THE GENERALIZATION OF THE HILDEBRAND RELATIONSHIP BETWEEN THE ENTHALPY OF VAPORIZATION AND THE SURFACE TENSION OF LIQUIDS

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INTRODUCTION

The physical properties of liquids such as surface tension, the heat of vaporization, internal pressure, cohesive energy density and static permittivity are macroscopic properties, all of which reflect intermolecular interactions.

The existence of relationships between some of these quantities is the direct consequence of the fact that all these quantities depend on the same interactions at molecular level. Research into such relationships is therefore a way of obtaining a better insight into the knowledge of the liquid structure as far as these relations can be explained on the basis of theoretical models. Many of the known relationships were discovered empirically and explained *a posteriori* on a theoretical basis. This is the case 1°) for COOMBER'S relationship [1,2] between the static permittivity and the internal pressure of non-polar liquids, 2°) for PAPAZIAN'S relationship [3,4] between surface tension and static permittivity, also relative to non-polar liquids and 3°) the relationship (equality) between the internal pressure and the cohesive energy density of several liquids described by HILDEBRAND [5-7].

Previously, Hildebrand pointed out the existence of a linear relationship between the free energy associated with the molar surface expansion of a liquid, $\gamma_0 S$, and the energy of vaporization [8], ΔE_V (γ_0: surface tension, $S = 4\pi r^2 N_{Av}$: molar area of an ensemble of spherical molecules or radius r). For spherical molecules, S is proportional to $V^{2/3}$($V = \frac{4\pi}{3} r^3 N_{Av}$: molar volume) and therefore, a proportionality can also be predicted between ΔE_V and $\gamma_0 . V^{2/3}$.

Such a relationship is in fact observed for non polar liquids [5] and a justification of this relationship has been derived by SCHONHORN [9] DAVIS and SCRIVEN [10] and VAVRUCH [11] on the basis of statistical thermodynamics. This theoretical approach leads to a linear relation between the cohesive energy density $\frac{\Delta E_V}{V}$ (where V is the molar volume) and $\gamma_0 . V^{-1/3}$ but the theoretical model does not explain the deviations to the Hildebrand's empirical relationship observed for polar and associated liquids. LEE [12] has tried to modify Hildebrand's empirical relationship in order to make it applicable, even in the case of polar and associated solvents.

Unfortunately, as Beerbower [13] observes, this modification breaks down the dimensional coherence of the relationship.

Beerbower [13] has also studied this problem by using a multiparametric empirical relationship. This approach does not bring any new fundamental results but the behaviour of approximately a hundred liquids can be described by the empirical equation.

In the present work we would like to attempt a theoretical relation between surface tension, γ_0, and vaporization enthalpy, ΔH_V, by focusing out attention on a single molecule situated in a cavity which, itself, is surrounded by a liquid which is considered to be a continuum.

THEORETICAL TREATMENT

From the pioneering work of Stefan [14], followed by that of Eyring [15], it is easy to show that the energy required to create a spherical cavity in a liquid (with a volume equal to the molecular volume: V/N_{Av}) is equal to the molecular energy of vaporization ($\Delta E_V/N_{Av}$) in the same conditions of temperature and pressure.

This conclusion is confirmed by calculations of the interactions of a single molecule with its all surroundings [16] and appears valid for all kinds of liquids (apolar, polar and associated). Strictly speaking, the treatment which leads to this result neglects the difference between the kinetic energy of the molecules in the bulk of the liquid, at its surface or in its gas phase. As far as different liquids can be compared with each other, the error associated with this omission seems negligible, however.

The work $\pi(r)$ associated with the formation of a spherical macroscopic cavity of radius r in a liquid can be described as the sum of two terms (see for example [17])

$$\pi(r) = \frac{4}{3}\pi r^3 p + 4\pi r^2 \gamma_0 \qquad (1)$$

where p is the external pressure. Under atmospheric pressure, the first term is nebligible compared with the second one for $r < 10^3$ Å. We therefore have

$$\pi(r) = 4\pi r^2 \gamma_0 \qquad (2)$$

If the cavity is formed at constant pressure, $\pi(r)$ is a Gibbs free energy.

We can assume that equation (2) also holds for a cavity of microscopical size if the macroscopic surface tension is corrected in order to take into account the curvature of the surface. On the basis of the work of Tolman [17], Kirkwood and Buff [18], Koenig [19], Wakeshima [20], Eyring [21] and Sinanoglu [22], it appears possible to apply to γ_0 a multiplicative corrective factor K(r) to obtain the correlaction due to the curvature of the surface. In these conditions, the Gibbs energy associated with the formation of a mole of cavities with volumes equal to the molecular volume is expressed by

$$\bar{G}_{cav} = 4\pi r^2 N_{Av} \gamma_0 K \qquad (3)$$

From the identity $H = G - T(\frac{\partial G}{\partial T})_P$ it is easy to derive the corresponding relationship giving $\bar{H}_{cav}$ i.e.

$$\bar{H}_{cav} = K^H N_{Av} 4\pi r^2 \gamma_0 \{1 - T(\frac{1}{\gamma_0}\frac{\partial \gamma_0}{\partial T} + \frac{2}{3}\alpha)\} \qquad (4)$$

where K^H itself is expressed by

$$K^H = K - \frac{T}{1 - T(\frac{1}{\gamma_0}\frac{\partial \gamma_0}{\partial T} + \frac{2}{3}\alpha)} \frac{\partial K}{\partial T} \qquad (5)$$

α is the coefficient of the thermal expansion of the liquid.

On the basis of the equality stated above between $\bar{H}_{cav}$ and ΔH_V, it therefore appears that equation (4) must be looked upon as a theoretically well-founded generalized from of Hildebrand's relationship.

If the product $K^H.A$, i.e.

$$K^H.\ A = K^H.\ \{1 - T(\frac{1}{\gamma_0}\frac{\partial \gamma_0}{\partial T} + \frac{2}{3}\alpha)\}$$

remains constant for a series of liquids, a proportionality must exist between ΔH_V and $4\pi r^2 \gamma_0$. On the other hand, if $K^H.\ A$ varies from one particular solvent to another, the proportionality between ΔH_V and $4\pi r^2 \gamma_0$ disappears.

The analysis we made for more than fifty pure liquids shows different kinds of behaviour. Apolar solvents are characterized by K^H and A values which are more or less constant leading to constant $K^H.\ A$ values and, therefore, to a excellent proportionality between ΔH_V and $4\pi r^2 \gamma_0$ (see Table 1). K^H and A values for the other liquids can be compared with those determined for apolar liquids.

Such a comparison makes it possible to analyse the origin of the deviations with respect to Hildebrand's relationship. In the case of dimethylsulfoxyde and formamide, the high values of K^H are partially compensated for by the small values of A, but a discrepancy still exists with regards to Hidebrand's relationship. Alcohols are characterized by very high K^H values whereas nitromethane and dimethylformamide are characterized by high A values. Low A values are observed for aniline and formic acid.

Table 1
K^H and A parameters for organic liquids at 25 °C

Solvent	K^H	A	$K^H.A$
n-hexane	0.687	2.428	1.668
cyclohexane	0.654	2.229	1.457
n-heptane	0.718	2.260	1.622
methylcyclohexane	0.690	2.129	1.469
n-octane	0.738	2.177	1.608
carbon tetrachloride	0.655	2.194	1.437
methylene chloride	0.649	2.441	1.584
chloroform	0.693	2.211	1.532
t-butyl chloride	0.653	2.525	1.649
chlorobenzene	0.778	1.872	1.456
carbon disulphide	0.647	2.143	1.387
benzene	0.660	2.227	1.470
toluene	0.711	2.080	1.479
mesitylene	0.800	1.908	1.526
dioxane	0.678	2.175	1.475
diethyl ether	0.677	2.688	1.820
cyclohexanone	0.871	1.680	1.463
acetone	0.826	2.298	1.898
acetonitrile	0.973	2.086	2.030
nitromethane	0.750	2.401	1.800
dimethylformamide	0.726	2.505	1.819
dimethylsulphoxide	0.999	1.758	1.756
formamide	1.826	1.289	2.354
methanol	1.819	1.919	3.489
ethanol	1.625	1.931	3.139
n-propanol	1.513	1.845	2.792
t-butyl alcohol	1.227	2.232	2.738
n-octanol	1.290	1.819	2.347
aniline	1.015	1.549	1.572
formic acid	0.692	1.683	1.164
acetic acid	0.710	1.985	1.409
water	1.359	1.598	2.172

K^H values were obtained from eq. (4) taking into account the equality between H_{cav} and ΔH_v

CONCLUSIONS

Our theoretical treatment leads to a generalization of Hidebrand's relationship. Equation (4) has the great advantage of permitting the determination of K^H from easily obtainable experimental parameters. Such a procedure has been used with success in a previous work [23]. The importance of this K^H factor has been ignored by Abdulnur [24] in his attempt to obtain a linear relationship between H_V and $V^{2/3}\gamma_0 A$. Our treatment also allows us to classify solvents according to the origin of the deviation with respect to the linear relationship ("abnormal" values fo K^H and/or A).

Our present aim is to give interpretation at molecular level of the high (or low) K^H and A values which characterize non-apolar solvents.

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ABSTRACT

The Hidebrand relationship which relates the enthalpy of vaporization to the surface tension of a liquid is derived on the basis of a theoretical model. Moreover, a generalized expression is obtained which makes it possible to explain deviations from the linear Hildebrand relationship. The theoretical model itself takes into account the work which is associated with the formation of cativities in liquids. A correct estimation both of this work and of the corresponding enthalpy contribution is important in the description of the dissolution process of a solute in a solvent.

RESUMO

Generalização da relação de Hildebrand entre a entalpia de vaporização e a tensão superficial de Líquidos.

A expressão de Hildebrand que relaciona a entalpia de vaporização com a tensão superficial de um líquido é deduzida neste trabalho a partir de um modelo teórico. Obtém-se assim uma expressão generalizada que permite dar uma explicação dos desvios à relação linear de Hildebrand. O modelo utilizado baseia-se no cálculo do trabalho associado à formação de cavidades em líquidos. O cálculo correcto deste trabalho, assim como o da contribuição entálpica correspondente, é importante para a descrição do processo de dissolução de um soluto num solvente.

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