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Short communication

An equation to calculate the actual methylene middle parameter as a function of temperature

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ABSTRACT

Methylene middle parameter $\left[\alpha_{CH_2}(\gamma_{CH_2})^{0.5}\right]$, the product of the methylene group's cross-sectional area (α_{CH_2}) and the root square of its dispersive free energy (γ_{CH_2}), is the key parameter to calculate the dispersive surface components of solids (γ_s^d) using inverse gas chromatography (IGC) at different temperatures. The only method reported to calculate $\alpha_{CH_2}(\gamma_{CH_2})^{0.5}$ as a function of temperature is the Dorris–Gray method. However, the conventional values of $\alpha_{CH_2}(\gamma_{CH_2})^{0.5}$ calculated by the Dorris–Gray method depend heavily on theoretical aspects. This paper establishes a novel equation calculating the actual $\alpha_{CH_2}(\gamma_{CH_2})^{0.5}$ as a function of temperature using the latest and most accurate surface parameters of seven successive n-alkanes. The obtained actual $\alpha_{CH_2}(\gamma_{CH_2})^{0.5}$ values are slightly higher those of the conventional $\alpha_{CH_2}(\gamma_{CH_2})^{0.5}$. At 20 °C, the actual $\alpha_{CH_2}(\gamma_{CH_2})^{0.5}$ generates γ_s^d values less than those generated using the conventional $\alpha_{CH_2}(\gamma_{CH_2})^{0.5}$ by ~3%, and this reduction in calculated γ_s^d values increases linearly to become ~5% at 100 °C. Therefore, using the new actual $\alpha_{CH_2}(\gamma_{CH_2})^{0.5}$ seems to mitigate the discrepancy between the γ_s^d values measured by IGC and those measured by the contact angle method.

1. Introduction

The surface energy of solids consists of dispersive (γ_s^d) and specific (electron acceptor and electron donor) components. Inverse gas chromatography (IGC) is a common technique to measure these components. The accuracy of γ_s^d calculation influences the calculated values of both γ_s^d and the specific components [1]. The calculation of γ_s^d was simplified by combining the Dorris–Gray equation [2] and the Schultz equation [3] within the chromatographic adhesion law [4], and its simplified equation to calculate γ_s^d is:

$$\gamma_s^d = \frac{0.477(T \ln K_{CH_2}^a)^2}{\alpha_{CH_2}^2 \gamma_{CH_2}} \text{mJ m}^{-2} \quad (1)$$

where α_{CH_2} is the cross-sectional area of a methylene group in units of Å^2, γ_{CH_2} is the dispersive free energy of the methylene group in units of mJ m^{-2}, $K_{CH_2}^a$ is the dispersive retention factor, and T is the column temperature (in degrees Kelvin).

The accuracy of $K_{CH_2}^a$ measurement and its effect on the accuracy of γ_s^d has been recently quantitated [5]. However, the values of the surface parameters of methylene (α_{CH_2} and γ_{CH_2}), and so the methylene middle parameter $[\alpha_{CH_2}(\gamma_{CH_2})^{0.5}]$, are still controversial. If $\alpha_{CH_2}(\gamma_{CH_2})^{0.5}$ is calculated according to the Dorris–Gray method, Eq. (1) generates the same values as the Dorris–Gray method, and if $\alpha_{CH_2}(\gamma_{CH_2})^{0.5}$ is calculated from the average of $\alpha_{C_{i+1}}(\gamma_{C_{i+1}}^d)^{0.5} - \alpha_{C_i}(\gamma_{C_i}^d)^{0.5}$, Eq. (1) generates the same values as the Schultz method [4,5].

Materials are processed at different temperatures, and their performance during processing depends on their surface free energy. To date, Dorris–Gray [2] is the only reported method to calculate $\alpha_{CH_2}(\gamma_{CH_2})^{0.5}$ as a function of temperature. They considered α_{CH_2} as 6 Å^2 and its value is temperature independent, but they calculated γ_{CH_2} as a function of temperature using the following equation:

$$\gamma_{CH_2} = 35.6 + 0.058(293 - T) \text{mJ m}^{-2} \quad (2)$$

where T is the temperature (in degrees Kelvin). Then, $\left[\alpha_{CH_2}(\gamma_{CH_2})^{0.5}\right]_{\text{Dorris–Gray}}$ is calculated using Eq. (2) and the constant value of α_{CH_2} being 6 Å^2.

Dorris and Gray calculated α_{CH_2} by multiplying the separation distance of two carbon atoms of n-alkanes (which is 0.1275 nm) with the average distance between centers of CH_2 groups in adjacent molecules (which is ≈0.47 nm). They derived Eq. (2) from

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the values of the surface tension of a linear polyethylene (containing only methylene groups) at different temperatures over the melt, and then from an extrapolation of the surface tension of low-molecular-weight n-alkanes to infinite chain length. Therefore, $\left[\alpha_{CH_2}(\gamma_{CH_2})^{0.5}\right]_{Dorris-Gray}$ depends heavily on theoretical aspects. However, due to the absence of an actual alternative of $\left[\alpha_{CH_2}(\gamma_{CH_2})^{0.5}\right]_{Dorris-Gray}$, most researchers have used it to calculate the dispersive surface energy at different temperatures [6–8]. In actuality, the methylene group represents the additive contribution of an n-alkane compared to its ascendant n-alkane to the adsorption to a tested solid. Therefore,

$$\left[\alpha_{CH_2}(\gamma_{CH_2})^{0.5}\right]_{actual} = \alpha_{C_{i+1}}(\gamma^d_{l_{C_{i+1}}})^{0.5} - \alpha_{C_i}(\gamma^d_{l_{C_i}})^{0.5} \quad (3)$$

where γ_l^d and α are the dispersive free energy and the cross-sectional area of the homologous n-alkanes, respectively, and the subscripts (C_{i+1} and C_i) indicate any two successive n-alkanes. This paper aims to derive an equation calculating $\left[\alpha_{CH_2}(\gamma_{CH_2})^{0.5}\right]_{actual}$ as a function of temperature using the latest and most accurate n-alkane parameters.

2. Discussion

Table 1 contains the latest data of n-alkanes' surface tensions (γ_l^d) of seven n-alkanes (n-pentane to n-undecane) within the temperature range 10–100 °C taken from Handbook of Chemistry and Physics, Chemical Rubber Company [9]. This temperature range is appropriate to derive $\left[\alpha_{CH_2}(\gamma_{CH_2})^{0.5}\right]_{actual}$ because IGC is typically used to characterise the surface at fairly low temperatures (below 100 °C) [10]. The last row of Table 1 contains the conventional values of γ_l^d which are usually taken from the latest SMS manual and from Schultz et al. [3]. The conventional γ_l^d values are available at 30 °C only. Table 2 contains different α values which are method dependent and temperature independent. These α values were measured by the Kiselev method or calculated using theoretical calculations such as Van der Waals (VDW) model, Redlich–Kwong (R–K) equation, geometric model, cylindrical model or spherical model [11]. Different hypotheses were tested to study the effect of temperature on the values of α, and it was found that the hypothesis assuming that α values are constant and temperature independent is the easiest method, which requires no additional assumptions, moreover, they fit the linearity of Eq. (4) of Schultz et al. [3] over a wide temperature range [10,12].

$$RT ln\, V_n = 2N(\gamma_s^d)^{0.5}\alpha(\gamma_l^d)^{0.5} + C \quad (4)$$

where C is a constant, N is the Avogadro number, R is the gas constant, V_n indicates the net retention volumes of n-alkanes.

These values of γ_l^d and α listed in Tables 1 and 2 were used to calculate $\left[\alpha_{CH_2}(\gamma_{CH_2})^{0.5}\right]_{actual}$ over the reported temperatures as follows:

$\left[\alpha_{CH_2}(\gamma_{CH_2})^{0.5}\right]_{actual}$ is the average of $\alpha_{C_{i+1}}(\gamma^d_{l_{C_{i+1}}})^{0.5} - \alpha_{C_i}(\gamma^d_{l_{C_i}})^{0.5}$, and so it is calculated from:

$$\left[\alpha_{CH_2}(\gamma_{CH_2})^{0.5}\right]_{actual} = \alpha_{C_{i+1}}(\gamma^d_{l_{C_{i+1}}})^{0.5} - \alpha_{C_i}(\gamma^d_{l_{C_i}})^{0.5} = \frac{\Delta\alpha(\gamma_l^d)^{0.5}}{\Delta n} \quad (5)$$

where n is the carbon number of the homologous n-alkanes.

Integration of Eq. (5) gives:

$$\alpha(\gamma_l^d)^{0.5} = \left[\alpha_{CH_2}(\gamma_{CH_2})^{0.5}\right]_{actual} n + \text{constant} \quad (6)$$

Also we can obtain Eqs. (5) and (6) by combining Eq. (4) of Schultz et al. [3] and Eq. (7) of Conder-Young [13].

$$lnt_n = An + B \quad (7)$$

where A and B are constants, t_n indicates the net retention times of n-alkanes. Further details of the mathematical derivation of Eqs. (5) and (6) are reported in the supplementary information.

The slope of Eq. (6) averages out $\left[\alpha_{CH_2}(\gamma_{CH_2})^{0.5}\right]_{actual}$ from the n-alkane line of $\alpha(\gamma_l^d)^{0.5}$ versus n. The error% of the slope reflects the accuracy of the obtained $\left[\alpha_{CH_2}(\gamma_{CH_2})^{0.5}\right]_{actual}$ and the considered n-alkanes' surface parameters (γ_l^d and α). The error% is calculated from:

$$\text{Error\%} = \left(\frac{\text{Standard deviation of the slope}}{\text{Slope}}\right) \times 100 \quad (8)$$

when the error% approaches zero, the correlation coefficient of Eq. (6) approaches one, and the used data (α and γ_l^d) obey Schultz and Conder-Young equations, the lower the error%, the more accurate $\left[\alpha_{CH_2}(\gamma_{CH_2})^{0.5}\right]_{actual}$.

Table 3 shows the typical consistency between correlation coefficient "r" of Eq. (6) and the error% values of its slope. Table 3 also shows that when the γ_l^d values taken from the Handbook of Chemistry and Physics [9] and the α values of Kiselev results [11] are used, the error% of $\left[\alpha_{CH_2}(\gamma_{CH_2})^{0.5}\right]_{actual}$ reaches its lowest values (less than 0.5%) at all temperatures with average of 0.2%. However, the average of error% increases when α values of the other tabulated methods are used. Also the error% increases in the case of using the conventional γ_l^d (last row of Table 3).

Although the conventional γ_l^d values (last row of Table 1) are still used by researchers, they lack accuracy. Shi et al. clarified the inaccuracy in the conventional γ_l^d values compared to those values reported in the solvents handbook [14]. This inaccuracy makes the calculated γ_l^d values depend on the n-alkane series used to probe the solid [15]. Also, the conventional values of γ_l^d cover only one temperature (30 °C). α_{CH_2} calculated from $\alpha_{C_{i+1}} - \alpha_{C_i}$ of Kiselev results equals 6 Å^2. However, other methods generate α_{CH_2} either higher or lower than 6 Å^2. Voelkel et al. cited different values of α_{CH_2} ranging from 3.1 to 7.7 Å^2, and they concluded that 6 Å^2 is the most accurate [16]. The above discussion and the values of "r" and Error% (Table 3) elucidate that the γ_l^d values listed in the Handbook of Chemistry and Physics and α values of Kiselev results are the most accurate and convenient to calculate $\left[\alpha_{CH_2}(\gamma_{CH_2})^{0.5}\right]_{actual}$ compared to their counterpart values. Therefore, we used them to derive the equation calculating $\left[\alpha_{CH_2}(\gamma_{CH_2})^{0.5}\right]_{actual}$ as a function of temperature. In this equation, we correlated $\left[\alpha^2_{CH_2}\gamma_{CH_2}\right]_{actual}$ instead of $\left[\alpha_{CH_2}(\gamma_{CH_2})^{0.5}\right]_{actual}$ with temperature to obey the first order linear correlation between surface tensions of liquids and temperature, which is prominent in Eq. (2) and the data of Table 1. These data show that all n-alkanes' γ_l^d values linearly correlate with temperature, and their Eqs. (9)–(15), which have correlation coefficient "r" 1.000000, are:

$$\gamma^d_{l,C5} = -0.111T + 48.486 \quad (9)$$

$$\gamma^d_{l,C6} = -0.102T + 48.379 \quad (10)$$

$$\gamma^d_{l,C7} = -0.099T + 49.068 \quad (11)$$

$$\gamma^d_{l,C8} = -0.095T + 49.494 \quad (12)$$

$$\gamma^d_{l,C9} = -0.094T + 50.268 \quad (13)$$

$$\gamma^d_{l,C10} = -0.092T + 50.801 \quad (14)$$

$$\gamma^d_{l,C11} = -0.090T + 51.084 \quad (15)$$