPERATURES

The precision on χ , as estimated from repeated measurements, is better than 5%.

Solute	Temperature (°C)		
	125	135	145
<i>n</i> -Nonane	2.055	1.963	1.883
<i>n</i> -Decane	2.186	2.097	2.010
<i>n</i> -Undecane	2.326	2.228	2.136
<i>n</i> -Dodecane	2.479	2.374	2.273
3,3,4,4-Tetramethylhexane	1.719	1.643	1.563
Cyclohexane	1.332	1.264	—
<i>n</i> -Butylcyclohexane	1.903	1.818	1.754
<i>cis</i> -Decalin	1.650	1.567	1.498
Benzene	0.370	0.365	0.354
<i>n</i> -Butylbenzene	0.950	0.910	0.881
Tetralin	0.832	0.799	0.769

Table III summarizes heats of solution (ΔH_s) and partial molar heats of mixing ($\Delta \bar{H}_1^\infty$) for the hydrocarbons in poly(vinyl acetate) at 135°C. The partial molar heat of mixing ($\Delta \bar{H}_1^\infty$) of the solute at infinite dilution in the polymer is given by

TABLE III

HEATS OF SOLUTION AND PARTIAL MOLAR HEATS OF MIXING OF SEVERAL HYDROCARBONS IN POLY(VINYL ACETATE)

Solute	Temperature range (°C)	$-\Delta H_s$ (kcal/mol)	$\Delta \bar{H}_1^\infty$ (kcal/mol)
<i>n</i> -Nonane	120–150	6.75 ± 0.03	2.57 ± 0.04
<i>n</i> -Decane	120–150	7.61 ± 0.04	2.72 ± 0.04
<i>n</i> -Undecane	120–150	8.38 ± 0.02	2.95 ± 0.02
<i>n</i> -Dodecane	120–150	9.21 ± 0.01	3.23 ± 0.02
3,3,4,4-Tetramethylhexane	120–150	7.26 ± 0.06	2.38 ± 0.07
Cyclohexane	115–135	4.57 ± 0.11	2.19 ± 0.12
<i>n</i> -Butylcyclohexane	120–150	7.72 ± 0.04	2.48 ± 0.05
<i>cis</i> -Decalin	125–145	8.24 ± 0.03	2.43 ± 0.05
Benzene	120–150	6.86 ± 0.03	−0.04 ± 0.03
<i>n</i> -Butylbenzene	125–145	9.46 ± 0.02	1.02 ± 0.03
Tetralin	125–145	10.31 ± 0.03	0.95 ± 0.03

$$\Delta \bar{H}_1^\infty = R \partial \ln(a_1/w_1)^\infty / \partial (1/T) \quad (12)$$

Heats of solution are obtained from the temperature dependence of the specific retention volume

$$\Delta H_s = -R \partial (\ln V_g) / \partial (1/T) \quad (13)$$

The uncertainty limits in Table III refer to the standard error in the slope, as given by a linear least squares analysis of the data.

The solubility parameter, δ_2 , for poly(vinyl acetate) at 135°C was evaluated in the manner previously discussed², by combining Flory theory with Hildebrand-Scatchard solution theory

$$\frac{\delta_1^2}{RT} - \frac{\chi}{V_1} = \frac{2\delta_2}{RT} \delta_1 - \frac{\delta_2^2}{RT} \quad (14)$$

TABLE IV

SOLUTE SOLUBILITY PARAMETERS AT 135°C

Solute	V_1 (135°) (cm ³ /mol)	ΔH_v (135°)** (kcal/mol)	$\delta_{1(135)}^*$	$\frac{\delta_1^2}{RT} - \frac{\chi}{V_1}$
<i>n</i> -Nonane	205.84	9.32 ± 0.07	6.43	0.04144
<i>n</i> -Decane	222.53	10.33 ± 0.08	6.53	0.04315
<i>n</i> -Undecane	239.61	11.33 ± 0.04	6.62	0.04473
<i>n</i> -Dodecane	256.91	12.44 ± 0.03	6.72	0.04644
3,3,4,4-Tetramethylhexane	206.64	9.65 ± 0.13	6.53	0.04463
Cyclohexane	126.87	6.76 ± 0.22	6.85	0.04790
<i>n</i> -Butylcyclohexane	196.14	10.20 ± 0.10	6.91	0.04961
<i>cis</i> -Decalin	170.66	10.67 ± 0.09	7.60	0.06204
Benzene	104.00	6.82 ± 0.05	7.60	0.06772
<i>n</i> -Butylbenzene	174.99	10.47 ± 0.05	7.43	0.06287
Tetralin	149.73	11.27 ± 0.06	8.35	0.08063

* $\delta_1 = [(\Delta H_v - RT)/V_1]^{1/2}$.** ΔH_v = molar heat of vaporization.

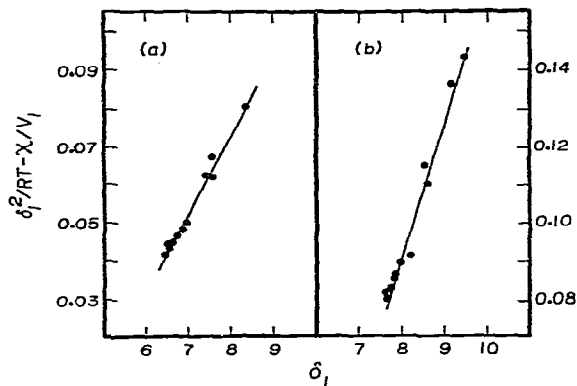


Fig. 1. Estimation of solubility parameter for poly(vinyl acetate): (a) 135°C, δ_2 (slope) = 8.4 ± 0.4 , δ_2 (intercept) = 8.6 ± 0.3 ; (b) 25°C, δ_2 (slope) = 10.1 ± 0.5 , δ_2 (intercept) = 10.3 ± 0.4 .

Molar volumes, V_1 , and solubility parameters, δ_1 , for the solutes are found in Table IV. A plot of $(\delta_1^2/RT - \chi/V_1)$ against δ_1 of the probe (11 data points) yields a straight line with a slope of $(2\delta_2/RT)$ and an intercept of $-\delta_2^2/RT$ (Fig. 1a). A least squares analysis yields an average value of 8.5 ± 0.4 for δ_2 at 135°C (Table V).

TABLE V

ESTIMATED SOLUBILITY PARAMETERS OF POLY(VINYL ACETATE)

	δ_2	
	135°C	25°C
Slope	8.4 ± 0.4	10.1 ± 0.5
Intercept	8.6 ± 0.3	10.3 ± 0.4
Literature		9.5-9.7*

* From ref. 20. Values as low as 8.8 and as high as 11.0 for δ_2 have also been reported in ref. 21.

The temperature dependence of the χ parameters in the range investigated (120–150°C) fits an equation of the form

$$\chi = \alpha + \beta/T \quad (15)$$

The constants α and β were determined from a linear least squares analysis and are summarized in Table VI. In most cases, the linear correlation is excellent. Assuming that this relationship remains valid at lower temperatures, extrapolation yields a value for χ at 25°C. The χ values so obtained are listed in Table VII. Literature values for V_1 are also included.

Using the δ_1 values for the solutes at 25°C from Table IV, values of δ_2 for the polymer were obtained from the slope and intercept of a plot of $(\delta_1^2/RT - \chi/V_1)$ against δ_1 . This is shown in Fig. 1b. The value of δ_2 for poly(vinyl acetate) at 25°C obtained in this manner is only slightly higher than the average δ_2 value obtained by conventional methods³. The solubility parameter defined by eqn. 14 is not identical

TABLE VI
TEMPERATURE DEPENDENCE OF THE χ PARAMETER OF SELECTED SOLUTES IN POLY(VINYL ACETATE)

Solute	Slope (β) ^a	Correlation coefficient	Intercept (α) ^a	Temperature range (°C)
<i>n</i> -Nonane	1426.1	1.0000	-1.532	120-150
<i>n</i> -Decane	1479.9	0.99966	-1.529	120-150
<i>n</i> -Undecane	1584.4	1.0000	-1.655	120-150
<i>n</i> -Dodecane	1711.3	1.0000	-1.821	120-150
3,3,4,4-Tetramethylhexane	1283.7	0.99645	-1.507	120-150
Cyclohexane	1247.0	0.99304	-1.796	115-135
<i>n</i> -Butylcyclohexane	1305.6	0.99837	-1.376	120-150
<i>cis</i> -Decalin	1263.2	0.99762	-1.531	125-145
Benzene	131.8	0.93933	0.041	120-150
<i>n</i> -Butylbenzene	573.1	0.99714	-0.492	125-145
Tetralin	504.7	0.99602	-0.436	125-145

^a The data were fitted to an equation of the form $\chi = \alpha + \beta/T$.

TABLE VII
EXTRAPOLATED χ VALUES AT 25°C FOR VARIOUS PROBES IN POLY(VINYL ACETATE)

Solute	V_1 (cm^3/mol)	δ_1	χ	$\frac{\delta_1^2}{RT} - \frac{\chi}{V_1}$
<i>n</i> -Nonane	179.67	7.64	3.251	0.08050
<i>n</i> -Decane	195.90	7.72	3.434	0.08314
<i>n</i> -Undecane	212.19	7.80	3.659	0.08553
<i>n</i> -Dodecane	228.58	7.84	3.919	0.08668
3,3,4,4-Tetramethylhexane	182.80	7.61	2.798	0.08251
Cyclohexane	108.74	8.19	2.386	0.09136
<i>n</i> -Butylcyclohexane	176.31	7.95	3.002	0.08973
<i>cis</i> -Decalin	154.81	8.68	2.705	0.10980
Benzene	89.40	9.15	0.484	0.13601
<i>n</i> -Butylbenzene	156.78	8.58	1.429	0.11524
Tetralin	136.82	9.49	1.256	0.14295

to that conventionally measured by swelling, solubility or surface tension data, since these are at concentrations where the probe is highly concentrated. In the present case, the probe is at infinite dilution in the polymer. However, there appears to be little difference between our δ_2^∞ value at 25°C for poly(vinyl acetate) and that found in the literature. This was also the case for polystyrene and poly(methyl acrylate)¹. This work suggests that the infinite dilution polymer solubility parameters (δ_2^∞) measured by gas chromatography may be useful in deriving fundamental information about polymer solubility, even at finite concentrations.

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