Estimation of Dispersion and Hydrogen Bonding Energies in Liquids

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It is proposed that the product of the molar volume and the internal pressure is a measure of the dispersion interaction energy in liquids regardless of the presence of other intermolecular forces. If this is true, then the energy of interaction due to hydrogen bonding may be estimated for hydrogen bonding liquids by the difference between the energy of vaporization and the product of the molar volume and the internal pressure. It is also shown that Small's group contribution technique provides a good estimate of internal pressure of hydrogen bonding liquids.

To study the thermodynamics of solutions involving liquids capable of hydrogen bonding, it is important to have some method of separating interaction energies due to dispersion forces from interaction energies due to hydrogen bonding. A possible method is to estimate the dispersion energy of a nonhydrogen bonding liquid of otherwise similar chemical structure. This is similar to the homomorph concept used by Blanks and Prausnitz (*2*) to separate polar and dispersion interaction energies. However, there is always some doubt as to how closely the chosen homomorph approximates the behavior which the hydrogen bonding liquid would show if it did not hydrogen bond. Thus an alternate method for estimating separately the dispersion and hydrogen bonding energies is needed.

The effect of dispersion forces in liquid solutions is described by the Hildebrand-Scatchard regular solution theory (*5*). According to this theory the entropy of mixing is ideal and the excess Gibbs free energy of mixing is given for a binary system consisting of components 1 and 2 by

$$G^E = H^m = (x_1V_1 + x_2V_2)(\delta_1 - \delta_2)^2\phi_1\phi_2 \qquad (1)$$

The solubility parameters (δ_1 and δ_2) can be defined as either the square root of the cohesive energy density

$$\text{CED} = \frac{E_v}{V} \qquad (2)$$

where E_v = energy of vaporization (cal./g.-mole) or as the square root of the internal pressure given by

$$P_i = \left(\frac{\partial E}{\partial V}\right)_T \qquad (3)$$

The cohesive energy density and the internal pressure are approximately equal in magnitude for most nonpolar liquids (*1*). However, in the case of either polar or hydrogen bonding liquids, the cohesive energy density is much greater than the internal pressure (*1*).

The internal pressure is experimentally determined either by measurement of the thermal expansion coefficient and the isothermal compressibility or by direct measurement of the thermal pressure coefficient defined as

$$\left(\frac{\partial P}{\partial T}\right)_V$$

The thermal pressure coefficient is related to the isothermal compressibility β and the thermal expansion coefficient α by

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\beta} \qquad (4)$$

According to the thermodynamic equation of state

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad (5)$$

For liquids the external pressure P is usually much less than the internal pressure P_i, so that approximately

$$P_i = T\left(\frac{\partial P}{\partial T}\right)_V = T\frac{\alpha}{\beta} \qquad (6)$$

McKinney et al. (*6*) have measured the thermal expansion coefficients and isothermal compressibilities of the first eight normal primary alcohols at 0°C. Thus the internal pressure of the first eight normal primary alcohols at 0°C. can be calculated from these data. McKinney et al. attempted to correlate the change of thermal pressure coefficient with carbon number for the first eight normal primary alcohols, but a simple relation was not observed.

In addition to the usual measurements of energy of vaporization and molar volume, the cohesive energy density of nonhydrogen bonding liquids may be estimated by a method proposed by Small (*8*). According to this approach a certain value is assigned to each chemical group. By adding these values, one may estimate the quantity

$$V\left(\frac{E_v}{V}\right)^{1/2}$$

TABLE 1. ESTIMATED HYDROGEN BONDING ENERGIES OF PURE LIQUIDS AT 20°C.

Liquid	V, cc./g.-mole	E_v/V, kcal./cc.	$(\partial E/\partial V)_T$, kcal./cc.	E_v, kcal./g.-mole	$V(\partial E/\partial V)_T$, kcal./g.-mole	$-E_{hb}$, kcal./g.-mole
Methanol	40.5	0.212	0.0681	8.59	2.76	5.83
Ethanol	58.4	0.168	0.0695	9.81	4.06	5.75
n-Propyl alcohol	74.8	0.145	0.0688	10.85	5.15	5.70
Isopropyl alcohol	76.5	0.132(3)	0.0670	10.10	5.13	4.97
n-Butyl alcohol	91.6	0.130(3)	0.0717	11.91	6.57	5.34
		0.116		10.63		4.06
Isobutyl alcohol	91.8	0.117(3)	0.066	10.74	6.06	4.68
t-Butyl alcohol	106.1	0.113	0.081	11.99	8.6	3.4
Ethylene glycol	55.7	0.212	0.120	11.81	6.68	5.13
Water	18.0	0.548	0.0351	9.86	0.632	9.23

[in (cal.$^{1/2}$)(cc.$^{1/2}$)/g.-mole]. Knowing the molar volume of the compound, one may then estimate the cohesive energy density at 25°C.

SEPARATION OF INTERACTION ENERGIES

Since the molecular interaction energy in the gaseous state is very small, the cohesive energy density must be a direct measure of the total interaction energy per unit volume of the liquid. On the other hand, the internal pressure is a measurement of the rate of change of the interaction energy with volume during a minute isothermal expansion of liquid. To determine the relationship between the cohesive energy density and the internal pressure rigorously, knowledge of how the interaction energy varies with volume at constant temperature would be required. However, we know empirically that the cohesive energy density and the internal pressure are approximately equal for liquids in which only dispersion forces are important. Thus in this case the product of the molar volume and the internal pressure is a good measure of the dispersion interaction energy.

If hydrogen bonding can be considered as forming associated complexes, it is not difficult to believe that hydrogen bonds are not broken by a very slight expansion of the liquid, and thus does not directly influence the value of the internal pressure. Therefore the product of the internal pressure and the molar volume may also represent the dispersion interaction energy for hydrogen bonding liquids. However, most of the hydrogen bonds must be broken during the evaporation of the liquid. Thus the energy of vaporization of a hydrogen bonding liquid must represent the energy required to break the hydrogen bonds plus the dispersion interaction energy. Therefore, it is proposed that the hydrogen bonding energy E_{hb} is given by

$$-E_{hb} = E_v - V P_i \tag{7}$$

The last column in Table 1 gives the results of the calculations of hydrogen bonding energies in pure liquids at 20°C. and is found from the difference between E_V and $V(\partial E/\partial V)_T$. Except for the data for water and the values of (E_v/V), annotated in Table 1 as being taken from reference 3, all the data in the table were given by Allen et al. (*1*). The values they tabulate for internal pressure are based on sound velocity measurements. The internal pressure of water was calculated from the sound velocity data of Vigoureux (9), taking the density of water as 1.00 at 20°C. In Table 2 the calculated hydrogen bonding energies are compared for three alcohols with those estimated with a previously developed alcohol-inert solvent solution theory (*10*).

EFFECT OF CARBON NUMBER ON DISPERSION INTERACTION ENERGY

Boiling point data of liquids suggest that the dispersion energy increases monotonically with increasing molecular weight, and hence the product of the molar volume and the internal pressure should be a monotonically increasing function. This is shown to be true in Figure 1, where the product of the molar volume and the internal pressure is plotted as a function of the carbon number for the first eight normal primary alcohols at 0°C. obtained from the data of McKinney et al. (*6*), and for the normal alkanes from pentane through decane at 20°C. obtained from the data of Allen et al. (*1*).

ESTIMATION OF THE INTERNAL PRESSURES OF HYDROGEN BONDING LIQUIDS

If internal pressure is a measure of dispersion forces only, Small's group contribution technique should yield a good estimate of the internal pressure, but not the cohesive energy density, for hydrogen bonding liquids at 25°C. Table 3 is a comparison of such estimates with the internal pressure data at 20°C. given by Gee (*1*). The value of 170 (cal.$^{1/2}$)(cc.$^{1/2}$)/g.-mole was used for the —OH group. This is the same value recommended by Small in the calculation of the cohesive energy densities of cellulose diacetate and cellulose dinitrate (*8*).

DISCUSSION

The estimations of the hydrogen bonding energies of various liquids at 20°C. given in Table 1 seem to be of the correct order of magnitude and seem to show logical trends with changes in chemical structure. Although estimates of the energy of an O—H hydrogen bond vary from 2 to 7 kcal./g.-mole (*7*), the present estimations seem to agree favorably with the value of 5.9 kcal./g.-mole given by Coulsen (*4*). This value also seemed to be a favorable choice from the alcohol-inert solvent solution theory (*10*). If this value is accepted, one can see in Table 1 that methanol is close to being completely

TABLE 2. COMPARISON OF ESTIMATED HYDROGEN BONDING ENERGIES WITH THOSE CALCULATED FROM ALCOHOL-INERT SOLVENT SOLUTION THEORY AT 20°C.

Liquid	$-E_{hb}$ Estimated, kcal./g.-mole	$-E_{hb}$ Solution theory (*10*), kcal./g.-mole
Methanol	5.83	5.89
Ethanol	5.75	5.82
n-Butyl alcohol	5.26 4.06	5.69

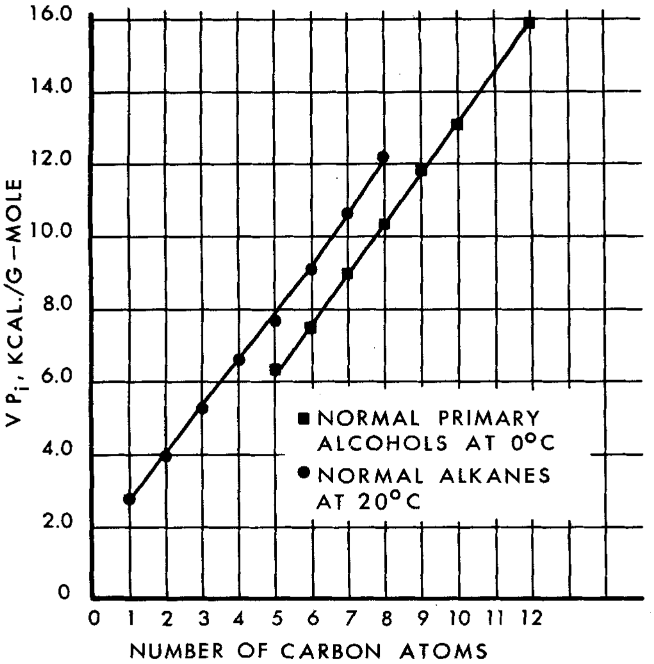

Fig. 1. Product of the molar volume and the internal pressure vs. carbon number for normal primary alcohols at 0°C. and for normal alkanes at 20°C.

hydrogen bonded. As the hydrocarbon portion of the alcohol is increased, steric hindrance prevents formation of hydrogen bonds, and the hydrogen bonding energy decreases. This is shown to be true in Table 1 where the hydrogen bonding energy is decreased by increasing the hydrocarbon chain or by adding a hydrocarbon branch to the alcohol. Both ethylene glycol and water are capable of forming twice as many hydrogen bonds per molecule as are the alcohols. This is demonstrated in the high estimated hydrogen bonding energy of water. However, the estimated hydrogen bonding energy of ethylene glycol is not as high as that of ethanol, although both have the same number of carbon atoms per molecule. This decrease in hydrogen bonding energy, which occurs in spite of the additional hydrogen bonding site, could be ascribed to steric hindrance effects arising from the extra OH group.

Since there is a discrepancy in the value of the energy of vaporization of *n*-butyl alcohol given by Gee (*1*) and by Burrell (*3*), both values have been included in Tables 1 and 2. Since all previous normal primary alcohols increase energy of vaporization as the number of carbon atoms is increased, the value given by Burrell seems to be the more logical choice.

In Table 2, where the estimated hydrogen bonding energies are compared with those calculated from the alcohol-inert solvent solution theory, there is excellent agreement for methanol and ethanol. However, for *n*-butyl alcohol there is less than 10% difference for one value and almost 30% difference for the other value. Probably more experimental work on both measurement of internal pressures of alcohols and on vapor-liquid equilibrium measurements of alcohol-inert solvent solutions will be required before it will be certain if there is agreement between these two methods of estimating the hydrogen bonding energies.

In Figure 1 the product of the molar volume and the internal pressure is plotted against the number of carbon atoms for the primary alcohols at 0°C. and for the normal alkanes at 20°C. Unlike that found by McKinney et al. (*6*) for the thermal pressure coefficient, Figure 1 indicates that the product of the molar volume and the internal pressure is a monotonically increasing function with increasing number of carbon atoms.

TABLE 3. COMPARISON OF CALCULATED AND EXPERIMENTAL INTERNAL PRESSURES

Liquid	Calculated $VP_i^{1/2}$, (cal.$^{1/2}$) (cc.$^{1/2}$)/ g.-mole	Experimental $VP_i^{1/2}$, (cal.$^{1/2}$) (cc.$^{1/2}$)/ g.-mole	Calculated P_i, cal./cc.	Experimental P_i, cal./cc.
Methanol	384	334	89.9	68.1
Ethanol	517	487	78.4	69.5
n-Propyl alcohol	650	621	75.5	68.8
Isopropyl alcohol	626	627	67.0	67.0
n-Butyl alcohol	783	775	73.1	71.7
Isobutyl alcohol	759	745	68.7	66.0
t-Butyl alcohol	719	955	45.9	81.0
Ethylene glycol	606	610	116.0	120.0

In Table 3 it is shown that by using only the group contribution values of Small (*8*), it is possible to estimate the internal pressures of hydrogen bonding liquids. The calculation of the internal pressure of *t*-butyl alcohol was not very close to the experimental value, but Small admits that the effect of packing of several large groups around a central atom is difficult to predict. This shows that Small's group contribution method may be an estimate of the internal pressure rather than the cohesive energy density as he intended. This also demonstrates that the assumption that hydrogen bonding does not greatly affect the internal pressure is a good one.

NOTATION

CED = cohesive energy density, Equation (2), cal./cc.
E = internal energy, cal./g.-mole
E_{hb} = hydrogen bonding energy, cal./g.-mole
E_v = energy of vaporization, cal./g.-mole
G^E = excess Gibbs free energy of mixing, cal./g.-mole
H^M = heat of mixing, cal./g.-mole
P = external pressure, cal./cc.
P_i = internal pressure, cal./cc.
T = absolute temperature, °K.
V = molar volume, cc./g.-mole
x = mole fraction

Greek Letters

α = thermal expansion coefficient, $1/V(\partial V/\partial T)_P$ 1/°K.
β = isothermal compressibility $1/V(\partial V/\partial P)_T$ cc./cal.
δ = solubility parameter, (cal./cc.)$^{1/2}$
ϕ = volume fraction

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