

Solubility Parameters of Two Chlorinated Polyethylene Polymers

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Synopsis

An equation that appears adequate for the calculation of the solubility parameter of random copolymers was tested with two nonrandom copolymers, chlorinated polyethylene (CPE) AK 227 and AK 243, containing 27.8% and 42.1% chlorine, respectively. Flory's equation relating the energy of interaction between polymer and diluent to the depression of the melting point of the pure polymer was used to estimate the solubility parameter of the polymers from solution temperature studies in chlorobenzene, toluene, *o*-xylene, and *p*-xylene. Using data obtained on PE as a criterion, agreement within 3% was obtained between the reported δ -value and that estimated from solution temperature studies when toluene, *o*-xylene, and *p*-xylene were used as diluents. In the case of the two CPE polymers, values for the gas constant and for the heat of fusion in units of cal/cm³ polymer °K and cal/cm³ polymer, respectively, were obtained by solving simultaneous equations. From the derived gas constant values, the weight of an average repeating unit of CPE polymer was obtained, 39.38 for AK 227 and 46.95 for AK 243, which compares favorably with values obtained using the expression $n_1M_1 + n_2M_2 = M_x$. For ΔH , the results showed that in going from PE to CPE, a reversal in the sign of ΔH occurs indicating that, in the diluents studied, the value of χ is positive in the case of PE and negative for the CPE polymers. Taking this into account, agreement between calculated δ -values and those estimated from solution temperature studies is within 2% for AK 227 (toluene, *o*-xylene, *p*-xylene) and within 1% for AK 243 when toluene and *o*-xylene were used as diluents. Anomalous results were obtained in the latter case when *p*-xylene and chlorobenzene were used as diluents and from solution temperature studies of PE in chlorobenzene. The results do indicate that the equation used to calculate the solubility parameter of random copolymers may also be used for nonrandom copolymers such as CPE.

INTRODUCTION

Equation (1)¹ appears adequate for calculating the solubility parameter of random copolymers from data obtained on the components of the copolymer.

$$\delta_x = \frac{(n_1M_1^2/\rho_1)\delta_1 + (n_2M_2^2/\rho_2)\delta_2}{\{n_1M_1 + n_2M_2\} \{[(n_1M_1^2/\rho_1) + (n_2M_2^2/\rho_2)][1/\rho_x]\}^{1/2}} \quad (1)$$

where n , M , ρ , and δ refer, respectively, to number of moles, monomer molecular weight, density, and solubility parameter, and the subscripts 1, 2, and x refer, in turn, to components 1, 2, and mixture. Solubility

parameter values calculated by use of eq. (1) for eight random copolymers agreed satisfactorily¹ with experimentally determined values in six instances. However, it was not known if the treatment may be applicable to nonrandom copolymers. Therefore, the solubility parameters of two nonrandom copolymers were determined experimentally in order to compare the results with values calculated by use of eq. (1). Chlorinated polyethylene (CPE) polymers obtained from ICI, Ltd., were used since they are reportedly² not obtained from solution chlorination and probably are not strictly random.

CPE is obtained² by chlorination of polyethylene, and the properties of the parent polyethylene affect the properties of the chlorinated product. Chlorination of PE results in a reduction in crystallinity leading to greater flexibility and a stiffening due to insertion of chlorine atoms.² CPE can be considered, then, as a polymer containing various concentrations of chlorine compounds arranged on a chain to provide monochloro- and *vic*-dichloro-substituted carbon atoms together with groupings of ethylene units which have no substituted hydrogen atoms. It is generally thought that CPE contains little, if any, groupings corresponding to vinylidene chloride substitution. If it is assumed that the distribution and amount of the chlorine compounds correspond to that normally found in a usual PVC homopolymer, then CPE can be visualized as a copolymer of ethylene and vinyl chloride, $(\text{CH}_2\text{CH}_2)_m(\text{CH}_2\text{CHCl})_n$, where the subscripts m and n refer to the number of PE and PVC units, respectively. The chlorine content of AK 227 was found to be 27.8%, while that of AK 243 was 42.1%. In order to obtain polymers corresponding to these chlorine contents, the values for m and n were taken, in the case of AK 227, as 66 and 28.5, respectively, and for AK 243, as 7 and 9. For convenience, the two CPE polymers can be represented in terms of mole weight fraction ethylene and vinyl chloride to provide, for AK 227, $(\text{CH}_2\text{CH}_2)_{0.697}(\text{CH}_2\text{CHCl})_{0.303}$, and for AK 243, $(\text{CH}_2\text{CH}_2)_{0.4375}(\text{CH}_2\text{CHCl})_{0.5625}$.

The solubility parameter of the polymers can be calculated by use of eq. (1). For PE, values used for M , ρ , and δ are 28.05, 0.902, and 7.9, respectively, and for PVC, in turn, 62.50, 1.40, and 9.52. The densities of the CPE polymers were found³ to be 1.069 g/cm³ and 1.174 g/cm³, respectively. Substitution of these values into eq. (1) affords δ_x 8.42 (cal/cm³)^{1/2} for AK 227, and for AK 243, 8.72 (cal/cm³)^{1/2}. Recalling that the relationship, eq. (1), $n_1M_1 + n_2M_2 = M_x$, the molecular weight of an average monomer unit of AK 227 is indicated to be 38.50, and of AK 243, 47.46.

Like polyethylene, CPE exhibits limited solubility in more common organic solvents at ambient temperature. Heat is required to dissolve the polymer. The results of studies for determining the energy of interaction between polymer and solvent at above ambient temperatures are often analyzed in terms of Flory's theory of melting point depression, expressed as⁴

$$1/T_M - 1/T_M^0 = (R/\Delta H_u)(V_u/V_s)(v_1 - \chi v_1^2) \quad (2)$$

where T_M^0 is the depressed melting point ($^{\circ}\text{K}$), T_M is the melting point of the pure polymer ($^{\circ}\text{K}$), V_u and V_s are the molar volumes of the polymer repeating unit and the diluent at T_M , respectively, R is the gas constant, ΔH_u is the heat of fusion per mole of polymer repeating unit, v_1 is the volume fraction of the diluent, and χ is the Flory interaction parameter. Solution temperature measurements have been used to estimate the interaction parameter. For example, Cernia et al.⁵ determined the interaction parameter for branched polyethylene in polar and nonpolar systems and presented values of the polar and nonpolar solubility parameters for a variety of solvents. Heat is also required to dissolve PVDC. Wessling⁶ judged the relative abilities of various solvents to dissolve crystalline PVDC by comparing the temperatures at which dilute solutions, $\sim 1\%$ by volume, become homogeneous.

In the studies reported here, the solubility parameters of PE and two CPE polymers were estimated by varying the concentration of polymer in various solvents and noting the temperature T_c ($^{\circ}\text{K}$) at which solution occurs. It can be assumed as a first approximation that when a polymer dissolves in a solvent forming a regular solution, an equation describing the relationship between the solution temperature and the interaction parameter would be of the form of eq. (2) to provide

$$1/T_M - 1/T_c = (R/\Delta H_u)(V_u/V_s)(v_1 - \chi v_1^2). \quad (3)$$

Since we are concerned with a single polymer in a single solvent and we want to study the effect of the change of polymer concentration on solution temperature, then

$$\begin{aligned} (1/T_c)_1 - (1/T_c)_2 = R/\Delta H_u[(V_u/V_s)_1 v_1 - (V_u/V_s)_2 v_2] \\ + R/\Delta H_u[(V_u/V_s)_2 \chi_2 v_2^2 - (V_u/V_s)_1 \chi_1 v_1^2] \quad (4) \end{aligned}$$

where the subscripts 1 and 2 now refer to polymer concentration in $\text{cm}^3/100 \text{ cm}^3$ diluent. Polymer volume concentration was obtained by multiplying the reciprocal of the polymer density in cm^3/g by the number of grams polymer used in each study.

Bearing in mind that for solvents forming regular solutions, or in which the diluent is nonpolar,

$$\chi = V_s/RT (\delta_s - \delta_p)^2 \quad (5)$$

where δ is the solubility parameter and the subscript p refers to polymer, substitution of eq. (5) into eq. (4) provides eq. (6) after the usual algebraic operations:

$$\delta_p = \delta_s - \left[\frac{\Delta H_u \left(\frac{T_{c2} - T_{c1}}{T_{c1} T_{c2}} \right) + R[(V_u/V_s)_2 v_2 - (V_u/V_s)_1 v_1]}{(V_u/T_c)_2 v_2^2 - (V_u/T_c)_1 v_1^2} \right]^{1/2}. \quad (6)$$

It was found that for the more concentrated solutions, T_c increases linearly with polymer concentration. The rate of increase depends on polymer and diluent types. By restricting our attention to the linear portions of the curve, the effect of small differences in polymer concentration on solution temperature can be studied. The change in solubility parameters and molar volumes of both the diluents and the polymers arising from temperature differences can be taken as small and to afford essentially constant values; the solubility parameter and molar volume of the diluents at 25°C were used.⁷ In this manner, the results from solution temperature studies can then be compared with values obtained by use of eq. (1).

In these studies, the molar volume of diluent, V_s , was taken as M/d , where M is the molecular weight and d is density at 25°C; the polymer volume was obtained by multiplying the polymer concentration, expressed as grams, by the reciprocal of the polymer density. For the heat of fusion of PE, a value of 1920 cal was taken.⁸ In order to adjust ΔH_u and R , in units of cal/cm³ polymer and cal/cm³ polymer-°K, in the case of polyethylene, the values of 1920 cal/mole and 1.986 cal/mole-degree, respectively, were divided by (28.05/0.902) 31.12; in the case of the two CPE polymers, values for ΔH_u and R were obtained by solving simultaneous equations based on eq. (6).

EXPERIMENTAL

The polymers used in the solution temperature studies were commercially available samples of PE 500 (Israel Petrochemicals Ltd., Haifa) and CPE AK 227 and AK 243 (ICI Ltd., England). The polymers and analytical reagent-grade solvents were used without further purification. The chlorine content and density³ of AK 227 were 27.8% and 1.069 g/cm³, while that of AK 243 were 42.1% and 1.174 g/cm³, respectively.

In a standard manner, the powder polymer was dispersed at room temperature in 25 cm³ diluent and heated slowly, with stirring, until the solid material contained in a test tube dissolved. With stirring, the solution was allowed to cool to room temperature. The polymer-diluent mass was reheated at a rate of 2-3°C/min with stirring to the temperature at which the transparency of two tubes, one containing the solution and the other the same volume of pure solvent at room temperature, appeared the same. The solution was allowed to cool again and the procedure was repeated 2-3 times. Temperature, measured with a thermometer, could be reproduced within 0.5°C.

RESULTS AND DISCUSSION

Figure 1 shows the change in solution temperature, T_c , with polymer concentration, V_u , in the various diluents. The data are given in Table I. The results show that for values of V_u lying between about 1 and 4 cm³/100 cm³ diluent, solution temperature varies linearly with polymer concen-

tration. In each case, a higher temperature is required to dissolve a particular volume of PE in a given diluent as compared to that needed for the same volume of the CPE polymers. This is to be expected, because of the higher degree of crystallinity of PE as compared to CPE. Solution of AK 243 was affected at the lowest temperature in each case, except when *o*-xylene was used as diluent. In this instance, a reversal was noted; solution of AK 227 occurred at the lowest temperature. Except for this reversal, as expected from eq. (2), an inverse relationship exists between solution temperature and the volume of polymer dissolved in a particular solvent. For example, at 335°K, the volume of polymer dissolved in toluene increases sevenfold from 0.55 cm³/100 cm³ diluent in the case of PE ($1/\rho = 1.1086$ cm³/g) to 3.6 cm³/100 cm³ diluent for AK 243 ($1/\rho = 0.8518$ cm³/g).

TABLE I
Effect of Diluent Type and Polymer Type and Concentration On
Solution Temperature^a

Polymer	V_u , ^b cm ³	Solution temperature T_c , °K			
		Chloro- benzene	Toluene	<i>o</i> -Xylene	<i>p</i> -Xylene
PE	4.4345		344.5	345	345
	3.3259		342	342	342
	2.2172	346	339.5	338.5	340
	1.1086	344	326.5	336	337.5
	0.5543	342	335	333	336
	0.2217	338	333	330.5	333
	0.1109	333	328	324	331
	0.0554		320	317	324
	AK-227	3.7418		338	335.5
2.8064			334.5	330.5	333.5
1.8709			330	327.5	331
0.9355			327	324	327
0.4677			320		
AK-243	3.4075	320.5	334.5	335	333.5
	2.5554	319	331	330.5	330.5
	1.7036	318	329	328	326
	0.8518	316	326.5	325	322
	0.4259	313			

^a Solubility parameter δ , (cal/cm³)^{1/2}/molar volume V_u , cm³, 9.67/102 for chloro-benzene, 8.90/107 for toluene, 9.06/121 for *o*-xylene, 8.83/124 for *p*-xylene. Data taken from ref. (7).

^b Volume of polymer was obtained by multiplying the weight of polymer, in grams, by the reciprocal of polymer density. Density of polymers used were 0.902, 1.069, and 1.174 g/cm³ for PE, AK-227, and AK-243, respectively. Density data for CPE samples taken from ref. 3.

The solubility parameter of PE was estimated from solution temperature measurements in the various aromatic solvents. The straight-line portions of the curves (Fig. 1) (polymer volume concentration greater than about 1

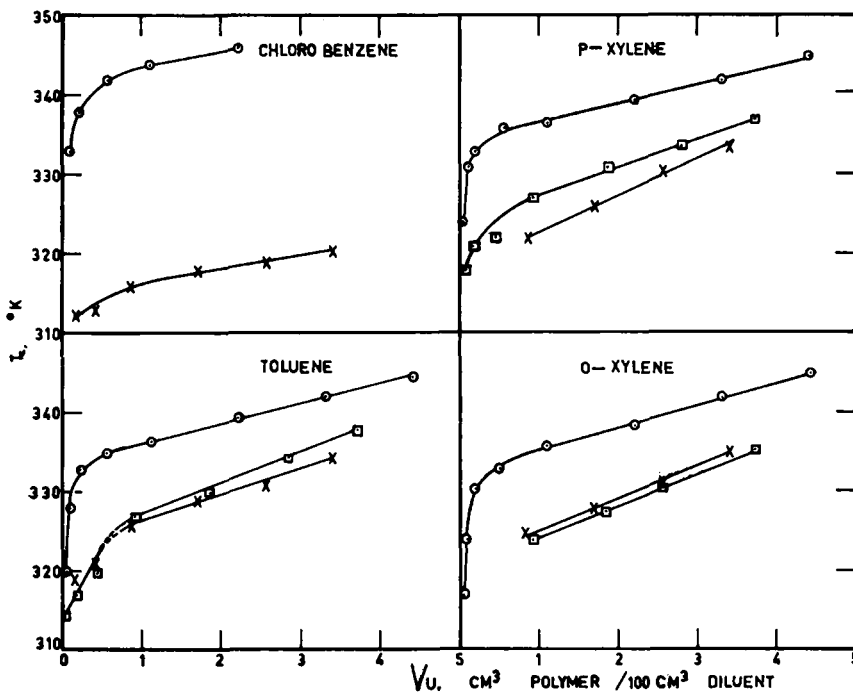


Fig. 1. Variation of solution temperature with polymer concentration in various diluents: (O) PE; (\square) AK 227; (\times) AK 243. Polymer concentration in units of $\text{cm}^3/100 \text{ cm}^3$ diluent was obtained by multiplying the weight of the polymer, in grams, by the reciprocal of the polymer density.

$\text{cm}^3/100 \text{ cm}^3$ diluent) were used for calculations of $(V_u/V_s)v$ and $(V_u/T_c)v^2$ at different concentrations. The values used for ΔH and R are shown in Table II. Estimates of δ from studies in various diluents, eq. (6), are given in Table III. The results show that when the three aromatic hydrocarbons, toluene, *o*-xylene, and *p*-xylene, are used as diluents, agreement between reported and estimated values is within 3%. For data obtained from studies using chlorobenzene as diluent, an anomalous value of 8.74 was obtained. Cernia et al.⁵ also obtained anomalous results from studies involving chlorinated aromatic hydrocarbons, including chlorobenzene. While they state that no definite explanation for the phenomenon is known,

TABLE II
Constants for PE and CPE Polymers

Polymer	Average molecular weight of monomer repeating unit	ΔH , cal/cm ³ polymer	R , cal/cm ³ polymer-°K
PE	28.05	61.70	0.0639
AK 227	39.38	42.42	0.0540
AK 243	46.95	26.65	0.0497

they tentatively suggest that steric hindrance and conformational differences may influence the interactions between the polymers and these diluents.

TABLE III
Solubility Parameter of PE and CPE Polymers

Polymer	Diluent	T_c , °K	$(V_u/V_s)v$ $\times 10^2$	$(V_u/T_c)v^2$ $\times 10^2$	δ_p , (cal/cm ²) ^{1/2}	
					Found ^a	Reported ^b
PE	chloro- benzene	346	2.170	0.6388	8.74	7.90 ^c
		342	1.086	0.3222		
	toluene	342	3.097	0.9694	8.08	
		336.5	1.036	0.3292		
	<i>o</i> -xylene	345	3.642	1.269	8.21	
		336	0.916	0.3300		
	<i>p</i> -xylene	345	3.554	1.269	8.05	
337.5		0.894	0.3280			
AK-227	toluene	338	3.484	1.0997	8.33	8.42
		334.5	2.617	0.8354		
	<i>o</i> -xylene	327.5	1.545	0.5702	8.47	
		324	0.773	0.2886		
	<i>p</i> -xylene	337	3.006	1.1029	8.26	
327		0.754	0.2859			
AK-243	chloro- benzene	320.5	3.307	1.057	9.59	8.72
		316	0.835	0.2700		
	toluene	334.5	3.175	1.013	8.77	
		329	1.591	0.5170		
	<i>o</i> -xylene	335	2.808	1.012	8.68	
		328	1.407	0.5192		
	<i>p</i> -xylene	333.5	2.756	1.016	8.35	
326		1.373	0.5221			

^a Equation (6).

^b Equation (1).

^c Reference (8).

In the case of the two CPE polymers, values for the constants, ΔH_u and R , were obtained by solving simultaneous equations. The straight-line portions of the curves (Fig. 1) were used with the approximation, eq. (6), $v_1 = v_2 = 1$. In order to obtain a figure of merit for the gas constant, in the case of AK 227, data obtained from studies in *o*-xylene and *p*-xylene were used:

For *o*-xylene:

$$\delta_p = 9.06 - \left\{ \left[\frac{(\Delta H_u)(6.5)}{(330.5)(327)} + R(1.5462 \times 10^{-2}) \right] / 5.604 \times 10^{-3} \right\}^{1/2}$$

For *p*-xylene:

$$\delta_p = 8.83 - \left\{ \left[\frac{(\Delta H_u)(10)}{(337)(327)} + R(2.2632 \times 10^{-2}) \right] / 8.249 \times 10^{-3} \right\}^{1/2}$$

The equations were set equal to each other and solved for ΔH in terms of R ; inserting this value into the original equations provided $R = 0.0540$ cal/cm³ AK 227 polymer-°K. In order to evaluate ΔH , solution temperature data in *o*-xylene only were used:

$$\delta_p = \delta_s - \left\{ \left[\frac{\Delta H_u(6.5)}{(330.5)(324)} + 0.054(1.5462 \times 10^{-2}) \right] / 5.604 \times 10^{-3} \right\}^{1/2}$$

$$\delta_p = \delta_s - \left\{ \left[\frac{\Delta H_u(3.0)}{(330.5)(327.5)} + 0.054(7.731 \times 10^{-3}) \right] / 2.776 \times 10^{-3} \right\}^{1/2}$$

A value of 42.42 cal/cm³ polymer was obtained which turned out to be negative. In a similar manner, for AK 243, values of 0.0497 and 26.65 were obtained for R and ΔH , respectively, from studies using chlorobenzene and toluene as diluents. Once again, the value of ΔH turned out to be negative.

The reversal in sign of ΔH is taken to indicate that, in the systems investigated, the value of χ is positive in the case of PE and negative for the two CPE polymers. A positive value of 61.70 cal/cm³ was used in eq. (6) to estimate the solubility parameter of PE from solution temperature studies. While highly crystalline polymers such as PE are normally insoluble except at temperatures near or above their melting points, polar crystalline polymers can be dissolved in certain specific solvents at temperatures much below their $T_M^{0.9}$; a common characteristic of such systems is a negative value of χ . On the other hand, polymer volume and configuration may be of importance too. In order to take into account the apparent reversal in the value of χ , the bracketed term, eq. (6), was multiplied by minus one.

The weight of a mole of CPE polymer repeating unit was obtained from the derived values of R . The gas constant, 1.986, was multiplied by the individual polymer density and divided by 0.054 and by 0.0497 to provide 39.38 and 46.95 as the molecular weight of an average repeating unit of AK 227 and AK 243, respectively. These results compare favorably with those calculated, eq. (1), above, 38.50 and 47.46, respectively. The derived values, 39.38 and 46.95, were used to estimate δ_x from solution temperature studies.

The solubility parameter of the CPE polymers was estimated using the derived figures of merit (Table II) and eq. (6) modified by the multiplication by minus one of the bracketed term. The results are given in Table III. In the case of AK 227, agreement within 2% exists between values obtained from calculations based on eq. (1) and those estimated from solution temperature studies using the three aromatic diluents, toluene, *o*-xylene, and *p*-xylene. For AK 243, agreement within 1% between predicted and estimated δ -values was obtained when toluene and *o*-xylene were used as diluents. Anomalous results, very high and low values, were obtained when chlorobenzene and *p*-xylene were used as diluents. Examination of Figure 1 shows that in solution temperature

studies involving toluene and *o*-xylene as diluents, polymer type (AK 227 or AK 243) has only slight effect on the volume of polymer dissolved at a given temperature. When *p*-xylene was used as diluent, the polymer volume concentration-solution temperature relationship is dependent on polymer type. While the reasons for the deviations cannot be explained at this time, the results do indicate that the equation used to calculate the solubility parameter of random copolymers may also be used to calculate the solubility parameter of nonrandom copolymers, such as CPE.

Equation (1) provides, in effect, a means for extending to copolymers the general method developed by Small¹⁰ for estimating the solubility parameter of polymers. The basis of eq. (1), the general method of Small, as well as its extension by other¹¹⁻¹³ are the findings of Scatchard¹⁴ which established that a linear relationship exists among several homologous series linking the square root of the product of the cohesive energy ΔE and molar volume V with the number of carbon atoms in the chain. Thus, Small found that, for a particular group, the quantity $(EV)^{1/2}$ is a constant, F , and is an additive property, $\delta = \xi F/V = (EV)^{1/2}/V = (E/V)^{1/2}$.

It is stated generally¹⁵ that for hydrocarbons, esters, or halogen-containing polymers, the agreement between these calculated values and experimental ones is quite good. Calculated values by Small's method for the two CPE polymers are 8.40 for AK 227 and 8.75 for AK 243. However, difficulties arise in cases where hydrogen bonding or strong polarity may affect the results.^{1,15,16} In addition, for a hydrocarbon copolymer containing 75% butadiene and 25% styrene, good agreement exists¹ between the δ -values obtained from solution studies, turbidimetry, or viscosity measurements and that calculated by use of eq. (1). On the other hand, values obtained from swelling measurements are much higher on this copolymer as well as styrene copolymers containing 85% or 60% butadiene. In order to carry out measurements by swelling, the polymers are crosslinked initially, usually with free-radical agents. Calculations using eq. (1) indicate¹ that, in this instance, groupings capable of excessive interactions may be formed; by the method of Small, use of the constants affords δ -values representative only of the crosslinked copolymers. Finally, it should be emphasized that the use of the F -values assumes that the interaction between polymer segments are analogous to the interaction between small solvent molecules. With eq. (1), the assumption is that the behavior of copolymers may be better estimated from the properties of its polymeric components. It may be that, under these circumstances, differences between calculated values and experimental ones can be related to the nonpolar and hydrogen-bonding components of the solubility parameter without the use of homomorphs.

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