Solubility Parameter of Acrylamide Series Polymers through Its Components and Group Contribution Technique

Husain Ahmad[a]

[a] Center for Materials Science and Technology Indian Institute of Technology, Delhi New, Delhi, India

PLEASE SCROLL DOWN FOR ARTICLE

Solubility Parameter of Acrylamide Series Polymers through Its Components and Group Contribution Technique

HUSAIN AHMAD

Center for Materials Science and Technology
Indian Institute of Technology, Delhi
New Delhi 110016, India

ABSTRACT

The chemical group contribution technique, based on the principle of additivity of molar refraction and polarization constants for groups in a molecule, has been used for determining the solubility parameters of acrylamide series polymers. The solubility parameter for a polymer is calculated through its components by using the contributions of chemical groups reported in the literature with the resultant values found to compare favorably. It is also noticed that the δ-values decrease with an increase in molar volume.

INTRODUCTION

Solubility parameter is one of the fundamental properties of a substance, is based on the theory of regular solution, and is being used quite extensively for finding out the miscibility of polymeric materials in individual solvents and their blends. Knowledge about solubility parameters [1-3] and other physical characteristics such as hydrogen bonding, polarity, molar volume, and wettability of different types of materials saves time and effort in finding their miscibility.

Scientists working in the field of solubility parameter have derived a number of mathematical expressions for the determination of the solubility parameter of low molecular weight substances [1, 2, 4]. But these expressions are not applicable in the case of polymers because the data on the physical constants, i.e., boiling point, molar volume, heat of vaporization, van der Waals and critical constants, compressibility factor, and surface tension, required for the calculation solubility parameter are not available.

The process of dissolution of the polymer in a solvent depends mainly on the heat of mixing which is negligible when the cohesive energy densities of the polymer and solvent are almost equal. The free energy of mixing ΔF_m of the polymer-solvent system can be expressed as

$$\Delta F_m = \Delta H_m - T\Delta S_m \tag{1}$$

and

$$\Delta H_m = V_m \left\{ (E_1/V_1)^{1/2} - (E_2/V_2)^{1/2} \right\} \phi_1\phi_2 \tag{2}$$

$$= V_m \left\{ \delta_1 - \delta_2 \right\} \phi_1\phi_2 \tag{3}$$

where ΔH_m = the heat of mixing

ΔS_m = the entropy of mixing

V_m = total volume of the two components

V_s = their molar volumes

E_s = their cohesive energies

ϕ_s = their volume fractions

δ_s = their solubility parameters

In systems where the long chains of the polymer uncoil in the course of dissolution, there is a high ΔS_m value, which in turn favors a negative ΔF_m. If the heat of mixing ΔH_m is not greater than $T\Delta S_m$, dissolution of the polymer in the solvent is possible. In the other case where the heat of mixing is very low ($\delta_1 \approx \delta_2$), the miscibility of the two components is assured but the extent of dissolution is governed by the entropy factor ΔS_m.

This theory has been developed for mixing of nonpolar substances. However, many of the solvents and polymers in common use are polar, i.e., have dipole moments and/or capabilities for hydrogen bonding. Hence these factors must be included in the theory.

It was Prausnitz et al. [5, 6] who divided the energy of vaporization into a nonpolar or dispersion part and polar part. Hansen [7] divided the polar part into a dipole-dipole contribution and hydrogen bonding contribution, both of which could be determined through solubility experiments. According to Hansen [7],

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{4}$$

where δ_d = solubility parameter due to dispersion forces

δ_p = solubility parameter due to polar forces

δ_h = solubility parameters due to hydrogen bonding forces

These three components of solubility parameters are separately related to the refractive index, the dipole moment, and the energy of hydrogen bonding, respectively.

Relation between Refractive Index n and δ_d

It was Sewell [8] who showed that the interaction energy between nonpolar molecules is dependent on the polarizability (London dispersion forces). The polarization, on the other hand, can be described by the Lorentz-Lorenz equation:

$$\frac{4}{3}\pi N/V\alpha = (n^2 - 1)/(n^2 + 2) \tag{5}$$

where N = number of molecules in 1 mol

α = polarizability

Using the concept of separation of cohesive energy density (C.E.D.) into three components, we expect a relationship between δ_d and n even for polar substances in which the interference of polar hydrogen bonding forces has vanished. Koenhem and Smolders [9] gave a relationship between δ_d and n applicable for polar substances:

$$\delta_d = 9.55n - 5.55 \tag{6}$$

The additive property correlating optical refraction with chemical structure is called molar refraction. According to Lorentz and Lorenz, the molar refraction R_{LL} is given by

$$R_{LL} = \frac{n^2 - 1}{n^2 + 2} \frac{M}{d} = \frac{n^2 - 1}{n^2 + 2} V_m \tag{7}$$

or

$$n = \left[\frac{1 + 2R_{LL}/V_m}{1 - R_{LL}/V_m} \right]^{1/2} \tag{8}$$

Relationship between Dipole Moment μ and δ_p

Beerbower [10] proposed a very simple and empirical relationship for the determination of δ_p:

$$\delta_p = A \frac{\mu}{V^{1/2}} \tag{9}$$

or

$$\delta_p = 9.5 \frac{\mu}{V^{1/2}} \tag{10}$$

where A is a constant [9] equal to 9.5.

It is possible to evaluate the dipole moment with the help of Debye's equation [11, 12]:

$$P_{LL} - R_{LL} = \left[\frac{\epsilon - 1}{\epsilon + 2} - \frac{n^2 + 1}{n^2 + 2} \right] V_m = \frac{4\pi}{9} \frac{N\mu^2}{KT} = 20.6 \ \mu^2 \tag{11}$$

or

$$\mu = \left[\frac{P_{LL} - R_{LL}}{20.6} \right]^{1/2} \tag{12}$$

where K = Boltzman constant

T = absolute temperature

ϵ = dielectric constant

$P_{LL} = \dfrac{\epsilon - 1}{\epsilon + 2}$ (molar polarizability)

The values of group contributions for R_{LL} and P_{LL} are available in the literature [12].

Relationship between Hydrogen Bonding Energy E_h and δ_h

Different hydrogen-bonded compounds have different E_h values. The following relationship was used to evaluate the value of δ_h:

$$\delta_h = (E_h/V_m)^{1/2}$$

The values of E_h for different groups are available in the literature [9].

The aim of this paper is to evaluate the δ-values of polyacrylamides through its components and group contribution technique.

Materials. The formulas of monomers, taken from Functional Monomers [13], were rewritten in the form of polymer repeating units of the corresponding polymers for calculating their solubility parameter values.

Procedure. The values of dipole moments μ and refractive index n were calculated with the help of molar polarizability P_{LL} and molar refraction R_{LL} as their values for the individual chemical groups are reported in the literature [12]. Molar volumes [14] of the polymers have been calculated by adding the contributions of atoms and bonds present in a single polymer repeating unit. The following two examples will illustrate the method of calculating V, n, μ, δ_d, δ_p, and δ_h.

Example 1. Poly-N-n-butyl acrylamide

$$\left[\begin{array}{l} -CH_2-CH- \\ \qquad | \\ \quad CONH.CH_2.CH_2.CH_2.CH_3 \end{array}\right]_x$$
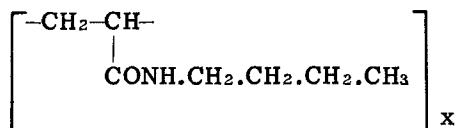
The molar volume of this polymer at 25°C is evaluated as shown in Table 1.

The evaluations of R_{LL}, n, P_{LL}, and μ are given in Table 2.

Using Eqs. (6), (9), and (13), the following values were obtained:

$$\delta_d = 9.55n - 5.55$$
$$= 9.55 \times 1.482 - 5.55 = 8.603 \ (cal/cc)^{1/2}$$

TABLE 1. Poly-N-n-butyl Acrylamide

Atoms and bonds	Molar volume
7 (C)	12.95
13 (H)	85.67
1 (O)	7.70
1 N	4.82
1 (=)	8.94
Polymer repeating unit (PRU)	2.97
	V = 123.05

TABLE 2.

Groups	R_{LL}	$n = \left[\dfrac{1 + 2R_{LL}/V}{1 - R_{LL}/V}\right]^{1/2}$	P_{LL}	$\mu = \left[\dfrac{P_{LL} - R_{LL}}{20.6}\right]^{1/2}$
1 (CH₃−)	5.64		5.64	
4 (−CH₂−)	18.60		18.60	
		1.482		1.051
1 (−CH−)	3.62		3.62	
1 (ĊONH−)	7.23		30.00	
	35.09		57.86	

$$\delta_p = \frac{9.5\mu}{V^{1/2}} = \frac{9.5 \times 1.051}{11.09} = 0.900 \ (cal/cc)^{1/2}$$

$$\delta_h = \left(\frac{E_{CONH}}{V}\right)^{1/2} = \left(\frac{3900}{123.05}\right)^{1/2} = 5.630 \ (cal/cc)^{1/2}$$

The total value of δ is

$$\delta = \left[\delta_d^2 + \delta_p^2 + \delta_h^2\right]^{1/2} = 10.320 \ (cal/cc)^{1/2}$$

TABLE 3. Poly-N-benzyl Acrylamide

Atoms and bonds	Molar volume
10 (C)	18.50
11 (H)	72.49
1 (O)	7.70
1 (N)	4.82
4 (=)	35.76
Six-membered ring	2.35
PRU	2.97
	V = 144.59

TABLE 4.

Groups	R_{LL}	$n = \left[\dfrac{1 - 2R_{LL}/V}{1 - 1R_{LL}/V}\right]^{1/2}$	P_{LL}	$\mu = \left[\dfrac{P_{LL} - R_{LL}}{20.6}\right]^{1/2}$
1 (–⬡)	25.51		25.00	
2 (–CH_2–)	9.15	1.491	9.30	1.043
1 (CONH–)	7.23		30.00	
	41.89		64.30	

Example 2. Poly-N-benzyl acrylamide

$$\left[\begin{array}{c} -CH_2-CH- \\ | \\ CONH.CH_2-⬡ \end{array}\right]_x$$
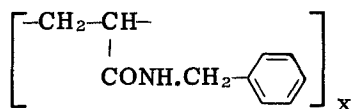
The molar volume of this polymer at 25°C is shown in Table 3.
The values of R_{LL}, n, P_{LL}, and μ are given in Table 4.
Using Eqs. (6), (9), and (13):

$$\delta_d = 8.689$$

TABLE 5. Solubility Parameter of Alkyl and Aryl Acrylamide Series Polymers

Name of polymer	Molar volume (V)	Solubility parameter $(cal/cc)^{1/2}$			
		δ_d	δ_p	δ_h	δ
1 Poly-N-methyl acryl-amide	77.96	8.35	1.13	7.07	11.00
2 Poly-N-ethyl acrylamide	92.99	8.46	1.04	6.48	10.71
3 Poly-N-isopropyl acrylamide	108.02	9.38	0.96	6.01	11.18
4 Poly-N-n-butyl acryl-amide	123.05	8.60	0.90	5.63	10.32
5 Poly-N-iso-butyl acrylamide	123.05	8.60	0.90	5.63	10.32
6 Poly-N-t-butyl acryl-amide	123.05	8.60	0.90	5.63	10.32
7 Poly-N,N-diethyl acrylamide	123.05	8.77	0.87	5.63	10.46
8 Poly-N-phenyl acryl-amide	129.56	9.41	0.85	5.49	10.92
9 Poly-N-(1-methyl-1-propyl butyl)acryl-amide	131.49	8.78	0.87	5.45	10.37
10 Poly-N-S-amyl acrylamide	138.08	8.63	0.85	5.31	10.17
11 Poly-N-S-isoamyl acrylamide	138.08	8.63	0.85	5.31	10.17
12 Poly-N-t-amyl acrylamide	138.08	8.63	0.85	5.31	10.17
13 Poly-N-cyclohexyl acrylamide	142.28	8.83	–	5.24	10.27
14 Poly-N-p-tolyl acrylamide	144.59	9.42	0.81	5.26	10.82
15 Poly-N-benzyl acrylamide	144.59	8.69	0.82	5.19	10.16
16 Poly-N-methyl-N-phenyl acrylamide	144.59	9.27	0.82	5.19	10.66
17 Poly-N-1,1-dimethyl butyl acrylamide	153.11	8.68	0.81	5.05	10.07

TABLE 5 (continued)

Name of polymer	Molar volume (V)	Solubility parameter $(cal/cc)^{1/2}$			
		δ_d	δ_p	δ_h	δ
18 Poly-N-1-methyl-1-ethyl propyl acrylamide	153.11	8.68	0.81	5.05	10.07
19 Poly-N-(1,1,2-trimethyl propyl)-acrylamide	153.11	8.68	0.81	5.05	10.07
20 Poly-N-p-methyl benzyl acrylamide	159.62	9.27	0.79	5.01	10.57
21 Poly N-n-heptyl acrylamide	168.14	8.72	0.77	4.82	9.99
22 Poly-N-(1,1-dimethyl-amyl) acrylamide	168.14	8.72	0.77	4.82	9.99
23 Poly-N-(1-methyl-1-ethyl butyl) acrylamide	168.14	8.72	0.77	4.82	9.99
24 Poly-N-1(1,1-diethyl propyl) acrylamide	168.14	8.72	0.77	4.82	9.99
25 Poly-N-(1-methyl-1-ethyl-2-methyl propyl) acrylamide	168.14	8.72	0.77	4.82	9.99
26 Poly-N-(1,1,2-trimethyl butyl) acrylamide	168.14	8.72	0.77	4.82	9.99
27 Poly-N-(1,1,3-trimethyl butyl) acrylamide	168.14	8.72	0.77	4.82	9.99
28 Poly-N-n-octyl acrylamide	183.17	8.76	0.74	4.61	9.93
29 Poly-N-(1,1-dimethyl hexyl) acrylamide	183.17	8.76	0.74	4.61	9.93
30 Poly-N-(1-methyl-1-ethyl amyl) acrylamide	183.17	8.76	0.74	4.61	9.93
31 Poly-N-(1,1-4-trimethyl amyl) acrylamide	183.17	8.75	0.74	4.61	9.92

TABLE 5 (continued)

Name of polymer	Molar volume (V)	Solubility parameter $(cal/cc)^{1/2}$			
		δ_d	δ_p	δ_h	δ
32 Poly-N-(1,4-dimethyl-1-ethyl amyl) acryl-amide	183.17	8.72	0.74	4.61	9.89
33 Poly-N-(1,1,3,3-tetra-methyl butyl)acryl-amide	183.17	8.74	0.74	4.61	9.91
34 Poly-N-(1,3-dimethyl 1-ethyl butyl) acrylamide	183.17	8.75	0.74	4.61	9.92
35 Poly-N,N-di-n-butyl acrylamide	183.17	10.44	0.69	4.61	11.43
36 Poly-N-(1,1-dibutyl amyl) acrylamide	191.61	11.02	0.72	4.51	11.93
37 Poly-N,N-diphenyl acrylamide	196.19	9.68	0.66	4.49	10.69
38 Poly-N-(1,1-dimethyl-heptyl) acrylamide	198.20	8.77	0.71	4.44	9.86
39 Poly-N-(1-methyl-1-propyl amyl) acryl-amide	198.20	8.77	0.71	4.44	9.86
40 Poly-N-(1-1-diethyl amyl) acrylamide	198.20	8.77	0.71	4.44	9.86
41 Poly-N-[1-(2-methyl-propyl-1-(3-methyl butyl)] acrylamide	213.23	8.79	0.68	4.28	9.80
42 Poly-N-(1-methyl-1-butyl-3-methyl butyl) acrylamide	213.23	8.77	0.68	4.28	9.79
43 Poly-N,N-dibenzyl acrylamide	226.21	9.33	0.66	4.15	10.23
44 Poly-N-(1-ethyl-1-butyl amyl) acryl-amide	228.26	8.81	0.66	4.13	9.75
45 Poly-N,N-dicyclohexyl acrylamide	234.81	9.13	0.56	4.08	10.02

TABLE 5 (continued)

Name of polymer	Molar volume (V)	Solubility parameter $(cal/cc)^{1/2}$			
		δ_d	δ_p	δ_h	δ
46 Poly-N-n-dodecyl acrylamide	243.29	8.83	0.64	4.00	9.72
47 Poly-N-(1-propyl-1-butyl amyl) acrylamide	243.29	8.82	0.64	4.00	9.72
48 Poly-N,N-di-(2-ethyl hexyl) acrylamide	303.41	8.31	0.57	3.59	9.07
49 Poly-N-n-octadecyl acrylamide	335.72	8.86	0.55	3.41	9.51

TABLE 6. Solubility Parameters of Functional Group Substituted Acrylamide Series Polymers

Name of polymer	V	δ_d	δ_p	δ_h	δ
1 Poly-N-(2,2,2-trifluoroethyl) acrylamide	83.12	9.00	1.17	6.85	11.37
2 Poly-N-hydroxymethyl acrylamide	85.66	9.10	1.16	6.75	11.39
3 Poly-N-acetyl acrylamide	87.61	8.81	1.18	6.66	11.11
4 Poly-N-(2-hydroxyethyl) acrylamide	102.69	8.25	1.06	6.16	10.35
5 Poly-N-methoxy methyl acrylamide	102.69	8.27	1.06	6.16	10.37
6 Poly-N-(2-cyanoethyl) acrylamide	111.02	8.38	1.05	6.30	10.54
7 Poly-N-(2-oxopropyl) acrylamide	111.28	8.36	1.05	5.92	10.30
8 Poly-N-(ethoxy methyl) acrylamide	115.72	7.89	1.00	5.81	9.85
9 Poly-N-hydroxymethyl-N-methyl acrylamide	115.72	8.62	0.93	8.76	12.33
10 Poly-N-(N',N'-dimethylaminomethyl) acrylamide	119.43	8.58	–	5.71	–

TABLE 6 (continued)

Name of polymer	V	δ_d	δ_p	δ_h	δ
11 Poly-N-(1-methyl-2-oxopropyl) acryl-amide	126.51	8.43	0.99	5.55	10.16
12 Poly-N-(n-propoxy methyl) acrylamide	130.75	8.53	1.02	5.46	10.18
13 Poly-N-(isopropoxy-methyl) acrylamide	130.75	8.52	1.02	5.46	10.18
14 Poly-N-(1-ethyl-2-hydroxyethyl) acrylamide	130.75	8.51	0.94	5.46	10.15
15 Poly-N-[1-(1-methyl-1-hydroxymethyl)] acrylamide	130.75	8.50	0.94	5.46	10.15
16 Poly-N-(n-butoxy-methyl) acrylamide	145.78	8.66	0.91	5.17	10.13
17 Poly-N-(isobutoxy-methyl) acrylamide	145.78	8.58	0.89	5.17	10.06
18 Poly-N-(3-dimethyl amino propyl) acryl-amide	149.49	8.72	–	5.11	–
19 Poly-N-[1,1,1-tris-(hydroxymethyl) methyl] acrylamide	152.74	8.26	0.90	5.05	9.72
20 Poly-N,N-bis(2-cyano-ethyl) acrylamide	159.11	7.95	0.83	5.55	9.73
21 Poly-N-[2-(2-methyl-4-hydroxy pentyl)] acryl acrylamide	160.81	8.59	0.85	4.92	9.94
22 Poly-N-[2-(2-methyl-4-oxopentyl)] acryl-amide	163.16	6.98	1.01	4.89	8.58
23 Poly-N-(2-dimethyl-aminoethyl) acryl-amide	164.52	8.76	–	4.78	–
24 Poly-N-benxyl oxo-methyl acrylamide	167.32	9.07	0.77	5.21	10.50

TABLE 6 (continued)

Name of polymer	V	δ_d	δ_p	δ_h	δ
25 Poly-N-[3-(1,5-di-methyl-2-oxohexyl)] acrylamide	171.60	8.59	0.85	4.77	9.86
26 Poly-N-(1-benzyl-2-oxopropyl acrylamide	193.14	9.02	0.80	4.55	10.13
2- or 3-Amino and 2- or 3-Alkoxy Acrylamide					
27 Poly-N-methyl-3-ethoxy acrylamide	115.72	8.46	1.00	6.20	10.54
28 Poly-N-ethyl-2-ethoxy acrylamide	130.75	8.52	0.94	5.83	10.37
29 Poly-N-ethyl-3-ethoxy acrylamide	130.75	8.52	0.94	5.83	10.37
30 Poly-N,N-dimethyl-3-ethoxy acrylamide	130.75	8.15	0.80	5.83	10.05
31 Poly-N-(n-propyl)-2-ethoxy acrylamide	145.78	8.58	0.89	5.52	10.24
32 Poly-N-(n-butyl-2-ethoxy acrylamide	160.81	8.62	0.85	5.26	10.13
33 Poly N,N-diethyl-3-ethoxy acrylamide	160.81	7.18	0.73	5.26	8.93
2- or 3-Halo Acrylamide					
34 Poly-N,N-diethyl-2,3-dichloroacryl-amide	151.71	8.96	0.89	5.20	10.40
35 Poly-N,N-diethyl-2-bromo-3-chloro acrylamide	156.98	8.83	0.78	5.05	10.20
36 Poly-N,N-diethyl-2-chloro-3-bromo acrylamide	156.98	7.94	0.24	5.05	9.41
37 Poly-N,N-diethyl-2,3-dibromo acrylamide	162.25	9.30	0.67	4.90	10.53

TABLE 7. Solubility Parameter of Polymers and Their Comparison with Experimental Values Reported in the Literature

Name of polymer	δ_d	δ_p	δ_h	δ	δ_{Lit} [16, 17][a]
1 Polyvinyl acetate	8.34	0.72	4.10	9.32	9.40 (C)
2 Polymethyl acrylate	8.34	0.72	4.10	9.32	10.1 (C)
					10.1 (V)
3 Polyethyl acrylate	8.39	0.67	3.74	9.21	9.40 (C)
					9.40 (V)
4 Polybutyl acrylate	7.90	0.56	3.24	8.56	8.76 (C)
					8.80 (V)
5 Polymethyl methacrylate	8.45	0.66	3.74	9.26	9.10 (C)
					9.50 (V)
					9.10 (V)
					9.40 (V)
6 Polyethyl methacrylate	8.55	0.61	3.46	9.24	8.95 (C)
7 Polybutyl methacrylate	8.66	0.61	3.05	9.20	8.75 (C)
8 Polyethylene	8.45	-	-	8.45	7.90 (C)
9 Polystyrene	9.66	-	-	9.66	8.60 (V)
					9.10 (V)
					9.10 (C)
10 Poly-N-methyl acrylamide	8.35	1.13	7.07	11.00	11.26 (H)
11 Poly-N-ethyl acrylamide	8.46	1.04	6.48	10.71	9.78 (H)
12 Poly-N-benzyl acryl-amide	8.69	0.82	5.19	10.16	10.62 (H)
13 Poly-N-(n-propoxymethyl) acrylamide	8.53	1.02	5.46	10.18	10.25 (H)
14 Poly-N-(n-butoxymethyl) acrylamide	8.66	0.91	5.17	10.13	9.95 (H)

[a](C) = experimentally determined from the maximum swelling of crystalline of cross-linked polymer; (V) = experimentally determined from the maximum in intrinsic viscosity; (H) = determined by Hoy's group contribution technique.

$\delta_p = 0.824$

$\delta_h = 5.193$

$\delta = 10.160 \ (cal/cc)^{1/2}$

RESULTS

The values of the components of solubility parameter i.e., δ_d, δ_p, δ_h, and total value of solubility parameter δ, are listed in Tables 5-7.

DISCUSSION

For the purpose of establishing the applicability of the additivity of group contribution technique, the total value of the solubility parameter was evaluated and compared with the practically determined ones. The results listed in Table 7 (Columns 4 and 5) indicate that the difference between calculated and experimentally determined solubility parameter values for a polymer is fairly small in most cases. However, the δ values obtained from such calculations depend greatly on the accuracy of the value of the contribution of the individual group, atom, and bond reported in the literature. Not many practical methods are available for the determination of solubility parameter of polymers, and the theoretical methods proposed by Small [15] and others [3, 12, 16] are not applicable to strongly hydrogen-bonded compounds. Hence it was felt worthwhile to evaluate the components of δ by the group contribution technique.

In Tables 5 and 6 the polymers are listed according to the increasing size of the substituent groups in them, hence they are arranged in the increasing order of their molar volumes. Scrutiny of the data reveals that a decrease of δ value is observed with an increase in molar volume. As the size of the polymer repeating unit increases, the value of both V and total cohesive energy also increases. But the decrease in δ value indicates that the increase in V and total cohesive energy is not exactly proportional.

In a particular homologous series, as the molar volume increases, the δ_d value also increases while the δ_p and δ_h values decrease (Table 5). But in the case of functional group substituted polymers (Table 6), a decreasing trend in all the components of the solubility parameter, i.e., δ_d, δ_p, and δ_h, is noticed. This may be because inclusion of a CH_2- group in a particular series (Table 5) contributes much to the dispersion components of energy and less to the molar volume. But in the case of functional group substituted polymers (Table 6), they contribute to the cohesive energy and, being bulkier in weight, they add more to the molar volume. Hence a decreasing trend in all the components of δ is observed.

REFERENCES

[1] J. H. Hildebrand and R. L. Scott, The Solubility of Non-electro-lytes, Reinhold, New York, 1949.

[2] H. Burrell, Off. Dig., 27, 726 (1955).

[3] K. L. Hoy, J. Paint Technol., 42, 76 (1970).

[4] H. Ahmad and M. Yaseen, J. Colour Soc., 13, 7 (1974).

[5] R. F. Blanks and J. M. Prausnitz, Ind. Eng. Chem., Fundam., 3, 1 (1964).

[6] R. F. Weiner and J. M. Prausnitz, Hydrocarbon Process. Pet. Refiner, 44, 237 (1965).

[7] C. M. Hansen and K. Skaorup, J. Paint Technol., 39, 511 (1967).

[8] J. H. Sewell, R. A. E. Technical Report No. 66185, June 1966.

[9] D. M. Koenhem and C. A. Smolders, J. Appl. Polym. Sci., 19, 1163 (1975).

[10] A. Beerbower and J. R. Dieky, ASLE Trans., 12, 1 (1969).

[11] P. Debye, Phys. Z., 13, 97 (1912).

[12] D. W. Van Krevelen and P. J. Hoftyzer, Properties of Polymers, Correlation with Chemical Structure, Elsevier, Amsterdam, 1972.

[13] D. C. MacWilliams, Functional Monomers, Their Preparation and Application, Vol. 1 (Yocum and Nyquist, eds.), Dekker, New York, 1973.

[14] J. H. Sewell, J. Appl. Polym. Sci., 17, 1741 (1973).

[15] P. A. Small, J. Appl. Chem., 3, 71 (1953).

[16] H. Ahmad and M. Yaseen, J. Oil Colour Chem. Assoc., 60, 99, 488 (1977); J. Coatings Technol., 50, 86 (1978); Polym. Eng. Sci., 19, 858 (1979).

[17] J. L. Gardon, J. Paint. Technol., 38, 43 (1966).