



# Standard Test Method for Solubility Range of Resins and Polymers<sup>1</sup>

This standard is issued under the fixed designation D 3132; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers determination of the solubility of resins and polymers in terms of the region of solubility parameter and hydrogen bonding of solvents in which complete solution occurs. In some cases dipole moment of the solvents may also be required to delineate more exactly the boundaries of solubility.

1.2 This test method is applicable only if the test solutions are of sufficient clarity and freedom from color to allow accurate visual judgement of complete solubility and of low enough viscosity for solution to take place.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For a specific hazard statement see Note 1 in 6.2.

## 2. Terminology

### 2.1 Definitions:

2.1.1 The solubility parameter  $\delta$  of a substance is defined as the square root of the “cohesive energy density,” or energy of vaporization per unit volume:

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

where:

$\Delta E$  = energy of vaporization, and

$V$  = molar volume.

The value of  $\delta$  for a volatile liquid can be calculated accurately from the latent heat of vaporization, or approximately from its boiling point. Solubility parameter values for large number of solvents are available in Table 1.

2.1.2 Solvents are also classified according to their hydrogen bonding power,  $\gamma$ . Numerical values for  $\gamma$  may be derived from spectroscopic analysis. In one method,<sup>2</sup>  $\gamma$  is defined as one-tenth the wavenumber shift observed by Gordy's tech-

nique,<sup>3</sup> and values range from 0 to about 25. Another method,<sup>4</sup> which limits values of  $\gamma$  to the range of 2.2 to 10, defines  $\gamma$  by the following equation:

$$\gamma = (0.0359 \times \Delta\nu) + 2.2 \quad (2)$$

where  $\nu$  is the wavenumber shift as determined by Gordy's method. Hydrocarbons, halogenated hydrocarbons and nitrohydrocarbons have low values of  $\gamma$ ; esters, ethers, etheralcohols, and ketones are intermediate; and alcohols, amines, and acids have high values.

2.1.3 The solubility parameter  $\delta_m$ , of a mixture of solvents having parameters,  $\delta_1$ ,  $\delta_2$ , etc., is a function of the molar fraction and molar volume of the components:

$$(\delta_1 x_1 V_1 + \delta_2 x_2 V_2) / (x_1 V_1 + x_2 V_2) \quad (3)$$

in which  $x_1$  and  $V_1$ ,  $x_2$  and  $V_2$ , etc., are the corresponding molar fractions and volumes, respectively. If the components have the same molar volumes ( $V_1 = V_2$ ),

$$\delta_m = x_1 \delta_1 + x_2 \delta_2 \quad (4)$$

Thus, in a mixture of two components A and B having the same molar volumes and solubility parameter values of  $\delta_A$  and  $\delta_B$

$$\delta_m = \frac{(\text{volume percent A} \times \delta_A) + (\text{volume percent B} \times \delta_B)}{100} \quad (5)$$

2.1.4 Similarly, the hydrogen bonding value,  $\gamma_m$ , of a mixture is determined by:

$$\gamma_m = \frac{(\text{volume percent A} \times \gamma_A) + (\text{volume percent B} \times \gamma_B)}{100} \quad (6)$$

and dipole moment by:

$$\mu_m = \frac{(\text{volume percent A} \times \mu_A) + (\text{volume percent B} \times \mu_B)}{100} \quad (7)$$

## 3. Summary of Test Method

3.1 Solubility of resinous and polymeric materials is dependent upon the solubility parameter, hydrogen bonding, and dipole moment of the solvents. Solubility parameter is the most important property of the three, followed by hydrogen bonding. Consequently, the solubility of most materials is sufficiently defined by the area of solubility parameter and hydrogen

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings, Materials, and Applications and is the direct responsibility of Subcommittee D01.33 on Polymers and Resins.

Current edition approved Aug. 31, 1984. Published January 1985. Originally published as D 3132 – 72. Last previous edition D 3132 – 72 (1984).

<sup>2</sup> Crowley, J. D., et al, “A Three Dimensional Approach to Solubility,” *Journal of Paint Technology*, JPIRA, Vol 38, No. 496, 1966, p. 269; Vol 39, No. 504, 1967, p. 19.

<sup>3</sup> Gordy, W., “Spectroscopic Evidence of Hydrogen Bonds,” *Journal of Chemical Physics*, JCPA, February 1939, February 1940, March, 1941.

<sup>4</sup> E. I. du Pont de Nemours & Co., Bulletin PA 12-770, “Solvent Formulating Maps for Elvacite Acrylic Resins, Serial A-70562, July 1970.

bonding of true solvents. A material is insoluble or incompletely soluble in a solvent if its solubility parameter and hydrogen bonding properties fall outside this region.

3.2 In this test method, the material is tested separately in solvents that cover the entire solubility diagram so that boundaries of complete solubility can be determined.

#### 4. Significance and Use

4.1 This test method is useful for an empirical determina-

tion of the solvent(s) in which a resin or polymer may be dissolved. This test method is also applicable to estimate the

solvents that may be useful for further dilution of a polymer or resin solution without formation of haze or without polymer or resin precipitation.

**TABLE 1 Solvent or Solvent Mixtures**

No.	Solvent or Solvent Mixture (Mixture Given in Volume Percent)	Solubility Parameter, $\delta$	Hydrogen Bonding		Dipole Moment, <sup>4</sup> $\mu$
			$\gamma^B$	$\gamma^C$	
1*	Diisopropyl ether	6.9	11.7	6.6	1.3
2	<i>n</i> -Pentane	7.0	0	2.2	0
3*	<i>n</i> -Heptane	7.3	0	2.2	0
4	50 % Diisobutyl ketone	7.4	10.1	5.9	2.0
	50 % Diisopropyl ether				
5*	Diethyl ether	7.4	13.0	6.9	1.2
6*	50% <i>n</i> -Heptane	7.6	4.2	3.7	1.4
	50 % Diisobutyl ketone				
7	25 % <i>n</i> -Heptane	7.7	6.3	4.5	2.0
	75 % Diisobutyl ketone				
8	Methyl cyclohexane	7.8	0	2.2	0
9	66.7 % <i>n</i> -Heptane	7.8	2.9	3.3	0.6
	33.3 % <i>n</i> -Butyl Acetate				
10*	Diisobutyl ketone	7.8	8.4	5.2	2.7
11*	57 % Diethyl ether	7.9	11.2	6.3	1.5
	43 % <i>n</i> -Butyl acetate				
12	66.7 % Diethyl ether	8.1	14.9	7.6	1.4
	33.3 % 2-Ethylhexanol				
13*	Cyclohexane	8.2	0	2.2	0
14	40 % <i>n</i> -Heptane	8.2	5.3	4.1	1.1
	60 % <i>n</i> -Butyl acetate				
15	71 % Cyclohexane	8.4	1.3	2.7	0.1
	29 % Toluene				
16*	<i>n</i> -Butyl acetate	8.5	8.8	5.4	1.9
17*	40 % Cyclohexane	8.6	2.7	3.2	0.2
	60 % Toluene				
18	50 % Cyclohexane	8.7	0	2.2	0
	50 % Benzene				
19	50 % <i>n</i> -Butyl acetate	8.7	6.7	4.6	1.2
	50 % Toluene				
20	50 % EGMBE (See No. 23)	8.7	10.9	6.2	1.8
	50 % <i>n</i> -Butyl acetate				
21*	33.3 % Diethyl ether	8.8	16.8	8.2	1.5
	66.7 % 2-Ethylhexanol				
22*	Toluene	8.9	4.5	3.8	0.4
23	2-Butoxyethanol	8.9	13.0	6.9	1.6
24*	Benzene	9.2	0	2.2	0
25	Propylene oxide	9.2	10.0	5.8	1.8
26	56 % EGMBE	9.2	15.5	7.8	1.6
	44 % 2-Ethylhexanol				
27	50 % Methylene chloride	9.3	3.0	3.3	1.0
	50 % Toluene				
28*	50 % Toluene	9.4	7.1	4.8	0.4
	50 % Dioxane				
29*	2-Ethylhexanol	9.5	18.7	8.9	1.7
30	Methyl acetate	9.6	8.4	5.2	1.7
31*	Methylene chloride	9.7	1.5	2.7	1.5
32	66.7 % Methylene chloride	9.8	4.2	3.7	1.1
	33.3 % Dioxane				
33	50 % Dioxane	9.8	5.6	4.2	1.0
	50 % Methylene chloride				
34*	Dioxane	9.9	9.7	5.7	0.4
35	Cyclohexanone	9.9	11.7	6.4	2.7
36*	2-Ethoxyethanol	9.9	13.0	6.9	1.6
37	75 % EGMBE	9.9	14.4	7.4	1.6
	25 % Methyl isobutyl carbinol				
38*	Carbon disulfide	10.0	0	2.2	0
39	30 % EGMBE	10.0	17.0	8.2	1.7
	70 % Methyl isobutyl carbinol				

**TABLE 1** *Continued*

No.	Solvent or Solvent Mixture (Mixture Given in Volume Percent)	Solubility Parameter, $\delta$	Hydrogen Bonding		Dipole Moment, <sup>A</sup> $\mu$
			$\gamma^B$	$\gamma^C$	
40	Methyl isobutyl carbinol	10.0	18.7	8.8	1.7
41	66.7 % Methylene chloride 33.3 % Nitroethane	10.2	1.8	2.8	2.2
42	66.7 % Dioxane 33.3 % Nitroethane	10.3	7.3	4.8	1.5
43*	50 % Toluene	10.4	5.4	4.2	2.2
44*	50 % Acetonitrile 50 % EGME	10.4	15.9	7.9	1.7
45*	50 % <i>n</i> -Amyl alcohol				
46	2-Ethylbutanol 33.3 % Methylene chloride 66.7 % Nitroethane	10.5 10.6	18.7 2.2	8.9 3.0	1.7 2.9
47	75 % Nitroethane 25 % Dioxane	10.8	4.3	3.8	2.8
48	75 % Dioxane 25 % Propylene carbonate	10.8	8.5	5.3	1.6
49	Dimethylacetamide	10.8	12.3	6.6	3.8
50	80 % EGME 20 % Methanol	10.8	14.1	7.3	1.6
51	33.3 % EGME 66.7 % <i>n</i> -Butanol	10.9	16.8	8.2	1.7
52	<i>n</i> -Amyl alcohol (pentanol)	10.9	18.7	8.9	1.7
53	48 % Benzene 52 % Nitromethane	11.0	1.3	2.7	1.8
54	50 % Dioxane 50 % Dimethylformamide	11.0	10.7	5.6	2.1
55*	Nitroethane	11.1	2.5	3.1	3.6
56	25 % <i>n</i> -Butyl acetate 75 % Acetonitrile	11.1	6.9	4.5	3.4
57*	<i>n</i> -Butanol	11.4	18.7	8.9	1.7
58*	50 % Nitroethane 50 % Acetonitrile	11.5	4.4	3.8	3.8
59	65 % EGME 35 % Methanol	11.5	15.0	7.6	1.6
60*	66.7 % <i>n</i> -Butanol 33.3 % Dimethylformamide	11.6	16.4	8.2	2.4
61*	50 % Dioxane 50 % Dimethyl sulfoxide	11.7	8.7	5.4	2.2
62	50 % Nitroethane 50 % Nitromethane	11.9	2.5	3.1	3.5
63*	Acetonitrile	11.9	6.3	4.5	3.9
64	30 % <i>n</i> -Butanol 70 % Dimethylformamide	11.9	13.8	7.2	3.2
65	<i>n</i> -Propanol	11.9	18.7	8.9	1.7
66	70 % Acetonitrile 30 % Dimethylformamide	12.0	8.0	5.1	3.9
67	68 % Dimethylformamide 32 % Acetonitrile	12.0	10.0	5.8	3.8
68*	Dimethylformamide	12.1	11.7	6.4	3.8
69	50% <i>n</i> -Propanol 50 % Ethanol	12.3	18.7	8.9	1.7
70	60 % Nitromethane 40 % Acetonitrile	12.4	4.0	3.7	3.6
71*	50 % Ethanol 50 % Dimethylformamide	12.4	15.2	7.7	2.8
72	23 % Dioxane 77 % Propylene carbonate	12.5	6.0	4.4	3.9
73	40 % Dimethylformamide 60 % Dimethyl sulfoxide	12.6	9.3	5.6	3.9
74	70 % Ethanol 30 % Dimethylformamide	12.6	16.6	8.2	2.3
75	80 % Dimethylformamide 20 % Methanol	12.6	13.1	6.9	3.4
76*	Nitromethane	12.7	2.5	3.1	3.4
77*	Ethanol	12.8	18.7	8.9	1.7
78*	72 % Dimethyl sulfoxide 28 % Ethanol	12.9	10.8	6.1	3.4
79*	Dimethyl sulfoxide	13.0	7.7	5.0	4.0
80	46 % Methanol 54 % Dimethylformamide	13.2	14.9	7.6	2.8
81*	Propylene carbonate	13.3	4.9	4.0	5.0
82	80 % Dimethyl sulfoxide 20 % Methanol	13.3	9.9	5.8	3.5

TABLE 1 Continued

No.	Solvent or Solvent Mixture (Mixture Given in Volume Percent)	Solubility Parameter, $\delta$	Hydrogen Bonding		Dipole Moment, <sup>A</sup> $\mu$
			$\gamma^B$	$\gamma^C$	
83	70 % Dimethylformamide	13.3	11.8	7.0	3.8
84	30 % Monomethylformamide	13.6	18.7	8.9	1.7
	50 % Ethanol				
85*	50 % Methanol	13.7	16.4	8.1	2.4
	66.7 % Methanol				
86*	33.3 % Dimethylformamide	13.9	14.0	7.8	2.7
	57 % Methanol				
87*	43 % Dimethyl sulfoxide	14.5	18.7	8.9	1.7
88*	Methanol	15.0	20.6	9.4	2.2
89	Propylene glycol	15.1	16.2	8.8	2.5
	63 % Methanol				
90	37% Monomethylformamide	17.1	20.6	9.6	2.3
	Ethylene glycol				

<sup>A</sup> McLellan, A. L., *Tables of Experimental Dipole Moments*, W. H. Freeman & Co., San Francisco, 1963.

<sup>B</sup> Crowley, J. D., et al, "A Three Dimensional Approach to Solubility," *Journal of Paint Technology*, Vol 38, No. 496, 1966, p 269; Vol 39, No. 504, 1967, p. 19.

<sup>C</sup> E. I. du Pont de Nemours & Co., Bulletin PA 12-770, "Solvent Formulating Maps for Elvacite Acrylic Resins," Serial A-70562, July 1970.

## 5. Apparatus

5.1 *Glass Vials*, with screw caps, capacity 5 to 20 mL.

5.2 *Mixing Rolls, Tumblers, or Other Rotary Mixing Machine*.

## 6. Reagents and Materials

6.1 Solvents and solvent mixtures used in this test method are listed in Table 1, in order of increasing solubility parameter. Those with an asterisk can be used in a preliminary survey to establish the general areas of solubility and nonsolubility. Intermediate solvents are then used to define more closely the solubility limits of a resin.

6.2 *Quality of Solvents*—Each solvent should be a good technical or commercial grade containing not less than 95 %, but preferably 99 %, of the specified compound and should be essentially anhydrous (<0.3 percent water).

NOTE 1—**Warning:** Diethyl ether, diisopropyl ether, and dioxane may form explosive peroxides on long storage, particularly if kept in glass bottles exposed to light.

6.3 Solvent mixtures, which are in volume percent, should be made by adding solvent from burets that have been washed with diethyl ether, dried at 65°C and rinsed twice with solvent before filling. Bottles containing mixtures should be tightly capped to prevent evaporation. Condensate above the liquid level should be well mixed in before using.

## 7. Procedure

7.1 *Preparation of Solutions:*

7.1.1 The ratio of solute to solvent should correspond as much as possible to the intended use of the material but should be chosen to avoid difficulty in effecting solution because the viscosity must be low enough for mixing to take place. For most film-formers the concentration range is from 40 % for low molecular weight resins to 10 % for polymers that give viscous solutions.

7.1.2 The precision of weighing the solute and solvent should ensure a maximum deviation of  $\pm 5\%$  in the desired concentration in each series of tests. Report the test concentration with the results since the solubility parameter range is somewhat dependent upon concentration.

7.1.3 Dry the clean vials at 65°C and label or mark them.

Select vials that are sufficiently large to promote flow of viscous solutions. A 15-mL vial containing 5 g of solution has been found satisfactory.

7.1.4 Reduce large lumps of aggregates in the resin or polymer to a convenient size by means that do not introduce contamination but not to a fine powder that may lead to packing or oxidation. With resins that give solutions of low viscosity, the solvent may be added to the solute or vice versa. The former is usually more convenient as the material can first be weighed into all the vials followed by the selected solvents. With high molecular weight resins that tend to gel, the order of addition markedly affects the time required to dissolve the resin and eliminate gel particles. Consequently, the solvent should be weighed into the vial and then the specimen in small portions.

7.1.5 In either procedure, after adding the correct amounts of solute and solvent, cap the vial tightly and mix the contents by shaking or swirling. Tumble or rotate the vials end-over-end for 24 h. One method is to place the vials in a quart or gallon can with their long axes perpendicular to the long axis of the can and rotate the can at a slow speed on mixing rolls. The rate of rotation should not be so fast as to prevent back and forth flow in the vials. One to five revolutions per minute are suitable speeds.

7.2 *Interpretation of Results:*

7.2.1 At the end of 24 h line up the vials for observation. Allow to stand for a few minutes and then classify the appearance of the contents according to the following ratings:

7.2.1.1 *Complete Solution*—A single, clear liquid phase with no distinct solid or gel particles.

7.2.1.2 *Borderline Solution*—Cloudy or turbid but without distinct phase separation.

7.2.1.3 *Insoluble*—Two phases: either a liquid with separate gel or solid phase or two separate liquids.

7.2.2 Maintain borderline samples at 20 to 27°C for 7 days and observe again to determine if the classification has changed.

7.2.3 Plot the solubility results on a graph using solubility parameter as abscissa, hydrogen bonding as ordinate, and symbols to distinguish the three solubility classes.

7.2.4 Identify areas of complete solubility and insolubility and select additional solvents from Table 1 to define more

closely the solubility limits of the resin. Repeat the test with these solvents and also with any that produced anomalous results, for example, borderline or insoluble between two complete solutions.

7.2.5 Plot the additional test results and draw in the limits of solubility. If anomalies are still present it may be necessary to plot solubility parameter versus dipole moment at eight levels of hydrogen bonding and draw in solubility limits (contour lines) for each level.

7.2.6 The solubility classification in 7.2.1 uses the simplified approach that there are no differences within the soluble and insoluble regions. Actually, it is possible to distinguish degrees of solubility and insolubility. The latter ranges from settling of an apparent or borderline solution, through various levels of gelling and wetting, to complete insolubility when the resin is absolutely unaffected by the solvent. Similarly in the soluble region, not all solutions are identical. With resins that are high in molecular weight or have a wide range in molecular weight distribution, there may be only a few solvents that produce perfectly clear solutions. The other solutions may vary from being slightly cloudy to fairly turbid. Viscosity measurements on the solution, allowing for solvent viscosity, might be used to determine the area of best solubility. Contour lines of degrees of solubility could be drawn if sufficient solvents were tested.

7.2.7 Because there is this gradation from complete solubility to total insolubility, where the borderline is placed may be a matter of personal choice or the end-use of the polymer. High clarity may be required for an unpigmented solution while some turbidity might be acceptable if the material will be pigmented in use.

## 8. Report

8.1 Results of this test are preferably presented in the form of a graph showing the region of solubility for the material under test. For written reports, state the minimum and maximum solubility parameter,  $\delta$ , and hydrogen bonding,  $\gamma$ , at which solution took place. If desired, the solubility parameter limits at several levels of hydrogen bonding can be given.

8.2 Report the concentration of resin used in the tests.

## 9. Precision

9.1 No statement of precision is presently available for this test method.

## 10. Keywords

10.1 dilution ratio; resin solubility; solubility parameters of resins

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