



Short communication

A method for improving the calculation accuracy of acid–base constants by inverse gas chromatography

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ABSTRACT

In this paper, studies were conducted in order to improve the calculation accuracy of acid–base constants measured by inverse gas chromatography. The conventional $a \cdot (\gamma_1^d)^{0.5}$ parameters of DCM (dichloromethane), TCM (trichloromethane), and EtAcet (ethyl acetate) were corrected as 185, 212, and $235 \text{ \AA}^2(\text{mJ}/\text{m}^2)^{0.5}$ by analyzing the relationship between $a \cdot (\gamma_1^d)^{0.5}$ and the boiling temperature of the probe solvents, where a is molecular area and γ_1^d is surface dispersive free energy of the probe solvents, respectively. To validate the availability of the new $a \cdot (\gamma_1^d)^{0.5}$ values, the acid–base constants of polystyrene were measured. It was found that when the new $a \cdot (\gamma_1^d)^{0.5}$ parameters were adopted, the final linear fit degree for the plot of $-\Delta H_a^s/AN^*$ versus DN/AN^* was enhanced from 0.993 to 0.999, and the standard deviation was decreased from 0.344 to 0.156. In addition, the availability of general application to improving the calculation accuracy of acid–base constants with the new $a \cdot (\gamma_1^d)^{0.5}$ parameters was also proved with a mathematical justification.

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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 are determined above room temperature [1]. Although using this technique to define the surface properties has been developed for more than 20 years, there are still some unsolved basic problems. One is there are three different methods for the calculation of surface dispersive free energy. Another is the calculation accuracy of acid–base constants is not enough high. For the first problem, in one of our published papers [2], we tried to solve it through comparing the two classical methods (Dorris–Gray and Schultz methods) with their basic equations and parameters. In this paper, the second problem is brought forward. The background of this research work is introduced in the following sections.

The traditional method of surface acid–base characterization is that the surface dispersive free energy of a solid stationary phase, γ_s^d , is initially determined by using a series of n -alkanes as non-polar probes at some temperatures. Then, the acid–base constants are calculated by using some polar liquids as the acid–base probes. The commonly used polar probes include three groups, which

are two absolute acidic sorbates: dichloromethane (DCM) and trichloromethane (TCM); basic sorbates: diethyl ether (DEE) and tetrahydrofuran (THF); and amphoteric sorbates: acetone (Acet) and ethyl acetate (EtAcet).

The universal process for the calculation of acid–base constants are: the adsorption free energy ΔG_a of the probes by the stationary phase is obtained from the net retention volume V_n by the following equation [3]:

$$-\Delta G_a = RT \ln(V_n) \quad (1)$$

where R is the gas constant, T is the temperature of column. When polar solvents are injected into the column, the adsorption free energy by acid–base interactions ΔG_a^s , is calculated by the following expression:

$$\Delta G_a = \Delta G_a^d + \Delta G_a^s \quad (2)$$

where ΔG_a^d is the adsorption free energy due to dispersive interaction, which is determined with a series of n -alkanes. $-\Delta G_a^s$ results from the distance between the $RT \ln(V_n)$ value of the polar solvent and a straight line plotted from the n -alkanes. Then, the adsorption enthalpy by acid–base interactions ΔH_a^s , is calculated according to the following expression:

$$\Delta G_a^s = \Delta H_a^s - T \Delta S_a^s \quad (3)$$

where ΔS_a^s is the adsorption entropy by acid–base interactions. ΔH_a^s results from the slope of a line, which is achieved by

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plotting $\Delta G_a^s/T$ versus $1/T$. The acid constant K_a and base constant K_b are calculated according to the following expression:

$$-\Delta H_a^s = K_a \times DN + K_b \times AN^* \quad (4)$$

where DN and AN^* are the Gutmann's donor and modified acceptor numbers of polar solvents, respectively. When plotting $-\Delta H_a^s/AN^*$ versus DN/AN^* , generally, a straight line is achieved. The slope of the line gives K_a , and the intercept gives K_b .

For the separation of ΔG_a^s from ΔG_a in Eq. (2), there are three methods [4,5]. Method (I): plotting $RT \ln(V_n)$ versus $a \cdot (\gamma_1^d)^{0.5}$, where a is the molecular area of the probe solvent, and γ_1^d is the surface dispersive free energy of the probe solvent; method (II): plotting $RT \ln(V_n)$ versus the logarithm of the saturation vapor pressure of the probe solvent, $\lg(P_0)$; and method (III): plotting $RT \ln(V_n)$ versus the normal boiling temperature of the probe solvent, T_b . It has been validated that the three methods can yield an equivalent ΔH_a^s [4,5].

Until now, hundreds of research papers on surface acid–base characterization with IGC using the above three methods have been published. Compared with the methods (II) and (III), most researchers were apt to choose the method (I). For example, since 2002, 6 papers [6–11] using method (I) were published on the *Journal of Chromatography A*. At the same time, 3 papers using method (III) has been validated that the three methods can yield an equivalent ΔH_a^s [12–14].

However, there exists a common problem for the three methods when choosing the probes, which is two absolute acidic probes, DCM and TCM can be chosen. For the calculation of acid–base constants by plotting $-\Delta H_a^s/AN^*$ versus DN/AN^* , the position of DCM and TCM locates on the vertical axis because their DN/AN^* values (abscissa) are zero. Because there was no reason to choose only DCM or TCM, the researchers often used DCM and TCM in one experiment [7,8,15–17]. This can produce a troublesome phenomenon that was the position of DCM and TCM was not same. According to the final plots of $-\Delta H_a^s/AN^*$ versus DN/AN^* [15–17], DCM often located above TCM on the vertical axis [7,15–17], and the differences in the vertical coordinates between DCM and TCM were about 0.5. Because the basic constant, K_b is dependent on the fitted line of the intercept value, the differences in the vertical coordinates of DCM and TCM had a very large influence on the basic constant. According to these results, it seemed that it was impossible to make the two different points to become one point.

In this paper, we attempt to amend the molecular parameters of DCM and TCM of method (I) to solve this problem. The following sections give the amended methods, a validation experiment, and a mathematical justification.

2. New $a \cdot (\gamma_1^d)^{0.5}$ parameters of DCM and TCM

Table 1 lists the conventional property parameters of the probe solvents. The values of boiling temperature, T_b were taken

Table 1
Conventional property parameters of probe solvents [7,10,11,13,17–24].

Name	T_b (°C)	a (Å ²)	γ_1^d (mJ/m ²)	$a \cdot (\gamma_1^d)^{0.5}$ (Å ² (mJ/m ²) ^{0.5})	AN^* (kJ/mol)	DN (kJ/mol)	DN/AN^*
C5	36.1	46.1	16.0	184	–	–	–
C6	68.7	51.5	18.4	221	–	–	–
C7	98.4	57.0	20.3	257	–	–	–
C8	125.7	63.0	21.3	291	–	–	–
C9	150.8	69.0	22.7	329	–	–	–
C10	174.1	75.0	23.4	363	–	–	–
DCM	40.0	31.5	27.6	165	16.4	0	0
TCM	61.2	44.0	25.9	224	22.7	0	0
Acet	56.0	42.5	16.5	173	10.5	71.4	6.8
EtAcet	77.1	48.0	19.6	213	6.3	71.7	11.4
THF	66.0	45.0	22.5	213	2.1	84.4	40.2

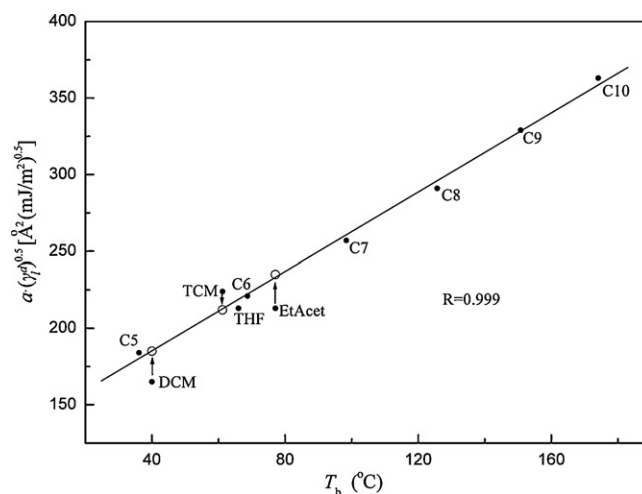


Fig. 1. Plots of $a \cdot (\gamma_1^d)^{0.5}$ versus boiling temperature of probes. (●) Conventional values; (○): new values.

from Refs. [13,18–20]. The other values were taken from Refs. [7,10,11,17,21–24]. There should exist a linear relation when plotting $a \cdot (\gamma_1^d)^{0.5}$ versus T_b if the above three methods could give consistent results. However, when we plotted $a \cdot (\gamma_1^d)^{0.5}$ versus T_b , we found that the linear relation was not very good as shown in Fig. 1. DCM, TCM, and EtAcet obviously deviate from the n -alkanes line.

We found that the conventional surface dispersive free energy of EtAcet, 19.6 mJ/m², was different from a value, 23.9 mJ/m² listed in the tables on the surface tension components of many liquids [25,26]. After we used the “new” dispersive free energy value to re-calculate $a \cdot (\gamma_1^d)^{0.5}$ of EtAcet, it was found that this polar probe was exactly located on the n -alkanes line! If we suppose that DCM and TCM should also distribute on the n -alkanes line, the “new” $a \cdot (\gamma_1^d)^{0.5}$ of DCM should be 185 and TCM should be 212 Å²(mJ/m²)^{0.5} as listed in Table 2. When the new $a \cdot (\gamma_1^d)^{0.5}$ values are introduced into method (I), the distance between DCM and TCM on the vertical axis will decrease, which is demonstrated in the Appendix A part and is validated through the following IGC experiment.

3. Experimental

In order to validate the availability of the new $a \cdot (\gamma_1^d)^{0.5}$ values, an IGC experiment was performed. The surface acid–base constants of polystyrene (PS) resin were measured in this experiment, which was purchased from Yanshan Petrochemical Co., China. PS was covered on chromosorb (80–100 mesh) by the general solution-evaporation method. First, 2 g PS was dissolved in 10 g toluene

Table 2
New $a \cdot (\gamma_i^d)^{0.5}$ values of DCM, TCM and EtAcet.

Name	Conventional γ_i^d (mJ/m ²)	"New" γ_i^d (mJ/m ²)	Conventional $a \cdot (\gamma_i^d)^{0.5}$ (Å ² (mJ/m ²) ^{0.5})	New $a \cdot (\gamma_i^d)^{0.5}$ (Å ² (mJ/m ²) ^{0.5})
DCM			165	185 ^b
TCM			224	212 ^b
EtAcet	19.6	23.9 ^a	213	235

^a Value is taken from Refs. [25,26].

^b Values are achieved from Fig. 1.

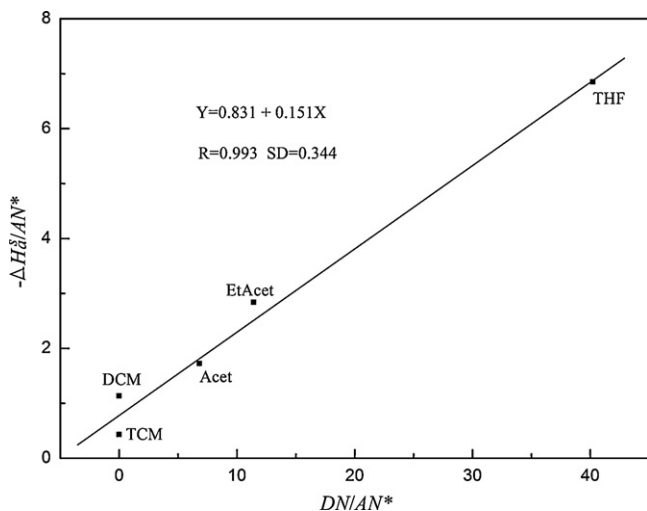


Fig. 2. Plots of $-\Delta H_a^s/AN^*$ versus DN/AN^* with conventional $a \cdot (\gamma_i^d)^{0.5}$ parameters.

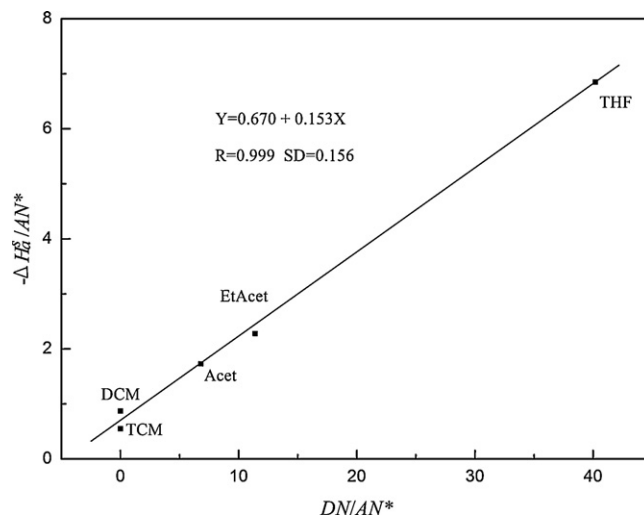


Fig. 3. Plots of $-\Delta H_a^s/AN^*$ versus DN/AN^* with new $a \cdot (\gamma_i^d)^{0.5}$ parameters.

at ambient temperature. Then, 5 g chromosorb was added to the solution and the solution was heated at 80 °C to vaporize toluene by continuous stirring. Finally, 1.54 g stationary phase coated with 0.44 g PS was packed into a stainless steel column. The column was conditioned at 90 °C and fast carrier gas flow rate for 12 h prior to measuring. The IGC instrument was a GC-900A gas chromatograph (Shanghai TianPu Analytical Instrument Ltd., China), equipped with a flame ionization detection (FID). The temperatures of injector and FID were 130 °C. High purity nitrogen (supplied by Qinghua Co., China) was used as the carrier gas. The flow rate was 25.0 mL/min, which was measured from the end of the column with a soap bubble flow meter. Methane was used as the non-interacting probe. The non-polar *n*-alkanes probes were *n*-pentane (C5), *n*-hexane (C6), *n*-heptane (C7), *n*-octane (C8), *n*-nonane (C9) and *n*-decane (C10). The polar probes were DCM, TCM, Acet, EtAcet and THF. They were analytical grade solvents and were purchased from Tianjin Kermel Chemical Reagents Development Centre, China. The IGC experiment was performed at 40, 50, 60, and 70 °C. The probe solvents were injected manually with a 1.0 mL Hamilton syringe. The injection volumes were 0.1 mL. The data were processed by a self-made program.

4. Results and discussion

Method (I) was adopted to calculate the surface dispersive free energy and acid–base constants of polystyrene. The expression for the calculation of the adsorption free energy is:

$$-\Delta G_a = RT \ln(V_n) = 2N_A a \cdot (\gamma_s^d)^{0.5} (\gamma_i^d)^{0.5} + K' \quad (5)$$

Table 3 lists $-\Delta H_a^s$ and $-\Delta H_a^s/AN^*$ values of DCM, TCM, and EtAcet calculated with the conventional and new $a \cdot (\gamma_i^d)^{0.5}$ parameters.

It can be found that when the new $a \cdot (\gamma_i^d)^{0.5}$ value is larger than the conventional value (e.g. DCM and EtAcet), the new values of

$-\Delta H_a^s$ will become smaller, and the new values of $-\Delta H_a^s/AN^*$ will also become smaller. On the contrary, the new $-\Delta H_a^s/AN^*$ value of TCM becomes large because the new $a \cdot (\gamma_i^d)^{0.5}$ value of TCM decreases. Compared with the difference in $-\Delta H_a^s/AN^*$ of DCM and TCM calculated from the conventional $a \cdot (\gamma_i^d)^{0.5}$ parameters, 0.704, the new difference decreases to 0.317. Figs. 2 and 3 show the plots of $-\Delta H_a^s/AN^*$ versus DN/AN^* calculated with the conventional and new $a \cdot (\gamma_i^d)^{0.5}$ parameters (listed in Table 3), respectively. They present that the linear fit degree is enhanced when using the new parameters, and the standard deviation becomes markedly small.

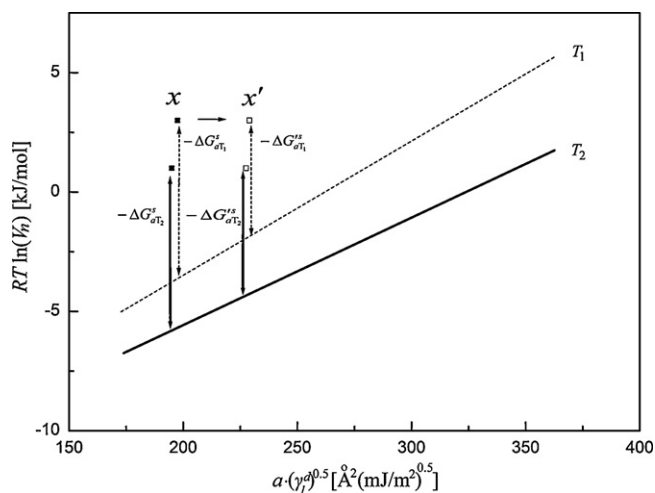


Fig. 4. Plots of $RT \ln(V_n)$ versus $a \cdot (\gamma_i^d)^{0.5}$. (■) Conventional $a \cdot (\gamma_i^d)^{0.5}$ values; (□) "new" $a \cdot (\gamma_i^d)^{0.5}$ values.

Table 3
Enthalpy values of DCM, TCM, and EtAcet calculated with conventional and new $a \cdot (\gamma_1^d)^{0.5}$ parameters.

Name	DCM		TCM		EtAcet	
	Conventional value	New value	Conventional value	New value	Conventional value	New value
$-\Delta H_a^s$ (kJ/mol)	18.62	14.25	9.78	12.53	17.90	14.36
$-\Delta H_a^s/AN^*$	1.135	0.869	0.431	0.552	2.841	2.279

5. Conclusions

In order to improve the calculation accuracy of acid–base constants, the conventional $a \cdot (\gamma_1^d)^{0.5}$ parameters of DCM, TCM, and EtAcet were amended as 185, 212, and $235 \text{ \AA}^2(\text{mJ}/\text{m}^2)^{0.5}$ through analyzing the relation between $a \cdot (\gamma_1^d)^{0.5}$ and the boiling temperature of the probe solvents. For the surface acid–base characterization of polystyrene in this experiment, when this new group of $a \cdot (\gamma_1^d)^{0.5}$ parameters were adopted, the final linear fit degree for the plot of $-\Delta H_a^s/AN^*$ versus DN/AN^* was enhanced from 0.993 to 0.999, and the standard deviation was decreased from 0.344 to 0.156. Consequently, using the new $a \cdot (\gamma_1^d)^{0.5}$ parameters could significantly improve the calculation accuracy of acid–base constants by inverse gas chromatography.

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Appendix A. Mathematical justification

In order to prove that when the new $a \cdot (\gamma_1^d)^{0.5}$ values are introduced into method (I), the decrease in the distance of $-\Delta H_a^s/AN^*$ between DCM and TCM on the vertical axis is a doubtless result, we will prove in this appendix part that there always exists a principle, which is $-\Delta H_a^s$ will decrease with the increase of $a \cdot (\gamma_1^d)^{0.5}$. There is a precondition that is the surface dispersive free energy of the solid stationary decreases with the increase of temperature.

In order to make the expressions to be concise, we let $a \cdot (\gamma_1^d)^{0.5} = x$. As shown in Fig. 4, from the $RT \ln(V_n)$ results measured at two different temperature conditions T_1 and T_2 ($T_1 < T_2$), $-\Delta H_a^s$ can be calculated with the following equation:

$$-\Delta H_a^s = \frac{-\Delta G_{aT_1}^s/T_1 + \Delta G_{aT_2}^s/T_2}{1/T_1 - 1/T_2} \quad (6)$$

When x increases to x' ($x < x'$), the new $-\Delta H_a^s$ (named as $-\Delta H_a^{s'}$) is:

$$-\Delta H_a^{s'} = \frac{-\Delta G_{aT_1}^{s'}/T_1 + \Delta G_{aT_2}^{s'}/T_2}{1/T_1 - 1/T_2} \quad (7)$$

Then, $-\Delta H_a^s$ minus $-\Delta H_a^{s'}$ is:

$$-\Delta H_a^s - (-\Delta H_a^{s'}) = \frac{T_1 \Delta G_{aT_2}^s - T_2 \Delta G_{aT_1}^s}{T_2 - T_1} - \frac{T_1 \Delta G_{aT_2}^{s'} - T_2 \Delta G_{aT_1}^{s'}}{T_2 - T_1} \quad (8)$$

or expressed as:

$$-\Delta H_a^s - (-\Delta H_a^{s'}) = \frac{T_2(-\Delta G_{aT_1}^s + \Delta G_{aT_1}^{s'}) - T_1(-\Delta G_{aT_2}^s + \Delta G_{aT_2}^{s'})}{T_2 - T_1} \quad (9)$$

Because the surface dispersive free energy decreases when the temperature increases, the slope of the n -alkanes line at T_1 is larger than the slope of the n -alkanes line at T_2 ($T_2 > T_1$). In addition, there are following relations: $-\Delta G_{aT_1}^s > -\Delta G_{aT_1}^{s'}$, $-\Delta G_{aT_2}^s > -\Delta G_{aT_2}^{s'}$, and $-\Delta G_{aT_1}^s - (-\Delta G_{aT_1}^{s'}) > -\Delta G_{aT_2}^s - (-\Delta G_{aT_2}^{s'})$. Consequently, we can obtain:

$$T_2(-\Delta G_{aT_1}^s + \Delta G_{aT_1}^{s'}) > T_1(-\Delta G_{aT_2}^s + \Delta G_{aT_2}^{s'}) \quad (10)$$

Therefore:

$$-\Delta H_a^s - (-\Delta H_a^{s'}) > 0 \quad (11)$$

It means that when $x < x'$, there always exists such relations: $-\Delta H_a^s > -\Delta H_a^{s'}$ and $-\Delta H_a^s/AN^* > -\Delta H_a^{s'}/AN^*$. For DCM, the new $a \cdot (\gamma_1^d)^{0.5}$ value, 185, is larger than the conventional value, 165, which means $x < x'$. But for TCM, the new value, 212, is smaller than the conventional value, 224, which means $x > x'$. Consequently, the distance of $-\Delta H_a^s/AN^*$ between DCM and TCM on the vertical axis is always smaller than the distance of $-\Delta H_a^s/AN^*$ between them.

Appendix B. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chroma.2012.01.090.

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