

On Some Irregularities of the Determination of the Surface Properties of Solid Materials

Tayssir Hamieh*

Laboratory of Materials, Catalysis, Environment and Analytical Methods Laboratory (MCEMA) and LEADDER Laboratory, EDST, Faculty of Sciences, Lebanese University, Hadath, Lebanon

Abstract

Inverse gas chromatography (IGC) at infinite dilution is one of the most used techniques to characterize the physicochemical and surface properties of solid substrates. The surface specific free energy of model organic molecules adsorbed on solid surfaces, as well as their dispersive component of the surface energy was determined by IGC technique since 1982. The specific surface enthalpy and entropy of adsorption of polar molecules derived from the determination of the variations of the specific free energy of interaction of such molecules with the solid particles as a function of the temperature. Using the concept of the donor and acceptor numbers of electrons of polar molecules, the acid base constants K_A , K_D of solid surfaces can be determined by an empirical relationship. Many methods and models were used in the literature to quantify the surface properties of solid materials. However, many irregularities were found when applying the different methods to various solid substrates. The conclusions concerning the dispersive surface energy and the acid base properties in Lewis terms of many solids revealed some errors committed by using the different models and methods of IGC.

Keywords: Specific free energy of adsorption • Dispersive surface energy • Enthalpy and entropy of adsorption • Acid base constants • Lewis concept • Hamieh model

Introduction

Inverse gas chromatography (IGC) at infinite dilution is the most important technique to characterize the surface properties of solid substrates such as oxides, polymers or copolymers in bulk or adsorbed phases IGC. This powerful technique first used by Conder and Young in 1970's [1-5] took an important development after 1980 where much research was devoted to the physicochemical determination of oxides, glass fibers and polymers [6-13]. Many specific thermodynamic variables were evaluated, especially, the free energy, the enthalpy and entropy of adsorption of organic model molecules on the solid substrates. Many studies treated the second order transition temperatures of polymers and copolymers in both the bulk and adsorbed phases.

Polar molecules and n-alkanes of known properties are injected in the column containing the solid. The retention times of these probes, measured at infinite dilution, allow us to determine the interactions between the organic molecules and the studied solid, if we suppose that there are no interactions between the probe molecules themselves. Measurements were carried out with a chromatograph equipped with a flame ionisation detector of high sensitivity. The retention data are obtained with a stainless steel column of length 15 to 60 cm and 2 to 5 mm internal diameter packed with 1 to 2 g of solid powders of fibres. The net retention volume V_n was calculated from:

$$V_n = jD(t_R - t_0) \quad (1)$$

where t_R is the retention time of the probe, t_0 the zero retention reference time measured with a non-adsorbing probe such as methane, D the flow rate and j a correction factor taking into account the compression of the gas [14].

The free energy of adsorption $-\Delta G_a^0$ of n-alkanes is given by:

$$-\Delta G_a^0 = RT \ln V_n + C \quad (2)$$

Where R is the ideal gas constant, T the absolute temperature and C a constant depending on the reference state of adsorption. In the case of n-alkanes, ΔG_a^0 is equal to the free energy of adsorption corresponding to dispersive interactions ΔG_a^d only.

If polar probes are injected into the column, specific interactions are established between these probes and the solid surface and ΔG_a^0 is now given by:

$$\Delta G_a^0 = \Delta G_a^d + \Delta G_a^{sp} \quad (3)$$

Where ΔG_a^{sp} refers to specific interactions. By plotting ΔG_a^0 as a function of the temperature, we can deduce the specific enthalpy ΔH_a^{sp} from:

$$\Delta G_a^{sp} = \Delta H_a^{sp} - T\Delta S_a^{sp} \quad (4)$$

Polar molecules used to determine the specific interactions with the solid substrates are characterized by their donor (DN) and acceptor (AN) numbers [15]. The concept of donor acceptor interactions is an extension of the Lewis acid base reactions, dealing with coordinate bonds which are formed by sharing a pair of electrons between donor and acceptor species. Knowing ΔH_a^{sp} of the various polar molecules, we will be able to determine the acidic constant K_A and basic constant K_D , the two constants characterizing the solid substrate, using the following relationship [16]:

$$-\Delta H_a^{sp} = (K_A DN + K_D AN) \quad (5)$$

And plotting $(-\Delta H_a^{sp}/A_N)$ as a function of (ND/NA) , according to equation

*Address for Correspondence: Tayssir Hamieh, Laboratory of Materials, Catalysis, Environment and Analytical Methods Laboratory (MCEMA) and LEADDER Laboratory, EDST, Faculty of Sciences, Lebanese University, Hadath, Lebanon, Email: tayssir.hamieh@ul.edu.lb

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(5). Model organic solvents are used in IGC at infinite dilution, such as n-alkanes (from n-pentane to n-dodecane) and polar organic molecules (toluene, methanol, ethanol, ethyl acetate, acetone, diethyl ether, benzene, dichloromethane, chloroform, tetrachloromethane, acetonitrile, etc...) as probes to examine the surface properties of solid materials. The methods proposed in literature used some thermodynamic parameters of organic molecules as the vapor pressure, P_0 [8,9], the dispersive component of the surface tension, γ_i^d [17], the boiling point, B.P. [18], the deformation polarizability, α_0 [19] or the standard enthalpy of vaporization, $\Delta H_{(vap.)}^0$, [20] and the topological index χ_T concept [21,22].

All the above methods are based on the linearity of the variations the free energy change of adsorption as a function the intrinsic thermodynamic parameters of n-alkanes and polar probes. Hamieh in a recent paper [23] showed a linear dependency of any thermodynamic parameters y_i as a function of another physicochemical variable x_j of n-alkanes. This linearity can be represented by:

$$y_i(x_j) = a_i x_j + b_i, i \neq j \quad (6)$$

Where a_i and b_i are constants relative to n-alkanes, y_i and x_j can be one of the above parameters (P_0 , γ_i^d , B.P., α_0 , $\Delta H_{(vap.)}^0$, χ_T , ...).

Any used couple (x_j , y_i) will lead to the specific interactions ΔG_a^{sp} between the polar solvents and the solid surfaces. The deduction of ΔH_a^{sp} from the variation of ΔH_a^{sp} allowed to obtain the acid base constants of the solids. However, by applying the different IGC methods, the obtained results presented large deviation. There is no universal method that can be used to better quantify the true values of the surface physicochemical properties of any solid substrates.

Principle Error Committed on the Dispersive Surface Energy of Solid Materials

By using the well-known relationship of Fowkes [24], Dorris and Gray [25] correlated the adhesion work W_a to the free enthalpy of adsorption by the help of the surface area a of adsorbed molecule and the geometric mean of the dispersive components of the liquid solvent γ_l^d and the solid γ_s^d .

$$\Delta G_a^0 = N a W_a = 2 N a \sqrt{(\gamma_l^d \gamma_s^d)} \quad (7)$$

Where N is the Avogadro's number. Dorris and Gray determined the dispersive component of the surface energy of a solid by supposing the surface area of methylene group a_{CH_2} equal to 6 Å² independently of the temperature.

Later, Schultz et al. [17] used the same concept of Fowkes and proposed the determination of the dispersive component of the surface energy of a solid substrate by plotting the variation of $RT \ln Vn$ versus $2Na (\gamma_l^d)^{1/2}$ of n-alkanes and by supposing the surface areas a of molecules constant at any temperature and obtained a straight line:

$$RT \ln Vn = (\gamma_s^d)^{1/2} [2Na (\gamma_l^d)^{1/2}] + C \quad (8)$$

Where C is constant. The slope of the alkane straight line given by relation (48) will give the value of $(\gamma_s^d)^{1/2}$ and therefore γ_s^d of the solid. These two methods were criticized by Hamieh's works [26-31] who demonstrated that the surface area of organic molecules varies as a function of the temperature and showed an important dependence of the surface area of molecules and also the methylene group a_{CH_2} versus the temperature. Hamieh et al. proposed other molecular models of the surface areas of organic molecules and obtained other values of the dispersive surface energy of solid materials.

Consequently, the results published by several scientists in literature by using the methods based on the Fowkes relation should be corrected.

Acid Base Constants of Solid Materials

The acid base constants K_A and K_D of solid surface were calculated by using the relation (5) in the following form:

$$(-\Delta H_a^{sp})/AN = K_A (DN/AN) + K_D \quad (9)$$

The representation of $(-\Delta H_a^{sp})/AN$ versus DN/AN will give in general a straight line of slope K_A and intercept K_D . However, in several cases, Hamieh et al. [26,29,31] proved the non-validity of equation (5) and introduced a third parameter K reflecting the amphoteric character of solid substrates according to:

$$(-\Delta H_a^{sp}) = K_A DN + K_D AN - K DN AN \quad (10)$$

The constants K_D , K_A and K can be obtained by resolution of the linear system (10) by using N organic solvents and give more accurate description of the acid base character of the solids.

General Method of IGC Technique

We proposed in this section a new general method for the determination of surface physicochemical properties of solid substrates. For n-alkanes (alk.), for example, we gave the following free energy of adsorption:

$$\Delta G_a^0(alk.) = A(B.P.)(alk.) + B \alpha_{0,i}(alk.) + C \Delta H_{vap.}^0(T)(alk.) + D \chi_T(alk.) + E \log P_0(alk.) + F$$

For polar molecules (pol.), one obtained the specific values of free energy of adsorption:

$$\Delta G_a^{sp}(pol.) = \Delta G_a^0(pol.) - A(B.P.)(pol.) - B \alpha_{0,i}(pol.) - C \Delta H_{vap.}^0(T)(pol.) - D \chi_T(pol.) - E \log P_0(pol.) - F$$

Where $\Delta G_a^0(alk.)$ and $\Delta G_a^0(pol.)$ are determined experimentally from the values of $RT \ln Vn$ of the various molecules, whereas, the constants A , B , C , D , E and F are determined by the physicochemical characteristics of the organic molecules.

Now the obtained values of $\Delta G_a^{sp}(pol.)$ of the polar solvents adsorbed on the solid surfaces will describe more accurately the solid surface properties.

Conclusion

In this editorial note, we presented the different methods of the inverse gas chromatography technique at infinite dilution by showing some irregularities resulting from the use of Fowkes relation, Dorris Gray and Schultz methods. The values of the dispersive component of the surface energy, the specific free energy of adsorption, the specific enthalpy and entropy of adsorption; and the acid base constants of silica particles should be reviewed and corrected on the light of the new findings proposed by hamieh et al. Finally, a new general essay was proposed to better quantify the acid base properties of solid surfaces.

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