

# Solubility Parameters of Amine-Crosslinked Aromatic Epoxies

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## Synopsis

For six epoxide-amine systems, based on mixtures of two different aromatic epoxides with four various aromatic amines, the solubility parameters  $\delta$  were determined by calculation, by using several literature sources and molar additive laws, and experimentally from equilibrium concentrations of 25 solvents, by using bidimensional solubility maps.  $\delta$  values ranging from 20 to 27 MPa<sup>1/2</sup> were found. Their variations with the epoxide and amine structure were discussed. The crosslink density was found to have a neglectable effect on the solvent absorption compared to interaction parameters.

## INTRODUCTION

Although an extensive literature exists on the concepts of the cohesive energy density  $e$  and solubility parameter  $\delta = e^{1/2}$ , and their applications to the prediction of some thermophysical and mechanical properties of glassy polymers,<sup>1-6</sup> little is known in this area on thermosets, especially crosslinked epoxies.<sup>7-10</sup> There are two ways to determine these characteristics:

(i) By calculation using additive laws and elemental group contributions established by several authors.<sup>1-4</sup> This approach is only possible when a network "monomer unit" can be defined, e.g., when the crosslinking is complete and stoichiometric without noticeable side reactions, which seems the case for many epoxide-amine systems.<sup>9</sup>

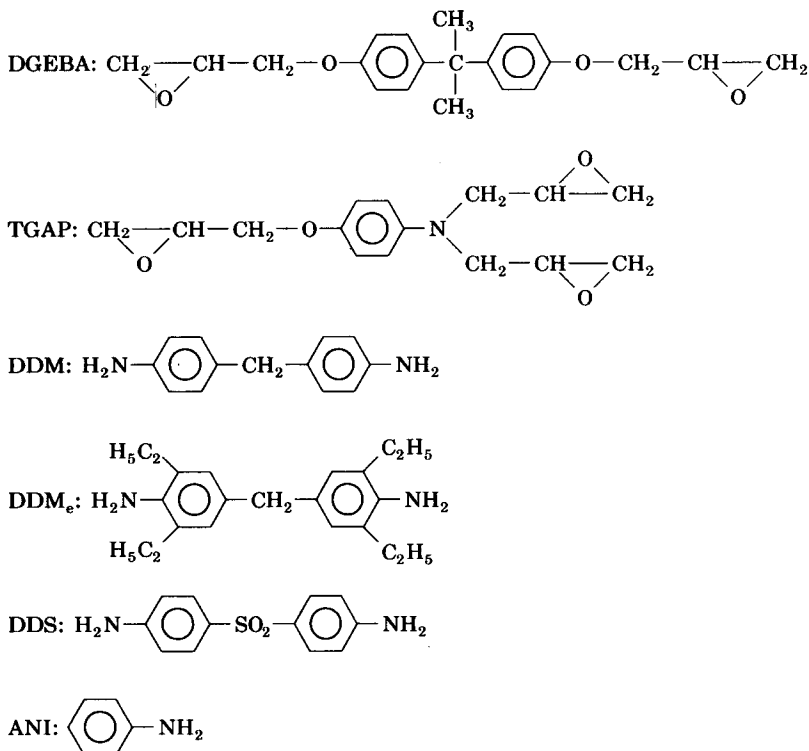
(ii) Experimentally from polymer-solvent interaction "spectra" or "maps."<sup>1,2</sup> In this case, sorption anomalies<sup>10</sup> presumably due to relaxation phenomena or damaging by swelling stresses and hydrogen bonding<sup>1,2</sup> involve serious complications. Despite these difficulties, it seemed to us interesting to use both approaches to try to determine the cohesive parameters of various epoxide-amine stoichiometric networks based on two epoxides: the diglycidyl ether of bisphenol A (DGEBA) and the triglycidyl derivative of amino phenol (TGAP), and four amines: the diamino diphenyl methane (DDM), its tetraethyl derivative (DDME), the diamino diphenyl sulfone (DDS), and the aniline (ANI).

## EXPERIMENTAL

### Materials

The codes and structures of epoxides and amines under study are recalled in Table I. The epoxides were nearly monomers according to their experimentally determined epoxide index: 5.9 *M*/kg for DGEBA and 10.8 *M*/kg for

TABLE I  
Structure and Designating Code of the Epoxides and Amines under Study



TGAP. The amines displayed a single peak in gel permeation chromatograms obtained with small porosity columns (500 Å and  $2 \times 100$  Å) and refractometric detection.

Some cure conditions and characteristics of the networks under study are summarized in Table II. No residual exotherm was observed in the DSC traces, and the glass transition temperature is close to its asymptotic value in all the cases. Sheets of 0.1 mm thickness were used for sorption measurements. Experimental data on hydrogen bonding,<sup>11</sup> glass transition temperature,<sup>12</sup> and water absorption<sup>13</sup> of these systems or similar ones have been already published. In all the cases, the epoxide and amine were in stoichiometric ratio and the amount of irregular structures due to side reactions was considered negligible on the basis of IR and DSC measurements. Then a network "monomer unit" containing three diamine (or six aniline) structural units and the corresponding number of epoxide units was used for the calculations. The corresponding molar weight and molar volume are given in Table II for the networks under study.

### Solvents

Twenty-five solvents were used. Their characteristics are listed in Table III.  $\delta$  is Hildebrand's solubility parameter, according to the data compiled by Van Krevelen.<sup>2</sup>  $\delta_h$ ,  $\delta_p$ , and  $\delta_d$  are, respectively, the hydrogen bonding, the dipolar

TABLE II  
Cure Conditions and Characteristics of the Networks Under Study

System	Cure conditions						$T_g$ (K)		
	First step <sup>a</sup>		Second step <sup>b</sup>		$M^c$ (g/mol)	$V^d$ (cm <sup>3</sup> /mol)			
	Time (h)	Temp (°C)	Time (h)	Temp (°C)					
DGEBA—DDM <sub>e</sub>	1	105	2	180	2970	2578	2.02	4.04	430
	1.5	140							
DGEBA—DDM	1	105	2	180	2634	2195	2.28	4.56	452
TGAP—DDM <sub>e</sub>	3	105	3	180	2038	1734	4.91	5.89	465
	0.5	150							
TGAP—ANI	3	180			1666	1327	2.40	7.20	396
TGAP—DDM	1	105	2	200	1702	1341	5.88	7.05	500
			1	230					
TGAP—DDS	1	105	4.25	230	1852	1392	5.40	6.50	522
	0.2	180							

<sup>a</sup>In air.

<sup>b</sup>In vacuum.

<sup>c</sup>Molar weight of the "monomer unit."

<sup>d</sup>Molar volume of the "monomer unit."

<sup>e</sup>Crosslink density expressed in moles of crosslink "mers" per kg.

TABLE III  
 Characteristics of the Solvents under Study According to Van Krevelen<sup>2</sup>

Solvent	V	M	V/M	$\delta_h$	$\delta_p$	$\delta_d$	$\delta_v$	$\delta_a$	$\delta$
1. Methylisobutylketone	125.8	100.16	1.260	4.1	6.1	15.3	16.5	8.5	17.2
2. Toluene	106.8	92.14	1.160	2.0	1.4	18.0	18.0	2.5	18.2
3. Ethylacetate	98.5	88.11	1.120	7.2	5.3	15.8	16.7	10.6	18.6
4. Chloroform	80.7	119.38	0.676	5.7	3.1	17.8	18.1	6.6	19.0
5. Methylacetate	79.7	74.08	1.080	7.6	7.2	15.5	17.1	11.7	19.6
6. Dioxane	85.7	88.11	0.973	7.4	5.9	17.5	18.5	7.6	20.2
7. Nitrobenzene	102.7	123.11	0.834	4.1	8.6	20.0	21.8	13.0	20.5
8. Aniline	91.5	93.13	0.983	10.2	5.1	19.4	20.1	11.4	21.0
9. Acrylonitrile	67.1	53.06	1.270	6.8	17.4	16.4	23.9	18.7	21.5
10. Pyridine	80.9	79.10	1.020	5.9	8.8	19.0	20.9	10.6	21.9
11. Dimethylphthalate	163.0	194.19	0.840	4.9	10.8	18.6	21.5	11.9	21.9
12. NN dimethylacetamide	92.5	87.12	1.060	10.2	11.5	16.8	20.4	15.4	22.1
13. Pentanol 1	108.2	88.15	1.230	13.9	4.5	16.0	16.6	14.7	22.3
14. Nitroethane	71.5	75.07	0.952	4.5	15.5	16.0	22.3	16.2	22.7
15. Propanol 2	76.8	60.10	1.280	16.4	6.1	15.8	16.0	17.5	23.5
16. Acetonitrile	52.6	41.05	1.290	6.1	18.0	15.3	23.6	19.0	24.1
17. Propanol 1	75.2	60.10	1.250	17.4	6.8	16.0	17.4	18.6	24.3
18. 2-Methoxyethanol	78.8	76.09	1.040	16.4	9.2	16.2	18.6	17.0	24.7
19. Dimethylformamide	77.0	73.09	1.050	11.3	13.7	17.4	22.1	17.8	24.9
20. Ethanol	58.5	46.07	1.270	19.4	8.8	15.8	18.1	18.1	26.0
21. Nitromethane	54.3	61.04	0.890	5.1	18.8	15.8	24.6	19.5	26.0
22. 2-Pyrrolidone	76.3	85.10	0.897	11.3	17.4	19.5	26.1	20.7	28.4
23. Methanol	40.7	32.04	1.270	22.3	12.3	15.1	19.5	25.4	29.6
24. Formamide	39.8	45.04	0.884	19.0	26.2	17.2	31.3	32.4	39.3
25. Water	18.0	18.02	1.000	42.3	16.0	15.5	22.3	45.2	47.4

<sup>a</sup>The solubility parameters are given in MPa<sup>1/2</sup>.

and dispersion components of the solubility parameter according to the data compiled by Van Krevelen.<sup>2</sup> Bidimensional solubility maps<sup>1,2</sup> were obtained by using

$$\delta_h \text{ and } \delta_v = (\delta_p^2 + \delta_d^2)^{1/2} \quad \text{or } \delta_d \text{ and } \delta_a = (\delta_h^2 + \delta_p^2)^{1/2}$$

### Sorption Tests

Samples of approximately 1 g weight were placed in a solvent saturated atmosphere at  $35 \pm 1^\circ\text{C}$  and periodically weighed. The equilibrium value  $v$  of the solvent concentration in the polymer, expressed in  $\text{cm}^3/100 \text{ g}$  of polymer, was used to determine the solubility parameters. The  $v$  values were arbitrarily ranged in three categories corresponding respectively to strong ( $v \geq 2/3$  of the maximum value), medium ( $2/3 > v \geq 1/3$  of the maximum value), and weak ( $v < 1/3$  of the maximum value) interactions, in order to make the bidimensional ( $\delta_h, \delta_v$ ) or ( $\delta_d, \delta_a$ ) solubility maps.

## RESULTS

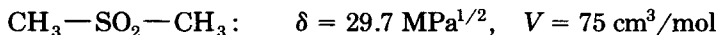
### Calculated Values

Two methods were used:

(a) Assuming the additivity of the cohesive energy molar contributions, the molar cohesive energy of the network "monomer unit" may be calculated as follows:

$$E_c = \sum_i H_{si}$$

where  $H_{si}$  is the molar contribution of the elemental group  $i$  determined in principle from measurements of the sublimation enthalpy of small molecules containing this group. Two literature sources, Fedors<sup>3</sup> and Bondi,<sup>4</sup> were used for these calculations. The corresponding  $H_{si}$  values are listed in Table IV. Noticeable discrepancies can be observed, especially for alkyl groups. Some group contributions were not available; they were determined from other  $H_{si}$  values using an additive law. In the case of the sulfone group, it was deduced from the experimental solubility parameter of the dimethyl sulfone given by Barton<sup>1</sup>:



$E_c = \delta^2 V = H_s(\text{SO}_2) + 2H_s(\text{CH}_3)$  so that  $H_s(\text{SO}_2) = \delta^2 V - 2H_s(\text{CH}_3)$ . Finally, from  $E_c$  and the molar volume of the "monomer unit" (Table II),  $\delta = (E_c/V)^{1/2}$  was calculated for each network. Both series of  $\delta$  values corresponding to Fedors and Bondi data are listed in Table V.

(b) According to Small,<sup>5</sup> the molar attraction constant  $F$  defined by  $F = (E_c V)^{1/2}$  has better additive properties than  $E_c$ . Two sources, Hoy<sup>6</sup> and Van Krevelen,<sup>2</sup> were also used in this case for the elemental group contributions.  $F(\text{SO}_2)$  was determined as before from the experimental data on the

TABLE IV  
Group Molar Contributions Used for the Calculations





	$H_s$ Fedors (J/mol)	$H_s$ Bondi (J/mol)	$F_{\text{Van Krevelen}}$ ( $\text{J}^{1/2} \text{cm}^3/2 \text{mol}^{-1}$ )	$F_{\text{Hoy}}$ ( $\text{J}^{1/2} \text{cm}^3/2 \text{mol}^{-1}$ )
—CH <sub>2</sub> —	4040	8360	280	269
—C(CH <sub>3</sub> ) <sub>2</sub> —	10,890	12,120	840	672.3
	31,940	29,260	1377	1442.2
	31,940	35,110	1517	1398.4
	31,940	28,420	1377	1442.2
—CH <sub>2</sub> —CH <sub>3</sub>	8750	17,970	700	572.4
—O—	3350	4180–1480	256	235.3
	33,230	34,280	894	638
—N—	4190	0	—	125
—SO <sub>2</sub> —	56,140	47,100	1388	1621

TABLE V  
Calculated Values of the Solubility Parameters

System	$\delta_{\text{Fedors}}$ ( $\text{MPa}^{1/2}$ )	$\delta_{\text{Bondi}}$ ( $\text{MPa}^{1/2}$ )	$\delta_{\text{Small-Hoy}}$ ( $\text{MPa}^{1/2}$ )	$\delta_{\text{small-Van Krevelen}}$ ( $\text{MPa}^{1/2}$ )
DGEBA-DDM <sub>e</sub>	22.6	24.3	21.5	23.1
DGEBA-DDM	23.5	24.4	22.1	23.3
TGAP-DDM <sub>e</sub>	23.9	25.9	22.2	23.9
TGAP-ANI	25.5	27.0	23.0	24.9
TGAP-DDM	25.7	26.7	23.5	24.7
TGAP-DDS	27.4	27.7	25.6	25.6

dimethyl sulfone. The elemental group contributions used for the calculations are listed in Table IV and the resulting solubility parameters in Table V.

### Interactions with Solvents

#### *Shape of the Sorption Curves*

In the great majority of cases, the sorption curves were apparently Fickian, and the solvent concentration reached equilibrium after many weeks. In some cases, with pyridine and formamide, for instance, no equilibrium was reached even after 2 months. The corresponding data were not used for the solubility parameter determinations.

#### *Hildebrand's Solubility Spectra*

The curves of the solvent equilibrium concentration  $v$  vs. Hildebrand's solubility parameter  $\delta$  are presented in Figures 1 and 2. As expected for the

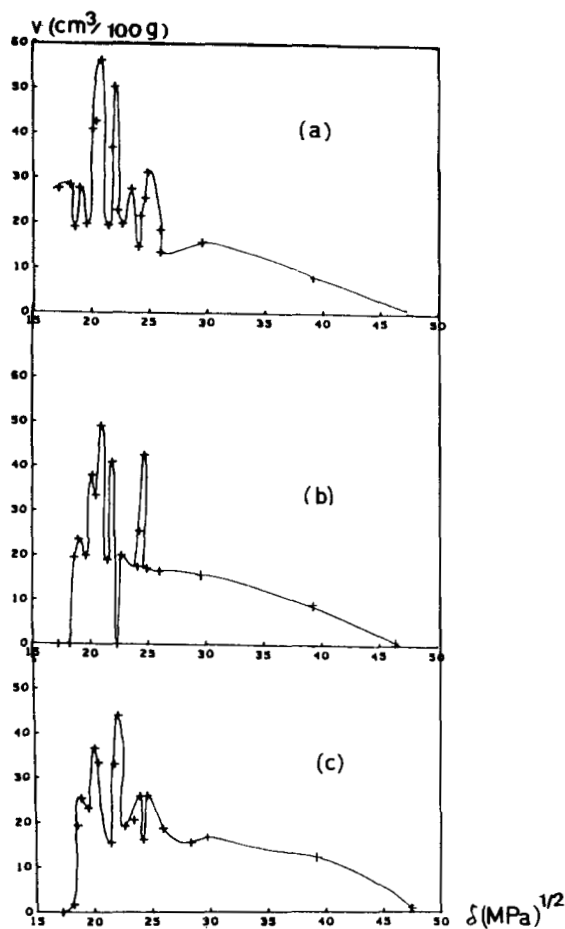


Fig. 1. Equilibrium solvent concentration vs. Hildebrand's solubility parameter for (a) DGEBA-DDM<sub>e</sub>; (b) DGEBA-DDM, and (c) TGAP-DDM<sub>e</sub>.

hydrogen bonding systems,<sup>1</sup> they display a very complex shape and cannot be used directly for a determination of the solubility parameter. However, they call for some interesting remarks:

For the solvents of low to moderate solubility parameter ( $\delta \leq 23 \text{ MPa}^{1/2}$ ), it is interesting to compare the average solvent equilibrium concentration  $v_{av}$  defined by

$$v_{av} = \frac{\sum_1^{14} v_i}{14}$$

where  $i$  is the solvent number in Table III. The values of  $v_{av}$  are listed in Table VI. Two sample families can be clearly distinguished: those for which  $v_{av} \geq 20 \text{ cm}^3/100 \text{ g}$ , DGEBA-DDM<sub>e</sub>, DGEBA-DDM, and TGAP-DDM<sub>e</sub>; and those for which  $v_{av} \leq 6 \text{ cm}^3/100 \text{ g}$ , TGAP-ANI, TGAP-DDM, and TGAP-DDS. Two structural effects are put in evidence:

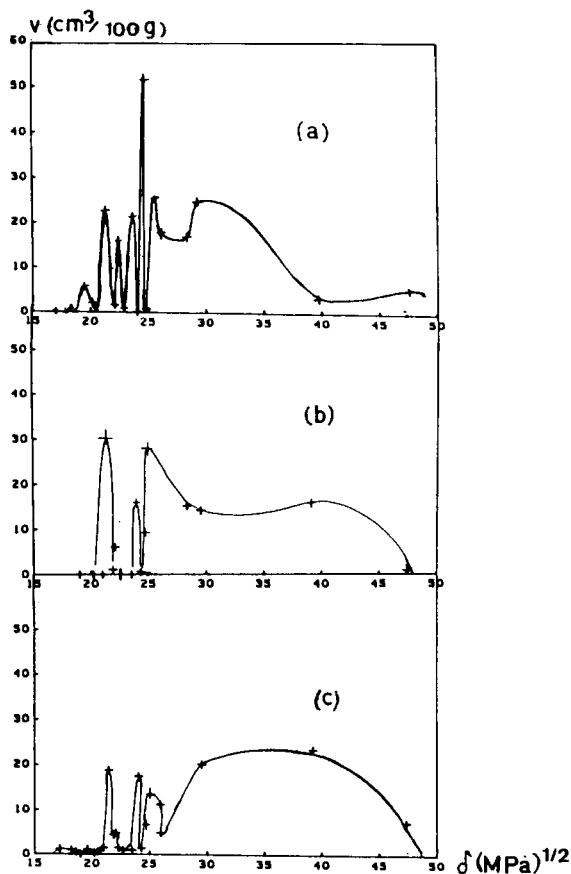


Fig. 2. Equilibrium solvent concentration vs. Hildebrand's solubility parameter for (a) TGAP-ANI; (b) TGAP-DDM, and (c) TGAP-DDS.

(i) The effect of the epoxide structure: DGEBA > TGAP, which is obviously related to the concentration of highly polar groups:  $[\text{OH}] \approx 7 \text{ M/kg}$  in TGAP systems against  $4\text{--}4.6 \text{ M/kg}$  in DGEBA systems.

(ii) The effects of the amine structure:  $\text{DDM}_e \gg \text{DDM} \approx \text{ANI} > \text{DDS}$ , which can be related partially to the overall cohesion effects (see the hierarchy of the calculated solubility parameters in Table V), partially to specific interaction effects at the amine level,<sup>11</sup> which will be discussed in the last section.

#### *Bidimensional Solubility Maps*

The maps  $(\delta_a, \delta_d)$  and  $(\delta_h, \delta_v)$  are presented in Figures 3 and 4. In all the cases, the inner and the outer areas correspond respectively to the most and the least active solvents. Thus, a "focal" region corresponding to the polymer solubility parameters can be more or less precisely defined. Indeed, the number of solvents under study (25) is largely insufficient for a precise



TABLE VI  
Experimental Data from Equilibrium Concentrations (See the Text)

System	$v_{av}$ ( $\text{cm}^3/100 \text{ g}$ )	$\delta_{h, av}$ ( $\text{MPa}^{1/2}$ )	$\delta_{p, av}$ ( $\text{MPa}^{1/2}$ )	$\delta_{d, av}$ ( $\text{MPa}^{1/2}$ )	$\delta_{h, graph}$ ( $\text{MPa}^{1/2}$ )	$\delta_{p, graph}$ ( $\text{MPa}^{1/2}$ )	$\delta_{d, graph}$ ( $\text{MPa}^{1/2}$ )	$\delta_{graph}$ ( $\text{MPa}^{1/2}$ )
DGEBA-DDM <sub>e</sub>	32	9.54	8.76	15.64	20.30	10.3	18.2	22.0
DGEBA-DDM <sub>c</sub>	22	9.39	10.11	17.36	22.17	10.0	18.5	22.2
TGAP-DDM <sub>e</sub>	22.4	10.41	10.40	15.88	21.65	11.2	17.9	22.5
TGAP-ANI	4.4	13.70	13.01	16.33	24.97	10.6	16.5	23.9
TGAP-DDM	4.8	13.02	15.38	16.40	25.98	7.7	16.7	24.8
TGAP-DDS	3.2	14.43	15.36	16.39	26.70	19.1	16.2	27.1

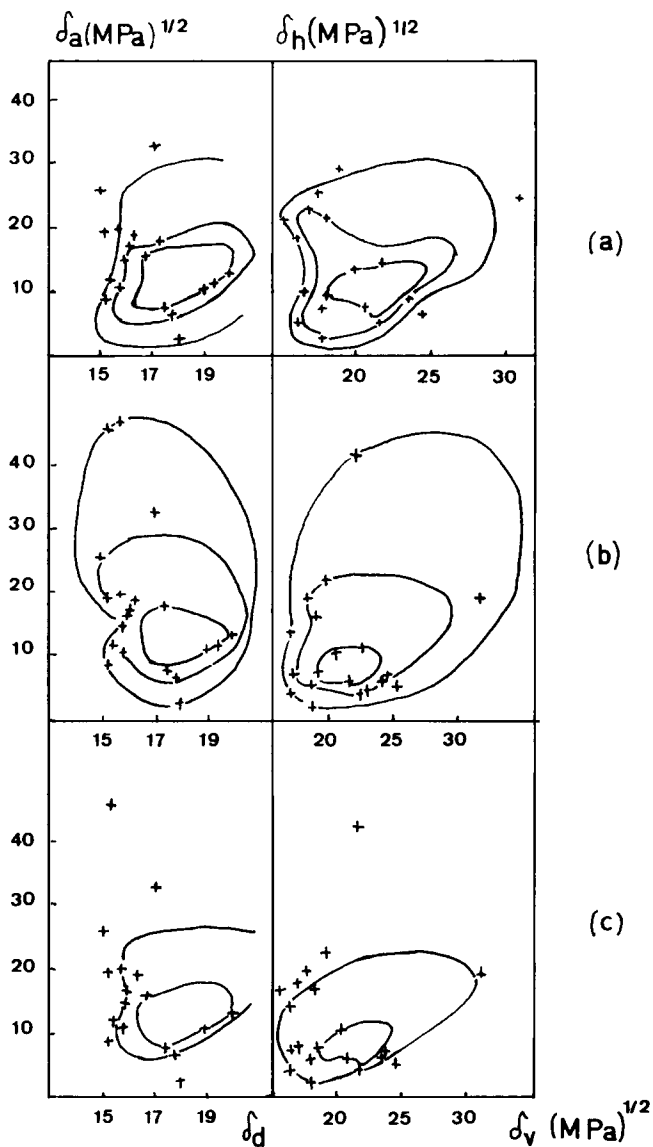


Fig. 3. Bidimensional solubility maps  $\delta_a = f(\delta_d)$  on the left side and  $\delta_h = f(\delta_v)$  on the right side for (a) DGEBA-DDM<sub>e</sub>, (b) DGEBA-DDM, and (c) TGAP-DDM<sub>e</sub>.

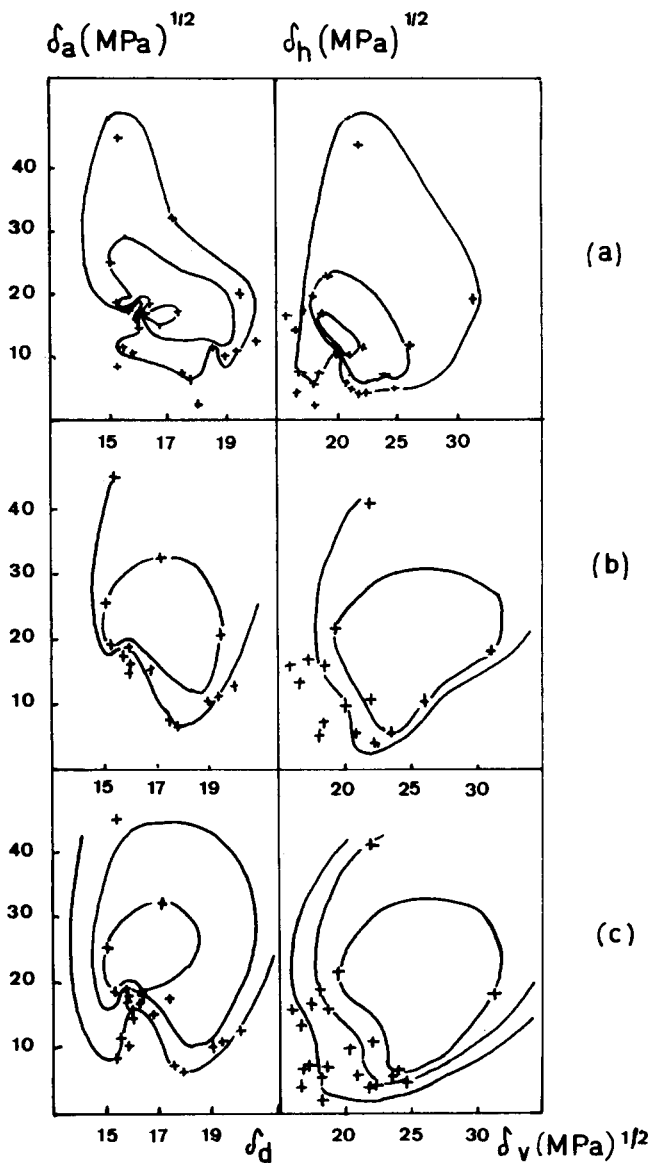


Fig. 4. Bidimensional solubility maps  $\delta_a = f(\delta_d)$  on the left side and  $\delta_h = f(\delta_v)$  on the right side for (a) TGAP-ANI, (b) TGAP-DDM, and (c) TGAP-DDS.

determination; however, we tried to obtain an order of magnitude by two methods:

(i) Average values: It is supposed that for each component of the solubility parameter, for instance,  $\delta_d$ , the polymer value is given by

$$\delta_{d,av} = \frac{\sum v_i \delta_{di}}{\sum v_i}$$

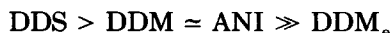
Indeed, the results should depend on the solvent's choice, but it can be assumed in a first approximation that the  $\delta_d$ ,  $\delta_p$ , and  $\delta_h$  values are almost homogeneously distributed among the solvent population (Table III). The results are listed in Table VI. The resulting overall solubility parameter was determined by the relation:

$$\delta_{av} = \left( \delta_{d,av}^2 + \delta_{p,av}^2 + \delta_{h,av}^2 \right)^{1/2}$$

(ii) Graphically determined values: By an analysis of the distribution of the  $v$  values along various axes, we tried to determine the most probable polymer coordinates in Figures 3 and 4. These coordinates are supposed to be schematically the center of gravity of the figure. The results are listed in Table VI. Here also, the overall solubility parameter  $\delta_{\text{graph}}$  was determined by the same relation.

## DISCUSSION

Despite noticeable discrepancies, all the above methods of determination of the solubility parameters agree with the following hierarchies:



The most probable  $\delta$  values range from 20 MPa<sup>1/2</sup> (DGEBA—DDM<sub>e</sub>) to 27 MPa<sup>1/2</sup> (TGAP—DDS), which corresponds to cohesive energy densities from 0.4 to almost 0.8 GPa. Determinations of the packing density<sup>14</sup> or the ultrasonic elastic moduli<sup>15</sup> led to practically the same hierarchy.

As previously quoted, the difference between TGAP and DGEBA can be attributed to the fact that the concentration of highly polar hydroxyl groups is higher in TGAP systems than in their DGEBA homologues. Concerning the amines, two structural effects are to be taken into account:

(i) The direct effect of the amine structure: the fact that DDM > DDM<sub>e</sub> is logical since the ethyl groups of low polarity have a diluting effect in the DDM<sub>e</sub> systems. In the same way, the fact that DDS > DDM can be attributed to the high polarity of the sulfone bridge compared to the methylene one. In principle, DDM and ANI systems should be very close owing to the similarity of their structure, as found for the calculated values (Table V). The solubility parameter is, however, expected to be slightly higher for an ANI system than for its DDM homologue since this latter contains more nonpolar methylene groups, which does not agree with the results of experimental determinations (Table VI).

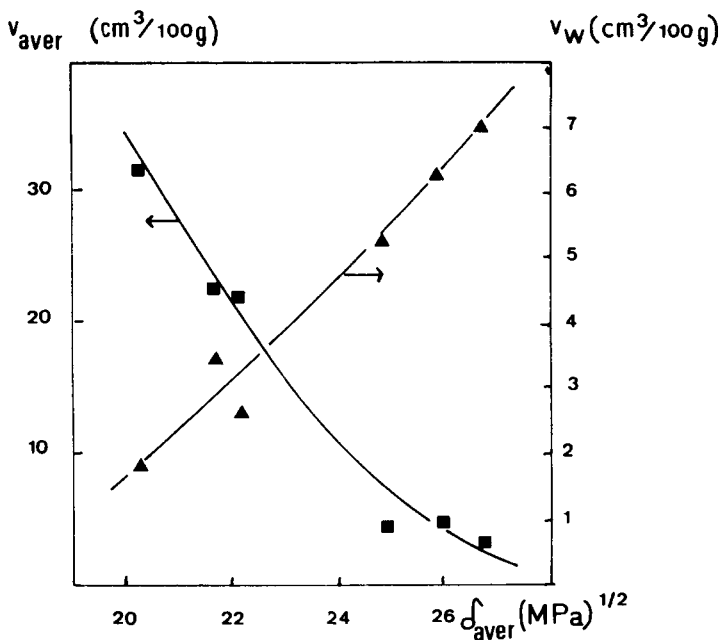


Fig. 5.  $v_{\text{av}}$  and  $v_w$  (see the text) vs. the experimental solubility parameter  $\delta_{\text{av}}$ .

(ii) The indirect effect of the amine structure on hydrogen bonding. The detailed studies of the structural effects on the water absorption<sup>13</sup> and the IR spectrum of hydroxyls<sup>11</sup> suggest the coexistence of inter and intramolecularly hydrogen bonded OH groups. Both types of studies lead to the following hierarchy of the concentration ratios [inter]/[intra]: DDS > DDM > ANI > DDM<sub>e</sub>. Since presumably intermolecular bonds (more than intramolecular ones) contribute to the cohesion, it is not surprising to find the same hierarchy in the experimental determination of  $\delta$  values (Table VI), and the difference observed before between DDM and ANI systems can be explained by these considerations. It is noteworthy that the calculation methods of  $\delta$ , implicitly based on the hypothesis that the various molar group contributions are not interdependent, cannot give accurate results in such cases where intrasegmental interactions are not taken into account. Another interesting point derived from experimental data can be illustrated by the Figure 5, where the average solvent equilibrium concentration  $v_{\text{av}}$ , for low to moderate solubility parameters as defined in the result section, and the water equilibrium concentration  $v_w$  are plotted vs. an arbitrarily chosen solubility parameter  $\delta_{\text{av}}$  (Table VI).  $v_{\text{av}}$  and  $v_w$  are almost monotonically decreasing or increasing functions of the solubility parameter and seem to be practically unaffected by the crosslink density. As a matter of fact,  $v_w$  is maximum for the most densely crosslinked networks: TGAP—DDM and TGAP—DDS, and  $v_{\text{av}}$  is considerably higher for TGAP—DDM<sub>e</sub> ( $n = 4.91 \text{ M/kg}$ ) than for TGAP—ANI ( $n = 2.4 \text{ M/kg}$ ). These trends were confirmed for all the individual solvents under study. In other words, for these systems, the solvent absorption is essentially governed by interaction factors so that the swelling ratio cannot be used to determine

the crosslink density, although, for limited structural series, it seems to give useful results.<sup>16</sup>

### CONCLUSION

Despite a considerable scatter in the experimental results, but also in the literature data, the solubility parameters of six epoxide-amine stoichiometric networks were estimated from calculations by additive molar functions and from experimental solubility maps. They vary between 20 and 27 MPa<sup>1/2</sup>. Two main structural parameters play an important role: the hydroxyl concentration which depends essentially, in the systems under study, on the epoxide structure; and the amine structure which governs the proportion of intramolecularly bonded hydroxyls having a relatively low contribution to the cohesion compared to the intermolecularly bonded ones.

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