Short communication

Comparison of Dorris–Gray and Schultz methods for the calculation of surface dispersive free energy by inverse gas chromatography

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ABSTRACT

Inverse gas chromatography (IGC) is an important technique for the characterization of surface properties of solid materials. A standard method of surface characterization is that the surface dispersive free energy of the solid stationary phase is firstly determined by using a series of linear alkane liquids as molecular probes, and then the acid–base parameters are calculated from the dispersive parameters. However, for the calculation of surface dispersive free energy, generally, two different methods are used, which are Dorris–Gray method and Schultz method. In this paper, the results calculated from Dorris–Gray method and Schultz method are compared through calculating their ratio with their basic equations and parameters. It can be concluded that the dispersive parameters calculated with Dorris–Gray method will always be larger than the data calculated with Schultz method. When the measuring temperature increases, the ratio increases large. Compared with the parameters in solvents handbook, it seems that the traditional surface free energy parameters of *n*-alkanes listed in the papers using Schultz method are not enough accurate, which can be proved with a published IGC experimental result.

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1. Introduction

Inverse gas chromatography (IGC) is an important technique for the characterization of surface properties of solid materials, especially powder materials. Generally, surface dispersive free energy and acid–base properties can be determined above room temperature [1]. A standard method of surface characterization is that the surface dispersive free energy (or named London force) of the solid stationary phase is firstly determined by using a series of linear alkane liquids (*n*-alkanes) as molecular probes. Then, the acid–base parameters can be calculated from the dispersive parameters with some acid–base liquid probes. However, for the calculation of surface dispersive free energy, generally, two different methods are now used, which are Dorris–Gray method [2] and Schultz method [3].

Until now, several hundreds of research papers on surface characterization with IGC have been published. Since 2000, 13 papers [4–16] using Dorris–Gray method have been published on the *Journal of Chromatography A*. At the same time, 12 papers [17–28] using Schultz method and four papers using both of the two methods have been published [29–32]. According to these papers, it can be found that at the same measuring conditions, the dispersive results calculated from Dorris–Gray method and Schultz method were generally different. Some data from Dorris–Gray method were larger than the data from Schultz method, but some results were opposite. Although the difference was not large (several mJ/m²), it still induced some difficult when comparing with the results or researching the law of surface dispersive properties of materials. Consequently, estimating which results are more reasonable is a necessary work for the development of inverse gas chromatography technique. In this paper, the comparison of Dorris–Gray and Schultz methods for the calculation of surface dispersive free energy is analyzed with their basic equations and parameters.

2. Discussion

2.1. Dorris–Gray method

The basic principle of Dorris–Gray method is [4–16]: when a series of liquid *n*-alkanes are used as probes, the adsorption dispersive free energy of one methylene group ΔG^{CH_2}, can be calculated from the slope of a line achieved by plotting the adsorption free energy of the probes $-\Delta G^{ads}$ versus the carbon number *n*. The equation for calculating ΔG^{CH_2} is:

$$\Delta G^{CH_2} = -RT \cdot \ln \left(\frac{V_{N,n+1}}{V_{N,n}} \right) \tag{1}$$

where *R* is the gas constant, *T* is the temperature (K), $V_{N,n}$ is the net retention volume of the *n*-alkane probe with the carbon number *n*. According to the Fowkes relation for the work of adhesion (W_a) by

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dispersive free energy between two phases [29], for one methylene group, the work of adhesion is:

$$W_{aCH_2} = 2\sqrt{\gamma_s^d \cdot \gamma_{CH_2}^d} \qquad (2)$$

where γ_s^d is the surface dispersive free energy of the solid stationary phase, and γ_{CH_2} is the surface dispersive free energy of a solid material only constituted by methylene groups, such as linear polyethylene. The common relation between dispersive free energy and temperature for polyethylene is:

$$\gamma_{CH_2} = 35.6 - 0.058t \qquad (3)$$

where t is the measuring temperature in °C. According to the following equation:

$$-\Delta G^{CH_2} = N \cdot a_{CH_2} \cdot W_{aCH_2} \qquad (4)$$

where N is the Avogadro's number, a_{CH_2} is the cross sectional area of an adsorbed methylene group, $6\,\text{Å}^2$. The surface dispersive free energy of the solid stationary phase can be obtained by:

$$\gamma_s^d = \frac{1}{4\gamma_{CH_2}}\left(\frac{-\Delta G^{CH_2}}{N \cdot a_{CH_2}}\right)^2 \qquad (5)$$

When combining Eq. (1) with Eq. (5), we can obtain:

$$\gamma_s^d = \frac{1}{4\gamma_{CH_2}}\left(\frac{RT \cdot \ln\left(\frac{V_{N,n+1}}{V_{N,n}}\right)}{N \cdot a_{CH_2}}\right)^2 \qquad (6)$$

2.2. Schultz method

The basic principle of Schultz method is [17–28]: when a series of liquid n-alkanes are used as probes, the adsorption dispersive free energy ΔG^{ads} of a probe with the carbon number n is:

$$\Delta G^{ads} = -RT \cdot \ln(V_{N,n}) + C \qquad (7)$$

where the constant C depends on the reference state. According to the Fowkes relation for the work of adhesion (W_a) by dispersive free energy between two phases, the work of adhesion of the probe is [29]:

$$W_a = 2\sqrt{\gamma_s^d \cdot \gamma_l^d} \qquad (8)$$

where γ_s^d is the surface dispersive free energy of the solid stationary phase, and γ_l^d is the surface dispersive free energy of the liquid alkane (probe). According to the following equation:

$$-\Delta G^{ads} = N \cdot a \cdot W_a \qquad (9)$$

where a is the cross section area of the alkane molecule, which can be calculated from the following equation:

$$a = 1.09 \times 10^{14} \cdot \left(\frac{M}{\rho \cdot N}\right)^{2/3} \qquad (10)$$

where M is the molar mass, and ρ is the density. After combining Eqs. (7) and (8) with Eq. (9), the following equation can be obtained:

$$RT \cdot \ln(V_{N,n}) = 2N \cdot a \cdot (\gamma_l^d)^{0.5} \cdot (\gamma_s^d)^{0.5} + C \qquad (11)$$

When plotting $RT \cdot \ln(V_{N,n})$ versus $a \cdot (\gamma_l^d)^{0.5}$ for the series of liquid n-alkanes, a line can be obtained. Then, the dispersive free energy of the solid stationary phase can be calculated from the slope of the line.

Table 1
Parameters of liquid n-alkanes for Schultz method [33,34].

Name	γ_l^d (mJ/m^2)	a (Å^2)	$a \cdot (\gamma_l^d)^{0.5}$ (Å^2 (mJ/m^2)$^{0.5}$)
n-C$_6$	18.4	51.5	220.9
n-C$_7$	20.3	57.0	256.8
n-C$_8$	21.3	63.0	290.8
n-C$_9$	22.7	69.0	328.8
n-C$_{10}$	23.4	75.0	362.8

Table 2
Calculated middle parameters for Eq. (13).

Carbon number n	6	7	8	9	Average	Standard deviation
$a_{n+1}\gamma_{l,n+1}^{0.5} - a_n\gamma_{l,n}^{0.5}$	35.9	34.0	37.2	34.0	35.3	1.565

2.3. Comparison of the two methods

In order to find the difference between the results from the two methods, the ratio between $\gamma_{s,\text{Dorris–Gray}}^d$ and $\gamma_{s,\text{Schultz}}^d$ will be calculated. Firstly, for the Schultz method, when two adjacent alkanes (carbon number is n and $n+1$) are used as probes, according to Eq. (11), the dispersive free energy of the solid stationary phase can be calculated from the slope as:

$$\gamma_s^d = \frac{1}{4}\left(\frac{RT \cdot \ln\left(\frac{V_{N,n+1}}{V_{N,n}}\right)}{N \cdot (a_{n+1}\gamma_{l,n+1}^{0.5} - a_n\gamma_{l,n}^{0.5})}\right)^2 \qquad (12)$$

When combining Eq. (6) with Eq. (12), for the same measuring conditions, the ratio of the two different methods is:

$$\frac{\gamma_{s,\text{Dorris–Gray}}^d}{\gamma_{s,\text{Schultz}}^d} = \frac{(a_{n+1}\gamma_{l,n+1}^{0.5} - a_n\gamma_{l,n}^{0.5})^2}{\gamma_{CH_2} \cdot a_{CH_2}^2} \qquad (13)$$

The common parameters of liquid n-alkanes (probes) for Schultz method are listed in Table 1. Table 2 lists the calculated middle parameter of $a_{n+1}\gamma_{l,n+1}^{0.5} - a_n\gamma_{l,n}^{0.5}$. The average value 35.5, is used to calculate the ratio. Table 3 lists the final calculated ratio at three temperatures, 30 °C, 40 °C, and 50 °C. The ratio values mean that the dispersive free energy calculated with Dorris–Gray method will always be larger than the data calculated with Schultz method. When the measuring temperature increases, the ratio increases.

Contact angle (CA) measurement is a technique for characterizing the surface free energy of smooth materials at room temperature. For the surface dispersive free energy measurements, some authors found that there was a good correlation between the results of CA and IGC methods [35–37]. However, we find that for the basic data of surface dispersive free energy of liquid n-alkanes, there is a slight difference between the papers using the traditional Schultz method and some handbooks for liquid solvents. Table 4 lists the surface dispersive free energy of liquid n-alkanes chosen from a handbook [38], which are used in CA measurement. The calculated "new" middle parameters of $a_{n+1}\gamma_{l,n+1}^{0.5} - a_n\gamma_{l,n}^{0.5}$ are listed in Table 5. Compared with the standard deviation 1.355 in Table 2, the standard deviation in Table 5, 0.411, is smaller. Table 6 lists the ratio values calculated with the "new" parameters and a set of ratio values calculated directly from an IGC experiment. It shows that the analyzed results absolutely equal to the experimental data. Therefore, the "new" surface dispersive free energy parameters listed in

Table 3
Ratio of $\gamma_{s,\text{Dorris–Gray}}^d / \gamma_{s,\text{Schultz}}^d$ calculated from Eq. (13).

Temperature (°C)	30	40	50
γ_{CH_2} (mJ/m^2)	33.86	33.28	32.70
Ratio	1.02	1.04	1.06

Table 4
"New" parameters of liquid n-alkanes.

Name	γ_l^d (mJ/m^2)[a]	a (Å^2)	$a \cdot (\gamma_l^d)^{0.5}$ (Å^2 (mJ/m^2)$^{0.5}$)
n-C$_6$	17.90	51.5	217.9
n-C$_7$	19.80	57.0	253.6
n-C$_8$	21.14	63.0	289.7
n-C$_9$	22.38	69.0	326.4
n-C$_{10}$	23.37	75.0	362.6

[a] Data are taken from Ref. [38].

Table 5
Calculated "new" middle parameters for Eq. (13).

Carbon number n	6	7	8	9	Average	Standard deviation
$a_{n+1}\gamma_{l,n+1}^{0.5} - a_n\gamma_{l,n}^{0.5}$	35.7	36.1	36.7	36.2	36.2	0.411

Table 6
"New" ratio of $\gamma_{s,\text{Dorris-Gray}}^d / \gamma_{s,\text{Schultz}}^d$.

Temperature (°C)	30	40	50
Calculated with "new" surface free energy of n-alkanes listed in Table 4	1.07	1.09	1.11
Calculated directly from experimental data in Table 2 of Ref. [39]	1.07	1.09	1.11

Table 4 should be better than the traditional parameters listed in Table 1.

3. Conclusions

In this paper, the surface dispersive free energy calculated from Dorris–Gray method and Schultz method is compared through calculating their ratio with their basic equations and parameters. It can be concluded that the dispersive parameters calculated with Dorris–Gray method will always be larger than the data calculated with Schultz method. When the measuring temperature increases, the ratio increases. Compared with the parameters in solvents handbook, it seems that the traditional surface free energy parameters of n-alkanes listed in the papers using Schultz method are not enough accurate, which can be proved with a published IGC experimental result.

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