average velocity, sq.cm./sec.
$\mathcal{D}$ = mutual diffusion coefficient of dilute gas, sq.cm./sec.
$\mathcal{D}_{12}$ = intradiffusion coefficient of dilute gas, sq.cm./sec.
$E(\sigma_k)$ = binary correlation of tray efficiency
$E^{(i)}$ = multicomponent tray efficiency
E_{ij} = constant
j_i = mass or mole flux relative to volume average velocity, g./(sq.cm. sec.) or mole/ (sq.cm./sec.)
P_{ij} = element of modal matrix of diffusion coefficients
S = constant, function of D_{ij}
t = time, sec.
V_i = volume of diaphragm cell compartment, cc.
x_i = mole fraction of species i
β = calibration constant of diaphragm cell, cm.$^{-2}$
ΔC_i = concentration difference in top, bottom diaphragm compartments
σ_i = eigenvalue of diffusion coefficients, sq.cm./sec.

Subscripts

A = top compartment of diaphragm cell
B = bottom compartment
0 = value at zero time
1, 2 = solute species
3 = solvent species

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Manuscript received December 2, 1968; revision received February 28, 1969; paper accepted March 3, 1969.

Calculation of Solubility Parameters of Polar Compounds

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A graphical method is presented for calculating solubility parameters and molar volumes of functional groups, as well as for calculating solubility parameters of high molecular weight members of a homologous series from data on low molecular weight members. These functional group solubility parameters and molar volumes have been used to extend the values of $\sqrt{EV}$ presented earlier by Small. Finally, it is shown that the use of group contributions to calculate cohesive energy is limited by the lack of information available on the intramolecular energies of interaction of functional groups on the same molecule.

In order to study the behavior of components in mixtures of nonelectrolytes, it is necessary to estimate the interaction energies between molecules in solution. Hildebrand (*1*) and Scatchard (*2*), in laying the groundwork for what is called *regular solution theory*, suggested that these interaction energies could be calculated from what they called *solubility parameters*. These solubility parameters are the square root of the cohesive energy density (that is, the cohesive energy per cubic centimeter of liquid) for the pure components. If one assumes that, in the gas phase, the compound for which the solubility parameter is to be calculated forms a perfect gas with no interactions between the molecules, the solubility parameters (δ) can be calculated directly from heat of vaporization data by Equation (1):

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TABLE 1. SOLUBILITY PARAMETERS (δ) AND MOLAR VOLUMES (V) OF FUNCTIONAL GROUPS

Group	δ	V, cc./mole
—NH_2	11.75	29.49
—F	6.58	30.30
—Cl	8.89	34.98
—Br	9.45	33.07
—I	9.68	42.30
—COOH	14.47	36.28
—OH	20.29	19.66
—CHO	10.83	37.22
—(CO)—	13.92	32.52
CH_3—(CO)—	11.31	53.49
—O—	10.04	27.96
—CN	14.86	31.23

$$\delta = \left(\frac{\Delta H_v - RT}{V} \right)^{1/2} \tag{1}$$

For materials for which heat of vaporization data are not available at the temperature of interest ΔH_v can be calculated from vapor-liquid equilibrium data. Hildebrand has outlined several other methods which can be used in the event that neither data on heat of vaporization nor vapor pressure are available (*1*).

However, these methods depend on the molecules of the compound being nonpolar or nearly nonpolar, or on being able to find data such as thermal expansion coefficient, liquid compressibility, internal pressure, etc., which are known for only a relatively few organic compounds. It is especially difficult to find such data, which must be obtained for the liquid state, if the compound of interest is a solid at normal temperatures and pressures. The work described in this paper was an attempt to circumvent these difficulties by devising methods for calculating the solubility parameters of compounds about which only a minimum amount of data is available.

SOLUBILITY PARAMETERS OF FUNCTIONAL GROUPS

It was found that, as shown in Figure 1, a straight line resulted when the solubility parameters of a homologous series of monofunctional compounds were plotted vs. the reciprocal of their molar volumes. As can be seen in this figure, the homologous series of hydrocarbons are an exception and do not fall on a line when plotted against 1/V. We have made similar plots using *n*-alkyl fluorides, chlorides, bromides, iodides, acids, nitriles, amines, and acetates.*

The largest scatter in the points plotted occurred for the case of methyl ketones and methyl esters. This is undoubtedly due to the well-known irregularity of the physical properties of the lower members of the methyl ketone and ester homologous series resulting from β-conjugation between the carbonyl group and the carbon hydrogen skeleton. If one now calculates the volume of the functional group, it should be possible, by reading off such a graph (or by solving the regression equation for the line), to obtain the solubility parameter for the functional group.

It should be noted that this method of plotting $\sqrt{E/V}$ ($=\delta$) vs. $1/V$ is exactly analogous to the method of plotting $\sqrt{EV}$ vs. n used by Scatchard (*3*) as long as the assumption is made that V is a linear function of n. This last assumption will be discussed in more detail below.

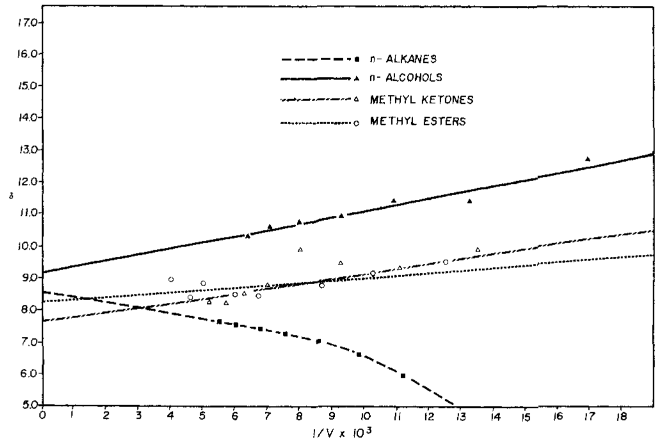

Fig. 1. Solubility parameters of organic compounds vs. the reciprocal of their molar volumes.

The homologous series of normal alcohols will be used as an illustration of this procedure. Figure 1 contains the plot of the solubility parameter of normal alcohols vs. the reciprocals of their molar volumes. The first step is to calculate an average molar volume of the CH_2 group in alcohols from the differences between the molar volumes of successive alcohols in the homologous series. This number and a value for the molar volume of an alkyl hydrogen obtained from Kopps rule (*4*) is then subtracted from the molar volumes of the alcohols to give an average value of the molar volume of an alcohol group, which turns out to be 19.66.

The equations of the best line through the points representing the alcohols in Figure 1 were found by the method of least squares. These equations are given below, together with the value of the solubility parameter (δ) calculated by solving for the values of the molar volume (V) of the OH group:

$$\delta_{ALC}(V) = 8.91769 + \frac{223.5137}{V} \tag{2}$$

$$\delta_{OH}(V) = \delta_{OH}\ (19.66) = 20.29 \tag{3}$$

We have made similar calculations for systems of *n*-amines, ketones, acids, esters, *n*-nitriles, *n*-halides, and *n*-alkanes. The results of these calculations are summarized in Table 1.

It should be noted that the molar volume calculated for the OH group roughly corresponds to that of water [$V(OH) = 19.66$; $V(H_2O) = 18.02$]. As might be expected, water, which hydrogen-bonds more extensively than alcohols, has the lower molar volume.

When the molar volumes calculated for the above-mentioned functional groups are compared with the molar volumes of their molecular analogues (Table 2), the corresponding situation is found (where a molecular analogue of a functional group is the molecule which consists of that functional group plus a hydrogen atom).

For most of these cases, the intermolecular forces are much lower than in water. Therefore, the molecular analogues tend to have larger molar volumes as a result of the volume of the extra hydrogen which they possess.

The method outlined not only has proved effective in calculating the molar volume and solubility parameters of functional groups, but also provides a good method for calculating the solubility parameters of compounds where the solubility parameters of other compounds in the homologous series are known.

It seemed worthwhile to see if we could use the solubility parameters of functional groups derived from the

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* These other plots and the data on which they are based can be obtained as order document NAPS-00234 from AISIS National Auxiliary Publications Service, c/o CCM Information Sciences, Inc., 22 West 34th Street, New York 10001, and may be obtained for $2.00 for microfiche or $5.00 for photocopies.

Table 2. Comparison of the Molar Volumes of Functional Groups to That of Their Molecular Analogue

Functional group	V, cc./mole	Molecular analogue	V, cc./mole
Acetate	58.46	Acetic acid	57.94
Acid	36.95	Formic acid	37.92
Nitrile	31.22	HCN	38.67
Amine	27.29	Ammonia	28.25
Hydroxyl	19.66	Water	18.02

plotting of data on monofunctional materials for the prediction of the values of δ for polyfunctional materials. We first calculated the solubility parameters of some difunctional and trifunctional compounds from vapor-pressure data, and some of the results are listed in Table 3. Further on in this paper, we will discuss the prediction of polyfunctional solubility parameters by a group contribution method.

The main advantage of this method of plotting a function of cohesive energy for a homologous series over the method used by Scatchard (3) and by Wiehe and Bagley (5), which was plotting $\sqrt{EV}$ vs. the number of atoms other than hydrogen in the molecule, is in the direction in which the plotted line can be extrapolated. Ideally, one would like to be able to predict the cohesive energy for high molecular weight compounds in a homologous series, for which data are scarce, from the more plentiful data on low molecular weight compounds. To make such an extrapolation on a graph, the ordinate of which was carbon numbers, would involve large graphs and extrapolation over large distances. On our graphs the solubility parameter of any compound in the homologous series can be easily determined, since the intercept of the lines with the Y axis represents the solubility parameter of an infinitely long member of the homologous series. Therefore, all higher members of the series fall on the line between the Y axis and the first datum point.

CALCULATION OF SOLUBILITY PARAMETERS BY A GROUP CONTRIBUTION METHOD

Despite the usefulness of the type of plot illustrated by Figure 1 for obtaining the solubility parameters of high molecular weight compounds for cases in which the solubility parameters of the lower molecular weight homologues are known, this method is still not general enough. The majority of compounds of chemical interest cannot be put neatly in homologous series for which data on the lower molecular weight homologues have been evaluated or can easily be evaluated. Therefore, it would be valuable to have a method by which the solubility parameters for functional groups, such as those calculated above, could be combined with the contribution to the solubility parameter of the carbon-hydrogen skeleton to give the total solubility parameter of the molecule. To do this we extended a method described by Small *(6)* in which he added together values of the quantity $\sqrt{EV}$ for each group in the molecule to predict the value of $\sqrt{EV}$ for the total molecule. As long as one knows the molar volumes of the groups involved and the molar volume of the molecule, δ and $\sqrt{EV}$ can easily be transformed one into the other by using the relationship

$$\sqrt{EV} = V \cdot \left(\frac{E}{V}\right)^{1/2} = V \cdot \delta \qquad (4)$$

Table 3. Solubility Parameters and Molar Volumes of Organic Compounds*

Compound	δ_{obs}	δ_{cal}	V, cc./mole
Ethylene glycol	15.83	15.84	55.9
1,2-propanediol	13.67	13.50	73.7
1,3-propanediol	13.94	14.05	72.5
1,3-butanediol	12.69	12.43	90.7
2,3-butanediol	12.65	12.09	91.3
1,4-butanediol	13.13	12.97	88.8
1,2-pentanediol	11.71	11.73	107.5
1,2-dichloroethane	9.27	9.48	79.30
1,2-dichlorobutane	8.54	8.70	114.25
1,1-dichloropropane	8.85	8.86	100.3
1,1-dichlorobutane	8.71	8.69	117.6
1,1-dichloropentane	8.65	8.58	134.6
1,3-dibromopropane	10.01	9.91	102.36
1,2-dibromopropane	9.48	9.43	104.98
1,4-dibromobutane	9.91	9.7	118.18
1,1-dibromobutane	9.68	9.66	121.03
1,1-dibromopentane	9.48	9.37	139.02
1,1-difluoropropane	7.88	7.80	87.04
1,1-difluorobutane	7.88	7.85	103.40
1,1-difluoropentane	7.91	7.95	118.82

* A complete list of the observed and calculated solubility parameters used can be obtained from ASIS. See footnote on p. 838.

This method, described by Small, has a major weakness resulting from the fact that certain combinations of groups are not additive in their effects. For example, as Wiehe and Bagley (5) point out, one cannot calculate the correct value of $\sqrt{EV}$ for a hydroxyl group by adding the contributions from an ether oxygen and from a hydrocarbon hydrogen. It is obvious that the value that Small obtains, which is 170, can only represent the cohesive energy resulting from dispersion forces and could not predict the much larger cohesive forces resulting from hydrogen bonding. This problem arises again in the addition of the individual contributions of several strongly interacting groups, such as two hydroxyl groups, to calculate their combined contribution to the total cohesive energy of the molecule. Some account must be taken of the fact that in polyfunctional compounds, in addition to intermolecular interactions, intramolecular interactions can occur between functional groups. We have found that in the example cited above, two hydroxyl groups are only 1.5 times as effective as one hydroxyl group in contributing to cohesive forces.

This we attribute to the fact that in a diol an appreciable fraction of the interactions possible between hydroxyl groups takes place intramolecularly, resulting in lowering the intermolecular cohesive energies.

This latter fact leads us to an even more serious problem with this method of calculating cohesive energies or solubility parameters. To analyze this problem, we must again look at the assumption that V is a linear function of n for a homologous series. Or, if stated in more general form, the assumption would be that the molar volume of a compound could be calculated by adding the so-called *group molar volumes* of the groups that it contains. These assumptions are nearly true if we limit ourselves to homologous series in the traditional sense of a series of

Table 4. Molar Volumes of Selected Compounds

Compound	V, cc./mole
1-propanol	75.1
1,2-propanediol	73.7
Glycerin	73.3

TABLE 5. GROUP COHESIVE ENERGIES ($\sqrt{EV}$) AT 25°C.

Group		$\sqrt{EV}$, (cal.)(cc.)$^{1/2}$/mole	
		Small	Our values
CH_3		214	—
CH_2	single bonded	133	—
—CH	single bonded	28	—
—C—	single bonded	−93	—
$CH_2 =$	double bonded	190	—
—CH =	double bonded	111	—
>C =	double bonded	19	—
CH ≡ C—		285	—
—C ≡ C—		222	—
Phenyl		735	—
Phenylene (*o, m, p*)		658	—
Naphthyl		1,146	—
Ring, 5-membered		105 to 115	—
Ring, 6-membered		95 to 105	—
Conjugation		20 to 30	—
S sulfides		225	—
SH thiols		315	—
O · NO_2 nitrates		440	—
NO_2 (aliphatic nitrocompounds)		440	—
PO_2 (organic phosphates)		500	—
H (variable)		80 to 100	—
CHO		—	403
O ethers		70	281
CO ketones		275	333
COO esters		310	—
—COOH		—	525
CN		410	464
Cl single		270	311
Cl as in $>CCl_2$		260	257
Cl as in $—CCl_3$		250	241[†]
Cl as in —C(Cl)—C(Cl)—		—	243
Br single		340	360
Br as in $>CBr_2$		—	331
Br as in $>CBr_3$		—	284[†]
Br as in —C(Br)—C(Br)—		—	308
F single		—	199
CF_2	*n*-fluorocarbons	150	152
CF_3	*n*-fluorocarbons	274	—
I single		425	410
OH single		170[*]	399[*]
OH in diols		—	310
NH_2		—	347

[†] Values are based on data for only one compound but were included in table for comparison.

[*] See text for explanation of discrepancy between values of $\sqrt{EV}$ for OH group.

compounds which differ from one another only in the number of CH_2 groups they contain.

However, if we redefine the term homologous to cover a series of compounds which differ from each other in the number of a particular functional group they contain, these assumptions break down. For example, Table 4 lists the molar volumes of three compounds which might be considered as constituting a homologous series of this second type. It would be hard to predict from any simple group contribution theory that these three compounds have essentially the same molar volumes.

Small has recognized these problems by assigning lower values of $\sqrt{EV}$ to the chlorine atoms in a dichloride (where both chlorine atoms are on the same carbon) than to the chlorine in a monochloride. We have found that the group contribution of chlorine to cohesive energy is relatively constant for 1,1-, 1,2-, and 2,3-chlorides. Table 5 lists a complete set of values of $\sqrt{EV}$, including our values and those of Small. Our values, which we calculated from the data on di and tri functional compounds, we feel compare favorably within the accuracy of the methods used for computing them. As an example of the feasibility of predicting solubility parameters by this method, calculated values of selected compounds are included in Table 3.

This method is convenient, then, for the calculation of solubility parameters of compounds with 1 or 2 functional groups. However, more work would have to be done, specifically studying the intramolecular interactions of various functional groups on the same molecule, before this method could be used with confidence on more highly polyfunctional materials. All the values of $\sqrt{EV}$ that we have calculated are for linear molecules. We feel that these values could also be used for ring compounds as long as the rings were not greatly strained or highly conjugated.

CONCLUSIONS

We have presented herein a graphical method for calculating solubility parameters and molar volumes of functional groups, as well as for calculating the solubility parameters of high molecular weight members of a homologous series from data on low molecular weight members. We have used the functional group solubility parameters and molar volumes to extend the values of $\sqrt{EV}$ presented earlier by Small. Finally, we have shown that the use of group contributions to calculate cohesive energy is limited by the lack of information available on the energies of interaction of functional groups on the same molecules. Therefore, more information would have to be gathered before such group contribution methods could be used to calculate cohesive energy densities of highly polyfunctional molecules.

ACKNOWLEDGMENT

The authors wish to acknowledge the Chemical Research Laboratory, Department of the Army, Edgewood Arsenal, Maryland, for funding the work described in this publication.

NOTATION

E = cohesive energy, cal./mole
ΔH_v = heat of vaporization, cal./mole
n = number of atoms in the molecule other than hydrogen (what Scatchard called γ)
R = gas constant, cal./(mole)(°K.)
T = temperature, °K.
V = molar volume, cc./mole
δ = solubility parameter, (cal./cc.)$^{1/2}$

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Manuscript received October 8, 1968; revision received January 31, 1969; paper accepted February 5, 1969.