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ADSORPTION ENTHALPY AND DESORPTION ENTHALPY DURING DISPLACEMENT OF ADSORBATE TO SOLVENT IN A LIQUID–SOLID SYSTEM*

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Abstract

The adsorption heat of the stoichiometric displacement process for the adsorption of a solute in a liquid–solid system was investigated. On the basis of the SDM-A and the rule of the additivity of energy, an expression which describes the dependence of the adsorption enthalpy on the nature and concentration of the solute, and on the solvent and adsorbent, was derived. The adsorption heat determined for the solute with the traditional method can be divided into two independent fractions, relating to the adsorption of the solute and to the desorption of the solvent. Experimental data on both isotherms from the literatures and precise calorimetry were used to test the adsorption heat and its fractions computed quantitatively via the equations presented in this study, and a satisfactory degree of conformity between them was obtained.

Keywords: adsorption enthalpy, desorption enthalpy, liquid–solid system

Introduction

A study of adsorption heat as one of the important means of exploring the adsorption mechanism is a basic feature of theoretical investigations of adsorption. When an adsorbate is adsorbed by an adsorbent from which solvent desorbs in a liquid–solid system, the traditionally named adsorption heat may in fact be divided in practice into two parts: the desorption enthalpy of solvent molecules (generally endothermic) and the adsorption enthalpy of adsorbate molecules (generally exothermic). However, the question of how to measure them separately has not yet been answered. The recently developed theory on the stoichiometric displacement model of adsorption (SDM-A) from a liquid–solid system, which is based on various interactions between solute, solvent and adsorbent molecules, as well as the equilibria between the adsorption of the

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solute by the adsorbent and the desorption of the solvent from it [1], laid a strong theoretical foundation for basic research of adsorption thermodynamics in a liquid–solid system. In the present paper, three linear equations are deduced theoretically according to the SDM-A and the rule of energy additivity, and the adsorption heat is divided into two independent energy fractions, separately corresponding to solute adsorption and solvent desorption, occurring simultaneously; a quantitative relation is then established between the adsorption heat (including the desorption enthalpy for the solvent) and the equilibrium activity in the bulk solution, and both fractions are computed from the equations presented in this study and tested with experimental data on both isotherms and precise calorimetry.

Theoretical

The SDM-A, which may be used for a precise description of the adsorption isotherms in dilute solutions in a liquid–solid system, can be expressed with the following equations [1]:

$$\log P_a = \beta_\alpha - (q/z)\log \alpha_{PD_m} \tag{1}$$

$$\beta_\alpha = \log K_\alpha + n\log P'_a \tag{2}$$

$$Z = n + q \tag{3}$$

where P_a and P'_a are the activity partition coefficients of the solute and the solvent in the two phases, respectively; α_{PD_m} is the equilibrium activity of the solvated solute; n and q are the numbers of moles of solvent molecules, D, released from the adsorbent and the moles of adsorbate during the stoichiometric displacement process, respectively, as one mole of solute molecule is adsorbed by the solvated adsorbent; Z is the sum of q and n and K_α is the equilibrium constant of adsorption. It should be pointed out that P'_a, n and q are constants under the conditions of a dilute solution, and therefore β_α and Z are also constants, and Eq. (1) should be a linear equation.

It was observed in a study [2] of the Gibbs adsorption free energy change of a solute, $\Delta G_{(P_a)}$, that it may be expressed as the sum of the two independent fractions: the affinity energy, $\Delta G_{(\beta_\alpha)}$, of the solute molecules for the adsorbent, and the desorption energy, $\Delta G_{(q/Z,PD_m)}$, of the solvent molecules from the adsorbent, i.e.

$$\Delta G_{(P_a)} = \Delta G_{(\beta_\alpha)} + \Delta G_{(q/Z,PD_m)} \tag{4}$$

Since P_a is considered to be an equilibrium constant describing a reversible equilibrium process, it can be shown that

$$\Delta G_{(P_a)} = -2.303\ RT \log P_a \tag{5}$$

Let us insert Eq. (1) into Eq. (5), and define the solute activity, α_{PD_m}, to be 1.0 mol·dm^{-3} as standard state. We then have

$$\Delta G_{(P_a)} = \Delta G^{o}_{(P_a)} + 2.303\ RT(q/Z) \log\alpha_{PD_m} \tag{6}$$

$$\Delta G^{o}_{(P_a)} = \Delta G_{(\beta_\alpha)} = -2.303\ RT\beta_\alpha \tag{7}$$

and

$$\Delta G_{(q/Z,PD_m)} = 2.303RT(q/Z) \log\alpha_{PD_m} \tag{8}$$

where $\Delta G^{o}_{(P_a)}$ or $\Delta G_{(\beta_\alpha)}$may be regarded as the standard Gibbs adsorption free energy change. At a given temperature, since β_α is a constant, and so is $\Delta G^{o}_{(P_a)}$ due to Eq. (7), $\Delta G_{(P_a)}$ should be a linear function of the logarithm of the solute activity in the bulk solution, as shown in Eq. (6). The term $\Delta G_{(P_a)}$ in Eq. (5) may also be expressed as the isotherm equation of enthalpy and entropy changes:

$$\Delta G_{(P_a)} = -2.303\ RT \log P_a = \Delta H_{(P_a)} - T\Delta S_{(P_a)} \tag{9}$$

or

$$\log P_a = -\frac{\Delta H_{(P_a)}}{2.303R} \times \frac{1}{T} + \frac{\Delta S_{(P_a)}}{2.303R} \tag{10}$$

where $\Delta H_{(P_a)}$ and $\Delta S_{(P_a)}$ are the general adsorption heat and adsorption entropy of the solute, respectively. They may all be considered as constants as long as α_{PD_m} is concerned and the temperature range studied is not too wide. Therefore, Eq. (10) should be a linear equation for $\log P_a$ *vs.* $1/T$.

As the values of β_α, Z and q in Eqs (2) and (3) are all constants as the temperature is given, so long as Eqs (7) and (8) hold, β_α and q/Z should be similar to P_a and can also be expressed in the same form as that in Eq. (9). We then have

$$\beta_\alpha = -\frac{\Delta H_{(\beta_\alpha)}}{2.303\ R} \times \frac{1}{T} + \frac{\Delta S_{(\beta_\alpha)}}{2.303\ R} \tag{11}$$

and

$$q/Z = \frac{\Delta H_{(q/Z,\mathrm{PD_m})}}{2.303\ R\ \log\alpha_{\mathrm{PD_m}}} \times \frac{1}{T} - \frac{\Delta S_{(q/Z,\mathrm{PD_m})}}{2.303R\ \log\alpha_{\mathrm{PD_m}}} \tag{12}$$

where $\Delta H_{(\beta_\alpha)}$ and $\Delta H_{(q/Z,\mathrm{PD_m})}$ denote the adsorption affinity enthalpy (or $\Delta H^{o}_{(\mathrm{P_a})}$, similar to that in Eq. (7)) of solute mulecules onto the adsorbent and the desorption enthalpy of the solvent molecules from both the adsorbent and the solvated adsorbate molecules, respectively, while $\Delta S_{(\beta_\alpha)}$ and $\Delta S_{(q/Z,\mathrm{PD_m})}$, are the entropy changes corresponding to ΔH_{β_α} and $\Delta H_{q/Z,\mathrm{PD_m}}$ respectively. Similarly, we can elucidate that there are linear relationships between both β_α and q/Z and $1/T$ in Eqs (11) and (12) under the same conditions as mentioned in Eq. (10).

From the rule of energy additivity, we have

$$\Delta H_{(\mathrm{P_a})} = \Delta H_{(\beta_\alpha)} + \Delta H_{(q/Z,\mathrm{PD_m})} \tag{13}$$

Equation (13) provides a possibility to study the contributions of the two fractions of enthalpy change.

Differentiating Eq. (6) with respect to T, inserting Eq. (12) into the differentiated equation, and combining the latter with the Gibbs-Helmholtz equation, we have

$$\Delta H_{(\mathrm{P_a})} = \Delta G_{(\mathrm{P_a})} - T \times \frac{\partial \Delta G_{(\mathrm{P_a})}}{\partial T}$$

because

$$\Delta H_{(\mathrm{P_a})} = \Delta H^{o}_{(\mathrm{P_a})} + 2.303\ R\ b\ \log\alpha_{\mathrm{PD_m}} \tag{14}$$

where

$$b = \Delta H_{(q/Z,\mathrm{PD_m})}\ /\ 2.303\ R\ \log\alpha_{\mathrm{PD_m}}$$

i.e. b is the linear slope of the plot of q/Z *vs.* $1/T$ of Eq. (12).

Equation (14) shows that the general adsorption heat is a linear function of the logarithm of the equilibrium activity of the solute in the bulk solution under the foregoing conditions. The significance of Eq. (14) is that, on the one hand, $\Delta H_{(\mathrm{P_a})}$ corresponding to the individual activity of the solute can be calculated from the data on different isotherms in a given system. At the same time, the fraction $\Delta H_{(q/Z,\mathrm{PD_m})}$ may also be considered. By comparing Eqs (14) and (13), we have

$$\Delta H_{(q/Z,\mathrm{PD_m})} = 2.303\ R\ b\ \log\alpha_{\mathrm{PD_m}} \tag{15}$$

On the other hand, the adsorption heat, $\Delta H_{(P_a)}$, derived from direct calorimetry may be divided into the two fractions $\Delta H^{o}_{(P_a)}$ and $\Delta H_{(q/Z,PD_m)}$, from which we can obtain more accurate information about the adsorption dynamics by plotting $\Delta H_{(P_a)}$ *vs.* $\log\alpha_{PD_m}$ in Eq. (14).

Experimental

Instruments and reagents

The Versatile Precision Semiconductor Calorimetric System [3] (made in the Thermal Chemistry Lab, Northwest University, Xi'an, China) uses a specially designed calorimetric unit: a precision environmental temperature controller (25±0.0001°C) is implemented by a microcomputer system.

1-Methyl-1'-(γ-sulfopropyl)-2,2'-cyanine (synthesized in the Photochemistry Lab, Northwest University, Xi'an, China) was recrystallized in ethanol-isopropynol (10:1, v/v), kept at 65±0.1°C for 2 h until constant weight, and was proved by DSC analysis to contain no detectable impurities.

AgBr suspensions were made in this laboratory with the double pouring method [4].

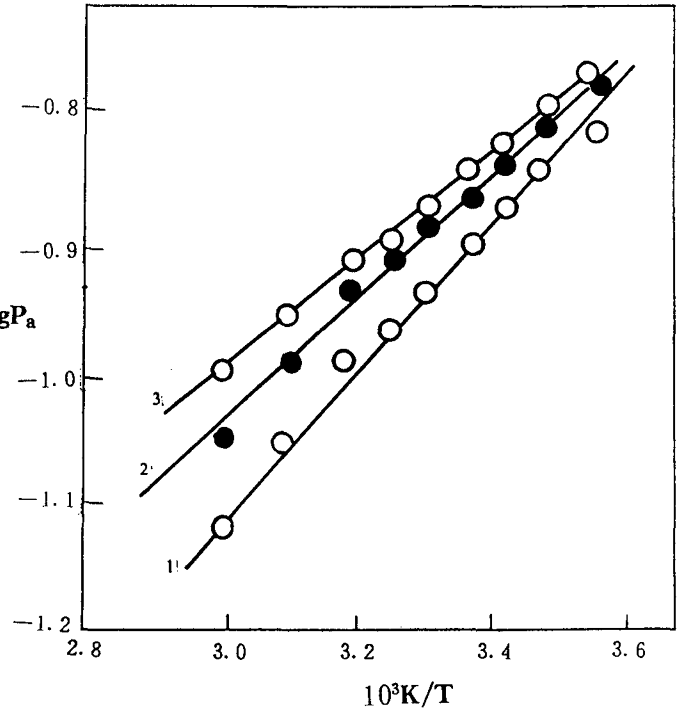

Fig. 1 Relationship between $\log P_a$ and $1/T$ for the system [6] *n*-heptane-EtOH/Graphon I. (1): 0.78 mol·dm^{-3}; (2): 2.14 mol·dm^{-3}; (3): 2.33 mol·dm^{-3}

N,N-Dimethylformamide (DMF) was of analytical grade.

Procedure

All calorimetric procedures were the same as reported previously [5].

Results and discussion

Calculations concerning $\Delta H_{(P_a)}$ and its fractions

In this study, when $\Delta H_{(P_a)}$ and its fractions $\Delta H_{(\beta_\alpha)}$ and $\Delta H_{(q/Z,PD_m)}$ are calculated with adsorption data from published works [6, 7] in which only dilute solutions are involved, the adsorption on each solid from the dilute solution is referred to as one from an ideal solution, and the adsorption layer thus formed is also treated as an ideal one in the data analysis. All data in this study were handled on a personal computer.

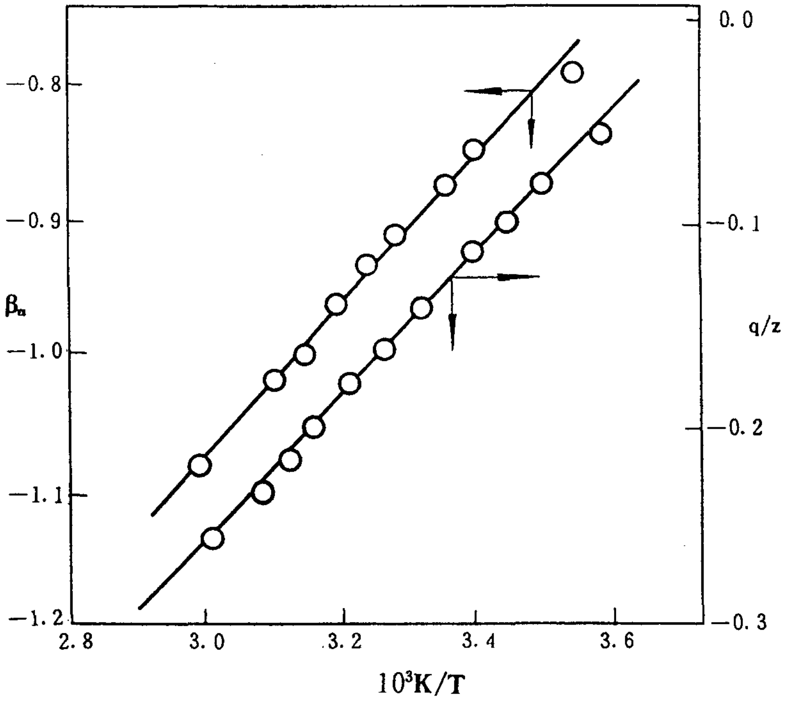

Fig. 2 Relationships between β_α, q/Z and $1/T$ for the system [6] *n*-heptane-EtOH/Graphon I

It is easy to obtain $\Delta H_{(\beta_\alpha)}$ and $\Delta H_{(q/Z,PD_m)}$ corresponding to $\Delta H_{(P_a)}$ from the linear slopes by plotting β_α and q/Z calculated from Eq. (1) *vs.* $1/T$ in a fixed concentration according to Eqs (11) and (12), respectively. On the basis of Eq. (13), the values of the two are added, corresponding to the individual concentrations. All results are listed in Table 1. In order to elucidate the reliability obtained from the linear plots of $\log P_a$, β_α and q/Z *vs.* $1/T$, respectively, plots for the system, *n*-heptane-ethanol/Graphon I, are shown in Figs 1 and 2. It is seen that all of these linear relationships are accurate in the two Figures, and the values of $\log P_a$, β_α and q/Z decrease with increase of temperature, which conforms to the well-known rule that the adsorbed amount decreases with increase of temperature, and shows that the proportions of solvent molecules desorbed from an adsorbent surface increase or, on the contrary, from PD_m molecules decrease.

Table 1 The calculated total adsorption heat and its fractions (kJ·mol^{-1})*

Adsorption systems	C /mol·dm^{-3}	$\Delta H_{(\beta_\alpha)}$	$\Delta H_{q/Z,PD_m)}$	$\Delta H_{(P_a)}$
	0.781	–10.1±0.2	–0.65±0.01	–10.8±0.2
n-Heptane–EtOH /Graphon I	1.36		0.81±0.02	–9.3±0.2
(282~333 K)	2.33		2.22±0.04	–7.9±0.2
	0.220	–3.62±0.07	–1.54±0.03	–5.16±0.10
EtOH–water /Graphon II	1.17		0.160±0.00	–3.46±0.07
(298~338 K)	1.52		0.43±0.01	–3.19±0.08
	2.56		0.95±0.02	–2.67±0.09
	4.89		1.60±0.03	–2.02±0.01

*The initial adsorption data were taken from the literatures [6, 7]

Table 1 shows that all values of $\Delta H_{(P_a)}$ are negative, demonstrating that adsorption heat deduced in this paper is a generally exothermic process, and that the absolute values of $\Delta H_{(P_a)}$ decrease with increase of the equilibrium concentration in the bulk solution. This is because a gradual decrease in the number of 'mean active sites' [8] distributed on the adsorbent surface leads to a decrease in the adsorption affinity enthalpy per molar adsorbate, which agrees with the general rule that the adsorption heat falls with increase in the adsorption equilibrium concentration.

In the two energy fractions of the calculated $\Delta H_{(P_a)}$ as listed in Table 1, $\Delta H_{(\beta_\alpha)}$ is a negative constant, much larger than $\Delta H_{(q/Z,PD_m)}$. This indicates that the adsorption affinity enthalpy between the adsorbate and the adsorbent makes the main contribution to the total adsorption heat $\Delta H_{(P_a)}$, and that the values of $\Delta H_{(q/Z,PD_m)}$ increase with increase of the equilibrium concentration of the adsorbate in the bulk solution. It suggests that the solvent desorption changes similarly as $\Delta H_{(q/Z,PD_m)}$, and the induction agrees well with the experimental result.

Reallocation of direct calorimetry for adsorption

Considering the calorimetric data of adsorption at different concentrations (restricted to dilute solutions) as $\Delta H_{(\mathrm{P_a})}$, according to the linear relationship between $\Delta H_{(\mathrm{P_a})}$ and $\log\alpha_{\mathrm{PD_m}}$ in Eq. (14), we can obtained $\Delta H_{(\beta_\alpha)}$ (or $\Delta H^{\circ}_{(\mathrm{P_a})}$) from the intercept and $\Delta H_{(\mathrm{q/Z,PD_m})}$ from the slope. The calorimetric data on the adsorption and their fractions for 1-methyl-1'-(γ-sulfopropyl)-2,2'-cyanine adsorbed from DMF by AgBr suspensions at 25±0.0001°C are listed in Table 2. The linear correlation coefficient for the foregoing system, based on Eq. (14), is 0.9714. It is clear in Table 2 that $\Delta H^{\circ}_{(\mathrm{P_a})}$ is −80.0 $\mathrm{kJ \cdot mol^{-1}}$ and exothermic making a main contribution to the total adsorption heat, while $\Delta H_{(\mathrm{q/Z,PD_m})}$ is positive (endothermic) and increases with increase of the concentration of the cyanine dye, much less than $-\Delta H^{\circ}_{(\mathrm{P_a})}$. This suggests that the desorption of DMF molecules from the surface of AgBr suspensions and from the solvolyte of molecules of the cyanine dye is weaker than the adsorption of the cyanine dye molecules onto the surface of AgBr suspensions. However, it may produce a significant error to use the adsorption heat ($\Delta H_{(\mathrm{P_a})}$) instead of the accurate adsorption affinity enthalpy ($\Delta H^{\circ}_{(\mathrm{P_a})}$). Unfortunately, not enough attention has been paid to the problem raised in this paper.

Table 2 The measured adsorption heat $\Delta H_{(\mathrm{P_a})}$ for cyanine dye adsorbed from DMF on AgBr surface at 25°C and the calculated fractions ($\mathrm{kJ \cdot mol^{-1}}$)

C /10^{-3} $\mathrm{mol \cdot dm^{-3}}$	$\Delta H_{(\mathrm{P_a})}$	$\Delta H^{\circ}_{(\mathrm{P_a})}$	$\Delta H_{(\mathrm{q/Z,PD_m})}$
24	−65.7	−80.0	14.3
149	−57.3		22.7
555	−54.8		25.2
627	−52.3		27.7
688	−50.6		29.4
863	−49.8		30.2
1132	−46.9		33.1

It should be pointed out that it is very useful to calculate the two fractions of $\Delta H_{(\mathrm{P_a})}$ obtained from the direct calorimetric data for adsorption that are considered to be most reliable. This is equivalent to indirectly measuring the two accurate fractions corresponding to an exothermic process (adsorption) and an endothermic one (desorption) from only one precise $\Delta H_{(\mathrm{P_a})}$. Moreover, the values of desorption enthalpy, $\Delta H_{(\mathrm{q/Z,PD_m})}$, and the total adsorption heat corresponding to the equilibrium concentrations in the bulk solution (also restricted to dilute solutions) may be calculated according to Eq. (14) from several (of course, not less than three) independent direct calorimetric data. Therefore, the reallocation of direct calorimetric data for adsorption is very helpful towards an understanding of the details of the entire adsorption process and of finding a new approach in investigations of the adsorption mechanism.

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Zusammenfassung — Für die Adsorption eines gelösten Stoffes in einem Flüssigkeit-Feststoffsystem wurde die Adsorptionswärme des stöchiometrischen Verdrängungsprozesses untersucht. Auf der Grundlage von SDM-A und der Additivität der Energie wurde ein Ausdruck erstellt, welcher die Abhängigkeit der Adsorptionsenthalpie von Art und Konzentration des gelösten Stoffes sowie von Lösungsmittel und Adsorbent beschreibt. Die für den gelösten Stoff mittels der herkömmlichen Methode bestimmte Adsorptionswärme kann in zwei unabhängige Teile gespalten werden, die sich auf die Adsorption des gelösten Stoffes und die Desorption des Lösungsmittels beziehen. Experimentelle Angaben von sowohl den Isothermen aus Literatur als auch aus präziser Kalorimetrie wurden benutzt, um die Adsorptionswärme und ihre mittels die vorliegend gegebene Gleichung quantitativ berechneten Teile zu testen und zwischen ihnen wurde ein zufriedenstellender Grad von Konformität erhalten.