Determination of the solubility parameter of poly(ethylene oxide) at 25°C by gas–liquid chromatography

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The solubility parameter of poly(ethylene oxide) at 25°C has been determined using the method developed by DiPaola-Baranyi and Guillet, by the extrapolation of the values of the interaction parameter χ, at high temperatures, ranging from 70°–90°, 90°–110° and 110°–130°C down to 25°C. The values of the solubility parameter obtained, depending on the temperature ranges employed, are 9.8, 9.9 and 10.1, respectively.

Keywords Poly(ethylene oxide); solubility parameters; interaction parameters; inverse gas chromatography; activity coefficients; heats of mixing

INTRODUCTION

The solubility parameter concept based on regular solution theory has been used extensively in practical applications of polymers in various solvents and solvent mixtures.

The solubility parameter, δ_1 (units of (cal cm^{-3})$^{1/2}$), for any compound is defined from Hildebrand—Scatchard solution theory as

$$\delta_1 \equiv (\Delta E_v/V_1)^{1/2} \tag{1}$$

i.e., as the square root of the cohesive energy density, which is itself defined as the ratio of the energy of vaporization, ΔE_v, to the molar volume V_1.

Solubility theory gives the energy of mixing of two liquids at constant volume, ΔE_m, as follows

$$\Delta E_m/\varphi_1\varphi_2 = V_m(\delta_1 - \delta_2)^2 \tag{2}$$

where φ_1 and φ_2 are the volume fractions of the components, V_m is the average molar volume based on mole fractions, and δ_1 and δ_2 refer to the solubility parameter of each liquid. As a first approximation and in the absence of strong interactions, such as hydrogen bonds, solubility can be expected if $\delta_1 - \delta_2$ is less than 1.7–2.0 (cal cm^{-3})$^{1/2}$, but not if it is considerably greater[1].

DiPaola-Baranyi and Guillet[2] have recently shown that inverse gas chromatography, using a polymer as the stationary phase, can be a simple and convenient method for estimating solubility parameters for polymers. The method is based on the principle that the Flory–Huggins χ parameters can be readily determined from retention data on various small molecule probes from the equation derived by Patterson *et al.*[3].

$$\chi = \ln(273.16Rv_2/P_1^0V_gV_1) - 1 - P_1^0(B_{11} - V_1)/RT \tag{3}$$

and that χ can be related to solubility parameters by Hildebrand–Scatchard theory combined with Flory theory[4] as follows

$$\chi = (V_1/RT)(\delta_1 - \delta_2)^2 \tag{4}$$

where χ has free-energy characteristics.

V_1 is the molar volume of the probe used, δ_1 is the solubility parameter of the probe, and δ_2 is the solubility parameter of the polymer. In a usual experiment, χ is determined under conditions approximating to infinite dilution of the probe in the polymer, and hence the value of δ_2 is more correctly designated δ_2^∞, since it is also an infinite dilution quantity. For reasons outlined previously[2], this quantity may have more fundamental significance than the value of δ_2 measured at finite solute concentrations by classical methods. Furthermore, at the high dilution of the experiment, it is possible that the assumptions on regular solution behaviour are more closely fulfilled.

The method has been successfully applied by DiPaola-Baranyi and Guillet to determine consistent δ_2^∞ values for polystyrene at 193°C, and poly(methyl acrylate) at 100°C, and by Ito and Guillet[5] for ethylene–propylene copolymer, *cis*-polyisoprene and amorphous polypropylene, using a variety of standard hydrocarbon solutes of different δ_1 values. δ_2^∞ values were also estimated at 25°C using interaction parameters calculated by extrapolation of the higher temperature data according to

$$\chi = \alpha + \beta/T \tag{5}$$

where the constants α and β should have characteristics of entropy and enthalpy respectively.

This empirical equation is usually valid only for relatively small ranges of temperature; however, the δ_2^∞ values thus obtained were shown to agree well with literature data, supporting the idea that the derived

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parameters might be of practical value in predicting polymer solubility even at finite concentrations.

This work extends the method to poly(ethylene oxide). As the interaction parameter varies with the temperature (or with its reciprocal) as shown in *Figure 1*, the value of the interaction parameter at 25°C, obtained by extrapolation at high temperatures, should be substantially different, depending on the temperature range used in the extrapolation.

EXPERIMENTAL

Materials

Solutes were reagent grade and were used without further purification. The following solutes of very different character were used: n-hexane, n-octane, acetone, ethyl acetate, methanol, ethanol, n-propanol, chlorobenzene, cyclohexane, benzene, toluene, and diethylene glycol diethyl ether. An effort was made to use solvent and non-solvent compounds of polymers of both polar and nonpolar nature, to extend the validity of the method to any type of solute.

The samples of poly(ethylene oxide) were obtained from Polysciences Ind., Warrington, USA ($M_w = 300\,000$).

Columns

The polymers were first dissolved in a suitable solvent (chloroform) and deposited onto an inert chromatographic support by slow evaporation of the solvent with gentle stirring and heating. After vacuum drying for *ca.* 48 h with slight heating, the chromatographic support was packed, with the aid of a mechanical vibrator, into 0.25 in o.d. stainless-steel columns. The weight and percentage of the stationary phase were determined by immediate weighing. Column parameters are described in *Table 1.*

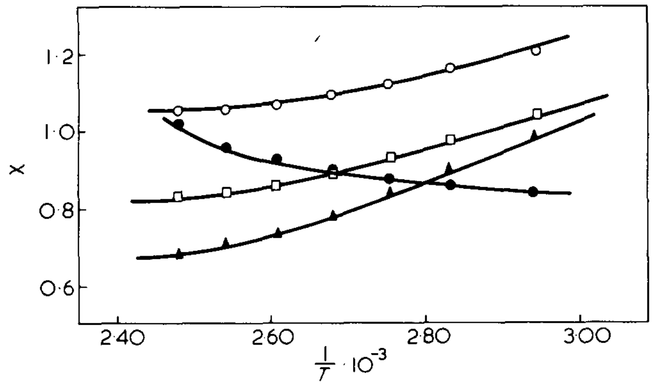

Figure 1 Variation of interaction parameter, χ, with reciprocal temperature (K) from methanol (○), n-octane (●), ethanol (□) and diethylene glycol diethyl ether (▲)

Instrumentation

Measurements were carried out on a Perkin Elmer 3920 B gas chromatograph, equipped with a dual flame ionization detector. Nitrogen was used as the carrier gas. Methane, as a non-interacting marker, was used to correct the dead volume in the column and the retention time was directly measured with a chronometer between the highest points of the peak of the methane and the solute. A minimum of 4 measurements were made for every molecular probe and for each temperature in both columns. Pressures at inlet and outlet of the column read from a mercury manometer (<0.05 mm Hg), were used to compute corrected retention volumes by the usual procedures. Flow rates were measured from the end of the column with a soap bubble flow meter. Three distinct gas flows, between 20 and 60 ml min^{-1} at 70°C were used to verify the non-variation of the volume retention with the flow. Throughout the experiment the flow was fixed at 30 ml min^{-1}. The oven was modified to accommodate a water bath to 90°C and an oil bath to 140°C. The bath temperature was controlled to within ± 0.1°C to 90°C and with a precision of ± 0.5°C for the oil bath.

The solute molecules, including a small amount of methane marker, were injected manually with a 10 μl Hamilton syringe (<0.01 μl).

To check the precision of the retention data from the Perkin-Elmer 3920 B gas chromatograph, specific retention volumes for benzene and toluene were compared with literature values[6].

DATA REDUCTION

Specific retention volumes, V_g, were calculated from the relation

$$V_g = (t_r F / w_L) J_2^3 (P_0 - P_w)/760 \qquad (6)$$

where t_r is the net retention time, F is the flow rate at 273.16 K, w_L is the mass of polymer, and J_2^3 is given by the relation

$$J_n^m = (m/n)[(P_i/P_0)^n - 1]/[(P_i/P_0)^m - 1] \qquad (7)$$

where $m = 3$, $n = 2$, and P_i and P_0 are the inlet and outlet pressures.

Solute vapour pressures were computed from the Antoine equation

$$\log P_1^0 = A - B/(t + C) \qquad (8)$$

where P_1^0 is the solute vapour pressure in mm Hg, t is the temperature (°C), and A, B and C are constants taken from standard sources[7], and also obtained from elsewhere[8,16].

Solute densities were obtained from Timmermans' compilation[8]. Second virial coefficients (B_{11}) were

Table 1 Experimental column parameters

Polymer	Coating solvent	Loading	Polymer mass (g)	Length (cm)	o.d. (inches)
Poly(ethylene oxide)	Chloroform	2.82	0.2886	100	0.25
"	"	6.04	0.7840	100	0.25

Table 2 Critical constants and deduced Antoine constants of diethylene glycol diethyl ether

T_c (K)	P_c (atm)	V_c (ml mol^{-1})	*A*	*B*	*C*
624	23.4	540	7.234284	1549.467	177.40209

Table 3 Weight fraction activity coefficients, $(a_1/w_1)^\infty$ of solute–poly(ethylene oxide) system at several temperatures

	Temperatures		
Solute	80°C	100°C	120°C
n-Hexane	15.82	14.55	13.73
n-Octane	10.54	11.13	11.94
Methanol	12.72	12.02	11.75
Ethanol	10.60	9.816	9.490
Propanol	9.208[a]	8.569	8.286
Acetone	7.725	7.625	7.736
Ethyl acetate	5.637[a]	5.672	5.864
Chlorobenzene	3.082	3.139	3.247
Benzene	4.490	4.512	4.606
DEGDEE	8.450	7.538	7.056
Cyclohexane	14.92	12.93	11.53
Toluene	5.009	4.977	5.017

[a] 82°C

computed from[9]

$$B_{11}/V_c = 0.430 - 0.886(T_c/T) - 0.694(T_c/T)^2 - 0.0375(n-1)(T_c/T)^{4.5} \quad (9)$$

for the n-hexane, n-octane, benzene, chlorobenzene, cyclohexane and diethylene glycol diethyl ether, where V_c and T_c are the critical volume and temperature respectively, T is the temperature (K) and n is the number of carbon atoms of the n-alkane, or an effective number of carbon atoms, n_a, was estimated and replaced n in equation (4)[10]. N_A takes on the value of n of the normal alkane having the same value for the vapour pressure parameter A, in the equation

$$\ln(P_c/P) = A(T_c - T)/T \quad (10)$$

where P_c and T_c are the critical pressure (mm) and temperature (K) of the solute.

Second virial coefficients for acetone, n-propanol, ethyl acetate, toluene, methanol and ethanol were determined by Kreglewski equations[11].

The vapour pressures for diethylene glycol diethyl ether, whose values were not given in the literature, were estimated by the correlations of Frost–Kalkwarf–Thodos[12]. The critical constants P_c, T_c, and V_c were evaluated by the Lydersen method[12]. The densities were measured experimentally in our laboratory. The critical constants and the deduced Antoine constants are shown in *Table 2*.

Weight fraction activity coefficients $(a_1/w_1)^\infty$ at infinite dilution were then calculated from the following relationship[3]

$$\ln(a_1/w_1)^\infty = \ln(273.16R/P_1^0 V_g M_1) - P_1^0(B_{11} - V_1)/RT \quad (11)$$

where V_1 and M_1 are the molar volume and molecular weight of the probe molecule, and R is the gas constant. χ parameters were calculated from

$$\chi = \ln(273.16 R v_2/P_1^0 V_g V_1) - 1 - P_1^0(B_{11} - V_1)/RT \quad (12)$$

where v_2 is the specific volume of polymer and is known from the literature[13].

RESULTS AND DISCUSSION

The experimental retention volumes, activity coefficients (weight fraction) and χ parameters for 12 solutes between 70° and 140°C were tabulated. Retention volumes were obtained for at least 8 temperatures, over each temperature range of 20°C.

Weight fraction activity coefficients (corrected for vapour phase non-ideality) of solutes in PEO at several temperatures are given in *Table 3*.

As shown in *Table 3* the activity coefficients do not necessarily decrease with the rise in temperature, which supposes that the solubility can increase or decrease according to the polymer–solute system. Thus, the solubility for n-octane decreases as the temperature rises. In the case of acetone a maximum solubility must exist at some temperature between 80° and 120°C.

The maximum activity coefficients are given for hydrocarbons, cyclohexanes and n-hexane, non-solvent compounds of the polymer and for the alcohols methanol and ethanol with hydrogen bonds in the liquid phase. The interaction parameters χ, similar to the activity coefficients, do not necessarily decrease with the rise of temperature, as can be seen in *Figure 1*, and as observed in literature.

The partial molar heat of mixing $\overline{\Delta H}_1^\infty$ of the solute at infinite dilution in the polymer is given by

$$\overline{\Delta H}_1^\infty = R\,\partial \ln(a_1/w_1)/\partial(1/T) \quad (13)$$

Therefore $\overline{\Delta H}_1^\infty$ was obtained from the slope of the best straight line through a plot of the logarithm of the activity coefficient vs. the reciprocal of the absolute temperature, as determined by a linear least-squares analysis. Partial molar heats of the 12 solutes in PEO are given in *Table 4* in the three temperature ranges, together with the corresponding heats of solution, determined in a similar manner from

$$\Delta H_s = -R\,\partial(\ln V_g)/\partial(1/T) \quad (14)$$

The molar enthalpies of vaporization at 100°C calculated from the relationship

$$\overline{\Delta H}_v^\infty = \overline{\Delta H}_1^\infty - \Delta H_s \quad (15)$$

are shown in *Table 4*.

Table 4 Partial molar heats of mixing, heats of solutions, enthalpies of vaporization and molar enthalpies of vaporization of several solutes in PEO

Solute	Temperature range (°C)	$\Delta\bar{H}_1^{\infty}$ (cal mol^{-1})	$-\Delta H_S$ (cal mol^{-1})	ΔH_V (at 100°C) (kcal mol^{-1})
n-Hexane	70–90	1159	5701	–
	90–110	992	"	6.69
	110–130	744	"	–
n-Octane	70–90	–572	9681	–
	90–110	–870	"	8.81
	110–130	–1159	"	–
Methanol	70–90	903	7470	–
	90–110	545	"	8.02
	110–130	112	"	–
Ethanol	70–90	1406	7966	–
	90–110	784	"	8.75
	110–130	–	"	–
Propanol	70–90	1523	8759	–
	90–110	871	"	9.63
	110–130	89	"	–
Acetone	70–90	270	6704	–
	90–110	–88.6	"	6.62
	110–130	–207	"	–
Ethyl acetate	70–90	–	7717	–
	90–110	–316	"	7.40
	110–130	–670	"	–
Chlorobenzene	70–90	–129	9360	–
	90–110	–384	"	8.98
	110–130	–605	"	–
Benzene	70–90	55.5	7396	–
	90–110	–181	"	7.21
	110–130	–421	"	–
DEGDEE	70–90	1787	11944	–
	90–110	1226	"	13.17
	110–130	712	"	–
Cyclohexane	70–90	2032	5217	–
	90–110	1783	"	7.00
	110–130	1585	"	–
Toluene	70–90	206	8304	–
	90–110	–17.2	"	8.29
	110–130	–214	"	–

Table 5 Solute solubility parameters at 80°, 100° and 120°C

Solute	25°C^a	80°C	100°C	120°C
n-Hexane	7.24	6.56	6.33	6.03
n-Octane	7.57	6.93	6.69	6.46
Methanol	14.5	13.26	12.74	12.15
Ethanol	12.7			
Propanol	11.9	10.96	10.40	9.76
Acetone	9.71	8.83	8.41	8.10
Ethyl acetate	9.04	8.13	7.75	7.38
Chlorobenzene	9.50	8.89	8.63	8.40
Benzene	9.15	8.39	8.10	7.82
DEGDEE	9.03	8.27	7.98	7.71
Cyclohexane	8.18	7.50	7.23	6.99
Toluene	8.91	8.24	7.99	7.75

^{a} Data obtained from literature

As can be seen the heat of mixing decreases with the temperature in all cases despite the fact that the activity coefficient increases in some cases. Thus, the activity coefficient for the n-octane increases as the temperature rises, while the mixing heat decreases. The enthalpy of vaporization for the n-octane is 8.81 at 100°C in good accord with data of DiPaola-Baranyi and Guillet[2] who give 8.79 at the same temperature.

The solubility parameters (δ_1) for the solutes were calculated for the different solutes from the relation:

$$\delta_1=[(\Delta H_v-RT)/V_1]^{1/2} \qquad (16)$$

where R is the gas constant and V_1 is the solute molar volume corresponding to temperature T(K), which was chosen as the midpoint of the temperature range investigated (80°, 100° and 120°C).

The units of δ_1 are (cal cm^{-1})$^{1/2}$. These calculated values are summarized in *Table 5*. The values which could be compared with those in the literature[2,5] are very much in agreement.

The solubility parameters for solutes at 25°C were obtained from the literature, excepting the diethylene glycol diethyl ether which was obtained by extrapolation of the values at high temperatures.

Following the method developed by DiPaola-Baranyi and Guillet which combines the theory of Flory with that of Hildebrand–Scatchard, equation (3) can be rewritten in the following way

$$(\delta_1^2/RT-\chi/V_1)=(2\delta_2/RT)\delta_1-\delta_2^2/RT \qquad (17)$$

Therefore a plot of $(\delta_1^2/RT-\chi/V_1)$ vs. δ_1 of the probe will give a straight line with a slope of $2\delta_2/RT$ and an intercept of $-\delta_2^2/RT$. The results at 80° and 100°C are illustrated in *Figures 2* and *3*. Slopes and intercepts were obtained from a linear least-squares analysis. Derived values of δ_2 for the polymer are listed in *Table* 6. The

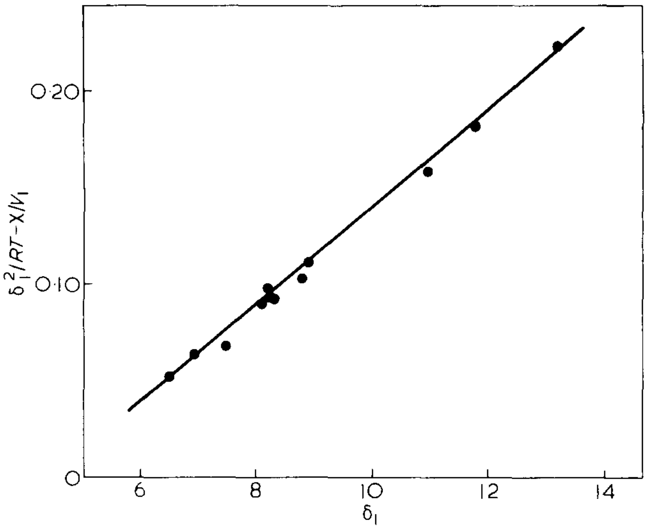

Figure 2 Estimation of solubility parameter (δ_2) of the PEO from the χ parameter at 80°C

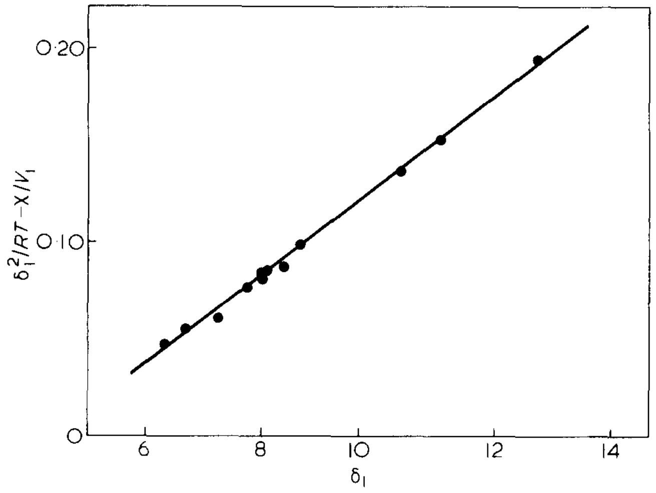

Figure 3 Estimation of solubility parameter (δ_2) of the PEO from the χ parameter at 100°C

Table 6 Solubility parameters of REO at 80°, 100° and 120°C

	80°C	100°C	120°C
Slope	8.99	8.60	8.18
Intercept	9.09	8.72	8.34

solubility parameters estimated in this way are 9.04, 8.66 and 8.26 at 80°, 100° and 120°C respectively.

Solubility parameters for poly(ethylene oxide) were not found in literature and it was possible to estimate their value at 25°C only by means of the Small method[15]. The value of the solubility parameter estimated in this way results as 10.2 (cal cm^{-3})$^{1/2}$. This does not clash, in any way, with the values obtained at high temperatures. In this work it can be seen that the method can be extended to the use of any type of solute, be it polar or non-polar, solvent or non-solvent of the polymer, etc. The correlation of the equation (17) by using all the solutes is very good.

As the solubility parameter was estimated at 25°C and as this parameter is normally given at this temperature in the literature, it was considered necessary to calculate that parameter at the described temperature. The interaction parameter χ at 25°C can be deduced from equation (5); the graphic representation of χ vs. $1/T$, for narrow temperature ranges, in general gives straight lines which can be extrapolated to 25°C. The constants α and β obtained by least-squares analysis in the 70°–90°C range, together with the correlation coefficient are shown in *Table 7*.

However, the interaction parameter must undoubtedly depend on the range of temperatures used, as equation (5) does not hold for a wide temperature range. On account of the lack of standards for the selection of an adequate temperature range, the extrapolation was carried out with three temperature ranges 70–90°C, 90°–110°C and 110°–130°C; the interaction parameters thus obtained are shown in *Table 8*.

As can be seen in *Table 7* the value for the interaction parameter obtained from three temperature ranges, shows a minimum variation of 6% for the n-hexane, and a maximum of 200% for the chlorobenzene.

Using the solubility parameter for the solutes at 25°C from *Table 5* values for δ_2 for the polymer were obtained from the slope and intercept of the plot of $\delta_1^2/RT-\chi/V_1$ against δ_1. The plots are shown in *Figure 4* and *Figure 5* in the temperature ranges 70°–90°C and 110°–130°C. The numerical values of δ_2 obtained in this manner are shown in *Table 9*.

The values obtained in this way are in agreement with the value estimated by the contribution of the groups,

Table 7 Dependence of the interaction parameter, χ, with the reciprocal temperature in the range 70°–90°C

Solute	Slope, β	Correlation coefficient	Intercept, α
n-Hexane	713.72	0.997	−0.840497
n-Octane	−215.95	0.995	1.46667
Methanol	514.87	0.997	−0.293372
Ethanol	807.51	0.992	−1.308776
Propanol	843.27	0.982	−1.507339
Ethyl acetate	92.861	0.726	0.197946
Chlorobenzene	−26.854	−0.515	0.16837
Benzene	92.570	0.983	−0.03883
DEGDEE	935.02	0.999	−1.745977
Cyclohexane	1096.14	0.9997	−1.801445
Toluene	179.007	0.992	−0.189591
Acetone	232.10	0.992	−0.011434

Table 8 Interaction parameters, χ, of solute–PEO systems at 25°C from three temperature ranges

Solute	From range 70°–90°C	From range 90°–110°C	From range 110°–130°C
n-Hexane	1.553	1.520	1.464
n-Octane	0.7424	0.6620	0.5834
Methanol	1.433	1.331	1.187
Ethanol	1.400	1.221	1.018
Propanol	1.321	1.139	0.8679
Ethyl acetate	0.5094	0.4368	0.3397
Chlorobenzene	0.0783	0.00772	−0.0722
Benzene	0.2716	0.2095	0.1327
DEGDEE	1.390	1.227	1.0432
Cyclohexane	1.875	1.805	1.733
Toluene	0.4108	0.3486	0.2735
Acetone	0.7670	0.6654	0.6150

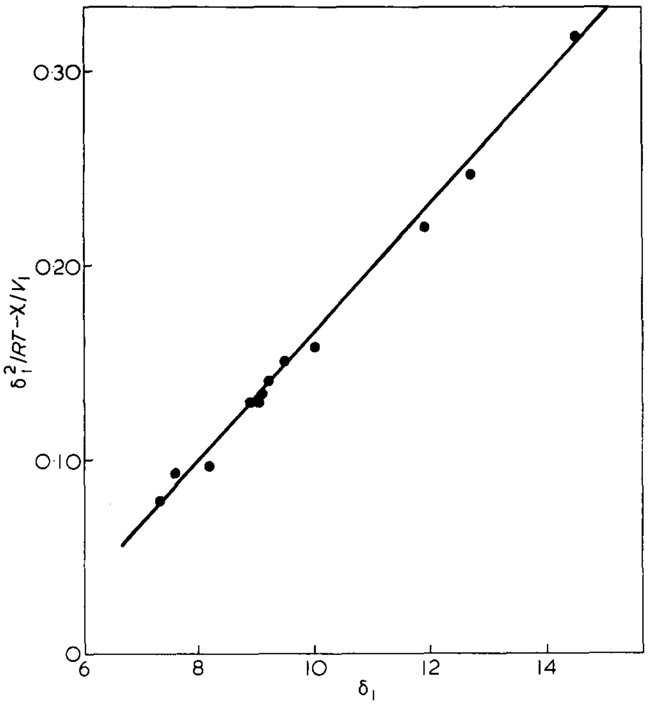

Figure 4 Estimation of solubility parameter (δ_2) of the PEO at 25°C from the interaction parameter values in the temperature range 70°–90°C

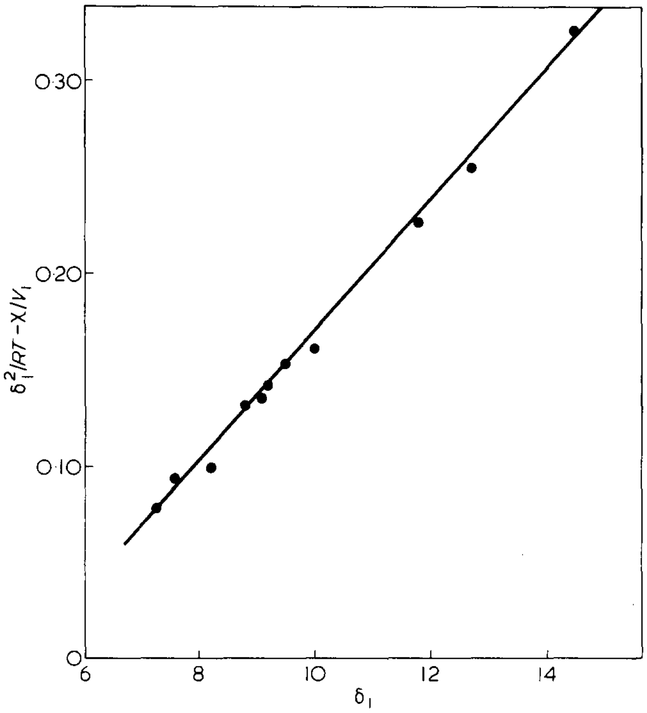

Figure 5 Estimation of solubility parameter (δ_2) of the PEO at 25°C from the interaction parameter values in the temperature range 110°–130°C

being 10.2. This suggests that the method is useful for the estimation of solubility parameters of polymers at any temperature, and that the value for the interaction parameter χ which was used does not have any great influence.

The validity of the use of extrapolation at high temperatures for obtaining the interaction parameter χ at 25°C, will require further study.

Table 9 Estimated solubility parameters of poly(ethylene oxide) at 25°C

	From temperature range, 70°–90°C	From temperature range, 90°–110°C	From temperature range, 110°–130°C
Slope	9.77	9.89	10.07
Intercept	9.88	9.97	10.1

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