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Correction of Some Thermodynamic Surface Properties of Sodium Alginate Determined by Inverse Gas Chromatography

Tayssir Hamieh[1,2*]

[1]Laboratory of Materials, Lebanese University, Lebanon

[2]University Gustave Eiffel, France

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Corresponding author:
Tayssir Hamieh,
Laboratory of Materials, Catalysis, Environment and Analytical Methods (MCEMA), EDST, Lebanese University, Lebanon, Tel: +33 7 69 16 00 92;
Email: tayssir.hamieh@ul.edu.lb

ABSTRACT

In their paper published in the Journal of Chemical Engineering Data, Ugraskan, et al. made several inaccuracies in the determination of the surface properties of sodium alginate by using the Inverse Gas Chromatography (IGC) technique. The proposed method to determine the dispersive component of the surface energy, γ_s^d, cannot be correctly evaluated, because it depends on the surface area of n-alkanes or of methylene group. This surface area supposed by Ugraskan, et al. constant strongly depends on the temperature. Therefore, the specific free energy of adsorption, ($-\Delta G^{sp}$), and consequently the specific enthalpy of adsorption, ($-\Delta H^{sp}$), cannot be known with accuracy. The wrong values of ($-\Delta H^{sp}$), certainly lead to inaccurate determination of the acid K_A and base K_D constants of the solid.

INTRODUCTION

Inverse Gas Chromatography (IGC) technique is a real source of physiochemical data of surfaces and interfaces allowing the determination of the specific interactions between oxides [1], polymers or polymers adsorbed on oxides and organic solvent systems [2-5]. This is an important tool, precise, sensitive, and more competitive to determine the heterogeneous surfaces of solids, their physicochemical properties [6], and to determine surface energy and surface area of powdered materials [7-10]. This IGC technique can advantageously determine the surface properties of solid materials, and especially, the Lewis acid base properties and mainly the adsorption thermodynamic parameters as specific free energy, enthalpy and entropy of adsorption, Lewis acid–base character of the surface, surface nanoroughness parameter, etc. [11-19]. In this paper, we propose to correct the surface properties determined by Ugraskan, et al. [1]. In fact, these authors had used the Schultz, et al. [20] and Dorris-Gray [21] methods, both, based on Fowkes relation [22]. The major problem of this method is the exact knowledge of the surface area of n-alkanes. Because the above method always supposed the surface area of n-alkanes constant. However, Hamieh, et al. [23] proved that the surface area of molecules depends on the temperature. Consequently, the specific free energy, enthalpy and entropy of adsorption of polar molecules become inaccurate and this leads to wrong values of the acid base constants of the solid.

METHODS AND CRITIQUES

Dorris and gray method or the increment method

Dorris and Gray [21] proposed the increment method by applying the well-known relationship of Fowkes which gives at the same time the dispersive component of the surface energy of solids γ_s^d by using the geometric mean of the dispersive components (exponent *d*) of the surface energy of the probe γ_l^d and the solid γ_s^d:

$$W_a = 2\sqrt{\gamma_l^d \gamma_s^d} \tag{1}$$

Where W_a is the work of adhesion between the probe and the solid.

This energy of adhesion was correlated to the free enthalpy of adsorption

$$\Delta G^0 = \mathcal{N} a W_a = 2\mathcal{N} a \sqrt{\gamma_l^d \gamma_s^d} \tag{2}$$

Where $\mathcal{N}$ is Avogadro's number and *a* the surface area of one adsorbed molecule on the solid.

Dorris and Gray [21] were the first who determined the dispersive component of the surface energy of a solid by considering the increment of ΔG^0_{-CH2-} per methylene group in the n-alkanes series of general formula $C_nH_{2(n+1)}$. They defined the increment ΔG^0_{-CH2-} by:

$$\Delta G^0_{-CH2-} = \Delta G^0\left(C_{n+1}H_{2(n+2)}\right) - \Delta G^0\left(C_nH_{2(n+1)}\right) \tag{3}$$

Where $C_nH_{2(n+1)}$ and $C_nH_{2(n+1)}$ represents the general formula of two consecutive n-alkanes.

By using the retention volumes $V_n\left(C_nH_{2(n+1)}\right)$ and $V_n\left(C_{n+1}H_{2(n+2)}\right)$ of two consecutive n-alkanes and relation (2), the dispersive component of the surface energy γ_s^d can be determined by the following equation:

$$\gamma_s^d = \frac{\left[RT \ln\left[\frac{V_n\left(C_{n+1}H_{2(n+2)}\right)}{V_n\left(C_nH_{2(n+1)}\right)}\right]\right]^2}{4\mathcal{N}^2 a^2_{-CH2-} \gamma_{-CH2-}} \tag{4}$$

Where a_{-CH2-} is the surface area of methylene group ($a_{-CH2-} = 6$ Å^2) and γ_{-CH2-} the surface energy of –CH2- group of a polyethylene polymer (with a finite molecular mass) given by:

$\gamma_{-CH2-} = 52.603 - 0.058\ T$ (T in K; γ_{-CH2-} in mJ/m^2) (5)

Therefore, relation (4) determined the dispersive component of the surface energy γ_s^d of solids.

Schultz et al. method or the n-alkane straight-line method

Table 1: Surface areas of various molecules (in Å^2) obtained from the various models of Van Der Waals (VDW), Redlich-Kwong (R-K) and Kiselev, compared to those obtained by geometrical, cylindrical or spherical models.

Molecule	VDW (in Å^2)	Kiselev (in Å^2)	Cylindrical (in Å^2)	R-K (in Å^2)	Spherical (in Å^2)	Geometrical (in Å^2)
C_5H_{12}	47.0	45	39.3	36.8	36.4	32.9
C_6H_{14}	52.7	51.5	45.5	41.3	39.6	40.7
C_7H_{16}	59.2	57	51.8	46.4	42.7	48.5
C_8H_{18}	64.9	63	58.1	50.8	45.7	56.2
C_9H_{20}	69.6	69	64.4	54.5	48.7	64.0
$C_{10}H_{22}$	74.4	75	70.7	58.2	51.7	71.8

This method also based on Fowkes approach [22] replaced the free enthalpy of adsorption by its values taken from relation (1) to obtain the following relationship:

$$RT \ln Vn + C = 2\mathcal{N} a \sqrt{\gamma_l^d \gamma_s^d} \tag{6}$$

By plotting $RT \ln Vn$ as a function of $2\mathcal{N} a \sqrt{\gamma_l^d}$ of n-alkanes, one obtains a typical straight line that allows to deduce, from its slope, the value of dispersive component γ_s^d of the surface energy of the solid. The two previous methods use the value of the surface area *a* of n-alkanes of the methylene group and suppose that these values of *a* remain constant whatever the temperature. In general, the values of surface areas of n-alkanes used are those proposed by Kiselev (Table 1). Hamieh, et al. Proposed several molecular models [23,24] to determine the surface areas of molecules (Table 1). They proved the effect of the temperature on the surface area of n-alkanes and polar molecules [24]. Hamieh, et al. [24] showed the areas *a* (T) of polar molecules adsorbed on Polytetrafluoroethylene (PTFE), linearly depend on the temperature. The following relation was proved:

$$a(T) = a_0 - \Omega\, T \tag{7}$$

with Ω the slope of the straight line depending on the nature of the adsorbed molecule and solid substrate, *a* (*T*) the surface area at temperature *T* and a_0 the molecule area extrapolated at 0K. Therefore, it will be impossible to deduce a precise value of the specific interaction for one polar molecule by using this method, because the surface areas of adsorbed molecules cannot be accurately determined. The limitations of Schultz, et al and Dorris-Gray methods are due, in part, to the fact that the molecular area *a* is not exactly known and varies both with the nature of the solid, and the temperature and surface coverage of molecule on the solid surface.

RESULTS

New results on the determination of the dispersive component of the surface energy of sodium alginate

In the calculation of γ_s^d, Ugraskan, et al. [1] not only supposed the surface areas constant but there is probably a certain error committed by considering constant the value of the dispersive component γ_l^d of the surface energy of organic molecules when the temperature changes. In fact, γ_l^d also depends on the temperature. On Table 2, we gave the different values of γ_l^d of n-alkanes and polar molecules versus the temperature. By taking into account the variations of γ_l^d as a function of the temperature, we were able to correct the values of γ_s^d following the Fowkes method. The results are presented on Table 3. The above values were obtained by taking the proposed results of Kiselev used for the surface areas of n-alkanes. Table 3 shows a difference of 2.33 mJ/m² between our values and those of Table 2 obtained by Ugraskan, et al. [1], probably due to their hypothesis that supposed γ_l^d constant.

Table 2: Values of γ_l^d (mJ/m²) of molecules as a function of the temperature.

Temperature/Molecules	303.2K	308.2K	313.2K	318.2K	323.2K	328.2K
C6	17.35	16.84	16.33	15.82	15.31	14.80
C7	19.14	18.65	18.16	17.67	17.18	16.69
C8	20.68	20.21	19.73	19.25	18.78	18.30
C9	21.86	21.39	20.93	20.46	19.99	19.53
C10	22.89	22.43	21.97	21.51	21.05	20.59
Acetone	19.22	18.78	18.35	17.92	17.48	17.05
THF	25.07	24.40	23.73	23.06	22.39	21.72
CH_2Cl_2	26.40	25.53	24.66	23.79	22.92	22.05
Chloroform	22.02	20.55	19.08	17.61	16.14	14.67
Ethyl acetate	22.49	21.89	21.29	20.68	20.08	19.48

Now, in order to prove the dependency of γ_s^d of solids on the choice of the molecular area models, we present in Table 4 our results obtained for the dispersive component of the surface area of sodium alginate for the different molecular surface area models. (Tables 3,4) prove an effect certain of the choice of chosen surface area model on the value of γ_s^d of the solid.

Table 3: Values of the dispersive component of the surface energy $\gamma_s^d(\mathrm{mJ/m^2})$ of Sodium Alginate by using Kiselev surface areas.

Temperature (K)	γ_s^d (mJ/m²)
303.2	44.44
308.2	44.22
313.2	43.30
318.2	42.93
323.2	42.63
328.2	41.95

Table 4: Values of the dispersive component of the surface energy $\gamma_s^d(\mathrm{mJ/m^2})$ of Sodium Alginate by using other molecular surface area models.

Area model/Temperature	VDW $(\mathrm{mJ/m^2})$	Cylindrical $(\mathrm{mJ/m^2})$	R-K $(\mathrm{mJ/m^2})$	Geometric $(\mathrm{mJ/m^2})$	spherical $(\mathrm{mJ/m^2})$
303.2 K	49.89	42.02	81.98	30.73	137.03
308.2 K	49.51	41.90	81.35	30.73	135.61
313.2 K	48.30	41.10	79.35	30.24	131.95
318.2 K	47.76	40.83	78.44	30.14	130.03
323.2 K	47.20	40.63	77.53	30.11	128.28
328.2 K	46.32	40.07	76.07	29.80	125.44

The difference between the results of those models can reach more than 100 % of deviation. Therefore, it is not admissible to continue using Shultz et al method based on the Kiselev surface areas of molecules and to suppose at the same time that these values are considered as absolute values without changing with the temperature.

New results on the determination of the acid base constants of sodium alginate

In the previous section, we demonstrated the non-validity of using the dispersive component of the surface energy of the solid by using Schultz, et al. [20] method or Fowkes relation [22]. The value of γ_s^d indeed depends on the choice of the molecular surface area model of molecules. These surface areas strongly depend on the temperature variation; However, Ugraskan, et al. [1] supposed that the surface area of n-alkanes remains constant even when the temperature changes. Many errors will result by applying this classical method, certainly, because of the dependency of the specific free energy depends on the values of the surface areas of n-alkanes and polar molecules. It becomes obvious that the calculations using this parameter can no longer be considered as absolute quantitative values, and, consequently the obtained values of acid base constants of sodium alginate become wrong. On the other hand, even when using the classical method of Schultz, et al. [20], our calculations give new results different from those obtained by Ugraskan, et al. [1], again because these authors supposed γ_l^d of polar and non-polar molecules as constant. Following Schultz, et al. method or Fowkes approach, *RTlnVn* values of the various solutes are first plotted versus $2\mathcal{N}a\left(\gamma_l^d\right)^{1/2}$. The points representative of n-alkanes define the so-called "alkane straight line", and the distance between this straight line and the points corresponding to *RTlnVn* (*polar molecule*) value of polar probes are then taken as a measure of the specific free energy of adsorption $-\Delta G^{sp}$, of polar molecule on the solid. It is given, for any temperature *T*, by the following equation:

$$-\Delta G^{sp}(polar\ molecule) = RTlnVn\ (polar\ molecule) - 2\mathcal{N}a\left(\gamma_l^d\right)^{1/2} - C \qquad (8)$$

Using relation (8), we obtained the results plotted on Figure 1.

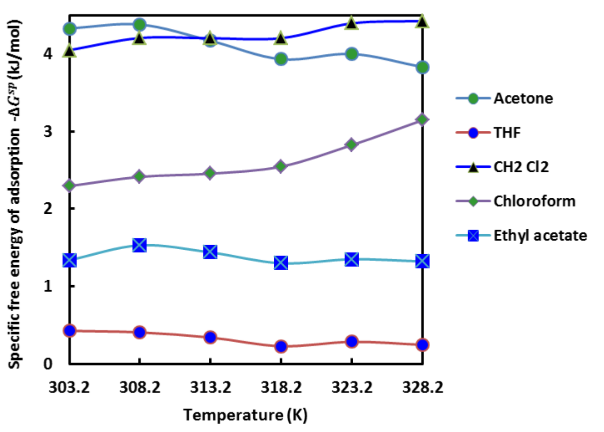

Figure 1: Evolution of the specific free energy of adsorption $(-\Delta G^{sp})$ (kJ/mol) of polar molecules on sodium alginate.

Our results presented in Table 5 give the various equations of the specific free energy $(-\Delta G^{sp})$ of adsorption and the values of specific enthalpy $(-\Delta H^{sp})$ and entropy $(-\Delta S^{sp})$ of adsorption of polar molecules on the SA solid. Table 5 clearly shows that he values of the linear regression coefficients ***r*²** for different polar molecules are comprised between 0.2169 and 0.8718. This implies that the linearity of $(-\Delta G^{sp})$ is not assured and therefore the values of specific enthalpy $(-\Delta H^{sp})$ and entropy $(-\Delta S^{sp})$ of adsorption cannot be considered as independent from the temperature. This will be another source of inaccuracies for the determination of the acid base constant. To prove that, we give on Table 6 the different values of acceptor *AN** and donor *DN* numbers of electrons relative to the various polar molecules with the corresponding ratios *DN*/*AN** *and* $(-\Delta H^{sp})$ /*AN**. The obtained results accumulate the errors committed on the values of acid KA and base KD constants of the sodium alginate.

Table 5: Equations of $(-\Delta G^{sp})$ (in kJ/mol) and values of $(-\Delta H^{sp})$ (in kJ/mol), $(-\Delta S^{sp})$ (in J K-1mol-1) and the linear regression coefficients r2 for different polar molecules adsorbed on sodium alginate.

Probes	$-\Delta G^{sp}$ **(T) (kJ/mol)**	$-\Delta H^{sp}$ **(kJ/mol)**	$-\Delta S^{sp}$ **(J K^{-1}mol^{-1})**	r^2
Acetone	$-\Delta G^{sp}(T)$=-0.0221T +11.089	11.089	22.1	0.8693
THF	$-\Delta G^{sp}(T)$ = -0.0079T + 2.810	2.8096	7.9	0.7942
CH_2Cl_2	$-\Delta G^{sp}(T)$= + 0.0140T - 0.180	-0.1795	-14	0.8718
Chloroform	$-\Delta G^{sp}(T)$= + 0.0319T - 7.451	-7.4511	-31.9	0.8914
Ethyl acetate	$-\Delta G^{sp}(T)$ = -0.0044T + 2.760	2.7596	-4.4	0.2169

On Figure 2, we plotted the evolution of $(-\Delta H^{sp})$ /*AN** of the various polar molecules as a function of the ratio *DN*/*AN**. The obtained curve on Figure 2 confirms that the linearity is not satisfied; the linear regression coefficient r^2 = 0.6234 very far from 1. In order to compare between our results and those obtained by Ugraskan, et al. [1], we give the following equation (even if the linearity is not satisfied):

$$\left(\frac{-\Delta Hsp}{AN^*}\right) = 0.033\left(\frac{DN}{AN^*}\right) + 0.112 \qquad (9)$$

From the classic relation:

$$\left(\frac{-\Delta H^{Sp}}{AN}\right) = K_A\left(\frac{DN}{AN}\right) + K_D \qquad (10)$$

One obtains the acid constants of the sodium alginate:

$$\begin{cases} K_A = 0.033 \\ K_D = 0.112 \\ \dfrac{K_D}{K_A} = 3.36 \end{cases}$$

These values obtained by our correction are different from those obtained by Ugraskan, et al. [1]:

$$K_A = 0.074;\ K_D = 0.437 \text{ and } \frac{K_D}{K_A} = 5.90$$

There is large difference between our results and the results obtained by Ugraskan, et al. [1] that neglected the variation of γ_l^d of n-alkanes and polar molecules with the temperature.

Table 6: Values of acceptor *AN** and donor *DN* numbers of electrons of the different polar molecules with the corresponding ratios *DN/AN* and* $(-\Delta H^{sp})$ */AN**.

Probes	***DN*** **(kJ/mol)**	***AN******(kJ/mol)**	***DN/AN****	$(-\Delta H^{sp})$ ***/AN****
CH_2Cl_2	0	16.3	0.00	-0.01
Chloroform	0	22.7	0.00	-0.33
Acetone	71.4	10.5	6.80	1.06
Ethyl acetate	71.1	6.3	11.29	0.44
THF	84.4	2.1	40.19	1.34

Nevertheless, we can find for these above values a certain tendency showing effectively for sodium alginate base character rather than acid behavior with an amphoteric property.

Standard deviation and error calculations: On the other hand, we gave below some relevant calculations of the errors on the different thermodynamic parameters.

We began with the error committed on the net retention time:

$$10^{-3}min \leq \Delta t_n(probe) \leq 3\times10^{-3}min$$

The relative standard deviation on the retention time is given by the following inequalities:

$$5\times10^{-5} \leq \frac{\Delta t_n(probe)}{t_n(probe)} \leq 10^{-4}$$

This gives a relative standard deviation on the net retention volume:

$$5\times10^{-5} \leq \frac{\Delta V_n(probe)}{V_n(probe)} \leq 10^{-4}$$

And therefore, we obtain for free enthalpy of adsorption the following error:

$$5\times10^{-4}kJ/mol \leq \Delta(\Delta G_a^0) \leq 3\times10^{-3}kJ/mol$$

Moreover, the relative deviation is given by:

$$3\times10^{-4} \leq \frac{\Delta(\Delta G_a^0)}{\Delta G_a^0} \leq 5\times10^{-4}$$

And the error on the specific free enthalpy reads as:

$$10^{-3}kJ/mol \leq \Delta(\Delta G_a^{sp}) \leq 6\times10^{-3}kJ/mol$$

Finally, the relative error committed on the acid-base constants K_A , K_B and K are:

$$1\times10^{-3} \leq \frac{\Delta(K_{A,B})}{K_{A,B}} \leq 2\times10^{-3}$$

Therefore, the error committed on the values of acid base constants is equal to 5×10^{-3}.

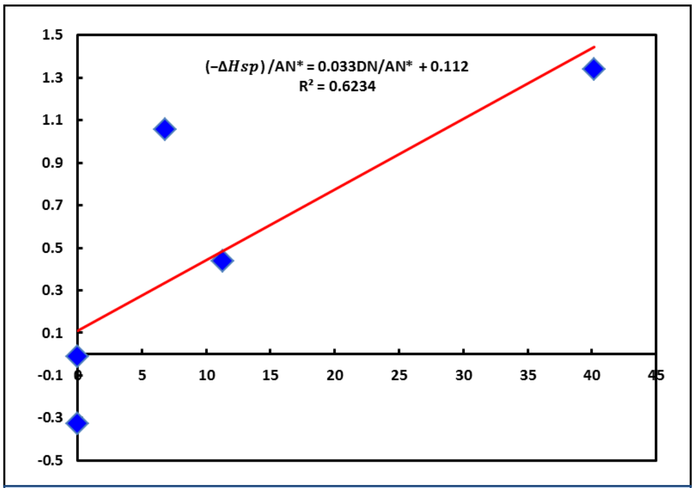

Figure 2: Evolution of $(-\Delta H^{sp})$ /AN* (in (kJ/mol) / (kJ/mol)) of the polar molecules versus the ratio DN/AN*.

CONCLUSION

We recalculated the dispersive component of the surface energy γ_s^d of the sodium alginate determined by Ugraskan, et al. [1] by taking into account the variation of the dispersive component of the surface energy γ_l^d of polar and non-polar molecules as a function of the temperature. This variation was neglected by Ugraskan, et al. On the other hand, we proved that γ_s^d strongly depends on the choice of the molecular surface area model. The application of the various models of the surface areas of n-alkanes gave an important deviation of γ_s^d values between the different models of the surface areas. The standard deviation in certain cases was proved reaching more than 100%. This leads to conclude that the determination of the specific free energy, enthalpy and entropy of adsorption of polar molecules on the sodium alginate cannot be determined with accuracy by using the Schultz method and consequently the obtained values of the acid base constants of the solid become false. Many serious errors were made by Ugraskan, et al. in their calculations of the acid base constants, we proved by calculations that the results obtained by these authors are inaccurate. Nevertheless, we confirmed a certain tendency of basic character of the sodium alginate stronger than the acid character.

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NOTES

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