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Study on the fractions of thermodynamic function changes for both adsorption and desorption from a liquid–solid system[1,2]

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Abstract

On the basis of the thermodynamics of the stoichiometric displacement model for adsorption of a solute, two equations to calculate separately two fractions of the Gibbs free energy for the solute adsorption and the solvent desorption to be the functions of temperature and the solute activity in bulk solution, were deduced. It was found that $\Delta G_{(\beta a)}$ (the affinity Gibbs free energy change between an adsorbate and adsorbent) in any equilibrium activity of the solute, α_{PDm}, and another fraction $\Delta G_{(q/Z,\mathrm{PDm})}$ (the desorption Gibbs free energy of a solvent from an adsorbent) under the same α_{PDm}, are linear functions of temperature. When temperature is fixed, $\Delta G_{(\beta a)}$ is a constant while $\Delta G_{(q/Z,\mathrm{PDm})}$ is proportional to log α_{PDm}. The changes in enthalpy and entropy corresponding to the solute adsorption and the solvent desorption can also be derived from the plot of the foregoing calculations of $\Delta G_{(\beta a)}$ and $\Delta G_{(q/Z,\mathrm{PDm})}$ vs. thermodynamic temperatures T, respectively. Experimental data on isotherms from the literature are used to test all of the fractions of thermodynamic function changes computed quantitatively with the equations presented in this study, and a satisfactory result was obtained. © 1998 Elsevier Science B.V.

Keywords: Fractions of thermodynamic function changes; Adsorption; Desorption; Liquid–solid system

1. Introduction

The adsorption of solute by adsorbent in a liquid–solid system is actually the displacement of solute to a solvent from the adsorbent. The thermodynamic function changes calculated for the system, up to now, should be corresponding to the ones of the displacement adsorption (the whole process of adsorption) [1]. The procedure of calculation is that the standard Gibbs function change was firstly attained by extrapolation (its precision is not satisfactory), and then the standard enthalpy and entropy changes can be obtained from the extrapolated standard Gibbs function change. Since the adsorption process of a solute onto a solid surface includes, at least, two steps: the adsorption of the solute molecules by the adsorbent, and in company with the desorption of the solvent molecules from the solid surface, therefore, the calculations of the thermodynamic function changes for the foregoing two steps under the conditions of various temperatures and concentrations may prompt us to explore the rule of adsorption in liquid–solid system from the standpoint of adsorption mechanism approach deeply. That would be more significant. The stoichiometric dis-

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placement model of adsorption (SDM-A) from a liquid–solid system [2,3] basing on various interactions including the equilibria between the foregoing two steps provides a strong theoretical basis for the calculations of the two fractions discussed above.

The traditional adsorption Gibbs free energy change (denoted with $\Delta G_{(Pa)}$) may be divided into two independent fractions [4] according to the SDM-A and the rule of energy additivity. However, the result obtained is not satisfactory enough, and especially it is necessary to pursue the study on the changes in the two fractions of $\Delta G_{(Pa)}$ with temperature changes. The two fractions of $\Delta G_{(Pa)}$, the Gibbs free energy changes of both adsorption and desorption, in the literature [4] would also be improved. In addition, based on the dividing $\Delta H_{(Pa)}$ into the independent two fractions of enthalpy change by author [5], the corresponding two fractions of $\Delta H_{(Pa)}$ into the independent two fractions of enthalpy change by author [5], the corresponding two fractions of $\Delta S_{(Pa)}$ would be further deduced.

2. Theoretical

Based on the expression of the SDM-A, the two fractions, $\Delta G_{(\beta a)}$ or $\Delta G^0_{(Pa)}$ and $\Delta G_{(q/Z,\mathrm{PDm})}$, of the traditional Gibbs free energy $\Delta G_{(Pa)}$ in a liquid–solid system may be expressed as following [5], respectively,

$$\Delta G_{(\beta a)} = -2.303RT\beta_a \tag{1}$$

and

$$\Delta G_{(q/Z,\mathrm{PDm})} = 2.303RT(q/Z)\log\alpha_{\mathrm{PDm}} \tag{2}$$

where $\Delta G_{(\beta a)}$ and $\Delta G_{(q/Z,\mathrm{PDm})}$ are the changes in the adsorption Gibbs affinity energy of the solute molecules onto the adsorbent and that in the desorption Gibbs free energy change of the solvent molecules from the adsorbent, respectively. Both β_a and q/Z is separately the parameters of the SDM-A relating to the corresponding adsorption and desorption, and both become constants under the condition of a fixed temperature in a given system. The term α_{PDm} is the equilibrium activity of the solvated solute in the bulk solution.

As temperature is given, $\Delta G_{(\beta a)}$ (called also standard Gibbs free energy change, $\Delta G^0_{(Pa)}$, because of corresponding to the $\Delta G_{(Pa)}$ of α_{PDm} being 1.0) should be constant due to Eq. (1), and the $\Delta G_{(q/Z,\ \mathrm{PDm})}$ should be a linear function of the log α_{PDm} due to Eq. (2).

When temperature varies, the calculations of $\Delta G_{(\beta a)}$ and $\Delta G_{(q/Z,\mathrm{PDm})}$ may be carried out by the linear relationships between the adsorption parameters of the SDM-A, βa and q/Z, and $1/T$ [4,5], respectively. Suppose the slopes and intercepts of the foregoing two linear correlations are k and b, as well as k' and b' respectively. That is

$$\beta a = k/T + b \tag{3}$$

and

$$q/Z = k'/T + b' \tag{4}$$

Inserting Eqs. (3) and (4) into Eqs. (1) and (2), respectively, we then have

$$\Delta G_{(\beta a)} = -2.303Rk - 2.303RbT \tag{5}$$

and

$$\Delta G_{(q/Z,\mathrm{PDm})} = 2.303Rk'\log\alpha_{\mathrm{PDm}} + 2.303Rb'\log\alpha_{\mathrm{PDm}} \cdot T \tag{6}$$

Eqs. (5) and (6) indicate that the adsorption Gibbs affinity free energy change, $\Delta G_{(\beta a)}$, of the solute onto the adsorbent is a linear function of temperature, and that so is the desorption Gibbs free energy change, $\Delta G_{(q/Z,\mathrm{PDm})}$, of the solvent from the adsorbent under the condition of the same α_{PDm}.Comparing both Eqs. (5) and (6) with the thermodynamic equation

$$\Delta G = \Delta H - T\Delta S \tag{7}$$

we have

$$\Delta H_{(\beta a)} = -2.303Rk \tag{8}$$

$$\Delta S_{(\beta a)} = 2.303Rb \tag{9}$$

$$\Delta H_{(q/Z,\mathrm{PDm})} = 2.303Rk'\log\alpha_{\mathrm{PDm}} \tag{10}$$

and

$$\Delta S_{(q/Z,\mathrm{PDm})} = -2.303Rb'\log\alpha_{\mathrm{PDm}} \tag{11}$$

where the $\Delta H_{(\beta a)}$ in Eq. (8) and $\Delta S_{(\beta a)}$ in Eq. (9), should be the intercept and the slope with a negative sign, respectively, of the linear plot $\Delta G_{(\beta a)}$ vs. T. by Eq. (5), denoting the changes in the adsorption affinity enthalpy and the adsorption affinity entropy, respectively, of the solute molecules onto the adsorbent. Similarly, the $\Delta H_{(q/Z,\mathrm{PDm})}$ and $\Delta S_{(q/Z,\mathrm{PDm})}$ in

Eqs. (10) and (11) correspond separately to that by plot $\Delta G_{(q/Z,\ \mathrm{PDm})}$ vs. T according to Eq. (6). Both separately represent the desorption enthalpy and entropy changes of the solvent molecules from the adsorbent. Moreover, the relations between the foregoing fractions of the thermodynamic functions and the traditional (displacement) adsorption enthalpy and entropy changes, $\Delta H_{(Pa)}$ and $\Delta S_{(Pa)}$, are as the follows:

$$\Delta H_{(Pa)} = \Delta H_{(\beta a)} + \Delta H_{(q/Z,\mathrm{PDm})} \tag{12}$$

$$\Delta S_{(Pa)} = \Delta S_{(\beta a)} + \Delta S_{(q/Z,\mathrm{PDm})} \tag{13}$$

Obviously, an assumption similar to that in the circumstance of van't Hoff Equation concerning with both the enthalpy and entropy changes (including the general ones and the fractions equivalent to this paper) to be independent of temperature is made, so long as the changes in temperature are not too broad.

It is necessary to emphasize that because the foregoing calculations of the fractions of thermodynamic functions are based on the adsorption isotherm of the solute, the calculated accuracy depends mainly on reliability of the absolutely adsorbed amounts of both the solute and solvent onto the adsorbent, n_1^s and n_2^s, and on that of the solute activity partition coefficient in the two phases, Pa.

Because of the co-adsorption of the solute and solvent onto the adsorbent in a liquid–solid system, only an apparent (mixture) adsorption isotherm can be attained by experimental measurement. From the assumption that adsorption is just limited to a monolayer and by the apparent adsorbed amount, $n_0\,\Delta x/m$, determined from experiment, the individual component (true) adsorbed amounts of the solute and solvent, n_1^s and n_2^s, may be solved by the following equation group [6]:

$$n_0\Delta x_1/m = n_1^s(1 - X_1) - n_2^s x_1 \tag{14}$$

$$n_1^s A_1 + n_2^s A_2 = A \tag{15}$$

where x_1 denotes the molar fraction of the solute concentration in the equilibrium solution, Δx_1 shows the change in molar fraction of the solute following adsorption, n_0 is the total moles of the solution, m descripts the gram of the adsorbent, and A_1, A_2, and A are the areas occupied separated by one mole of the solute and of solvent molecules adsorbed, and by one gram of adsorbent. The assumption that A_1 and A_2 are independent of temperature in the range approached was used.

For convenience, the solute activity on the surface phase and that in the bulk solution are regarded with the corresponding concentration [2,3], and then the solute activity partition coefficient, Pa, may be simply expressed as

$$Pa = C_1^s/C_1^{\prime} \tag{16}$$

where C_1^s and $C_1^{\prime}$ denote the mole concentration of the solute on the surface phase and the one in the bulk solution, respectively. Although the strict calculation of the C_1^s should be made by the adsorbed layer volume or thickness, we have not found any reliable treatment method (the attempting approaches are various, and the results of them differ considerably from each other) in literature being available here. In this approach, supposing the adsorbed layer to be an ideal one, we have

$$\begin{aligned} C_1^s &= 1/(V_1 + V_2 n_2^s/n_1^s) \\ &= 1/(M_1/\rho_1 + M_2 n_2^s/\rho_2 n_1^s) \end{aligned} \tag{17}$$

where M, ρ, and V denote the molar mass, the density, and the molar volume, respectively, and the subscripts "1" and "2" separately show the solute and solvent.

As using Eq. (16), the solute concentration in bulk solution, $C_1^{\prime}$, should be molar concentration instead of molar fraction, and the conversion between them can be carried out by Eq. (18).

$$C_1^{\prime} = 1/[M_1/\rho_1 + M_2(1 - x_1)/x_1\rho_2] \tag{18}$$

Inserting Eqs. (17) and (18) into Eq. (16), we can calculate the solute partition coefficients, Pa, at various temperatures and in different concentrations.

The other two adsorption parameters, β_a and q/z, in a given temperature may be obtained by the intercept and the slope of the linear plot logPa vs. logα_{PDm} with the expression of the SDM-A [2,3]

$$\log Pa = \beta a - q/Z \cdot \log\alpha_{\mathrm{PDm}} \tag{19}$$

Further with Eqs. (1), (2) and (6) to combine with Eqs. (8)–(11), we can obtain the aim to attain all the fractions of thermodynamic function changes at various temperatures and in different concentrations, we need.

3. Results and discussion

The adsorption data taken from literature [7,8] were used for calculating in the paper. However, only four adsorption systems, ethanol–water/Graphon II, benzene–ethanol/Graphon I, heptane–ethanol/Graphon I and methanol–water/Graphon II, can be used for this study for the following two reasons. Firstly, the experimental works are very onerous, because it needs to get a lot of very dense experimental data at various temperatures, in which only very few of them are suitable for our using. Secondly, the available data obtained only under the conditions of the equilibrium concentrations of solute at various temperatures must be identical. Moreover, due to the assumption of the literature [3,5], the data adsorbed should be carried out from dilute solution. In order to make the calculated results be systemic and explicit, the calculation and discussion in the paper mainly focus on the one of the four adsorption systems, ethanol–water/Graphon II. The other three systems have similar behaviors to that of this system we chose, and therefore we did not discuss them in this paper. Also, the used assumption that the solute activity coefficients in both solid and liquid phases are regarded as unity was carried out in this paper. Thus the solute concentrations were to be instead of activities in this study, and it was proved to be well in the published papers [2–5].

3.1. Solute activity partition coefficient Pa

The correct and quantitative calculations of $\Delta G_{(\beta a)}$ and $\Delta G_{(q/Z,\ \mathrm{PDm})}$ under the conditions of different temperatures and various concentrations studied depend, as shown in Eqs. (1) and (2), on the reliability of the linear adsorption parameters, βa and q/z. Thus, a satisfactorily linear correlation coefficient, r, for the plot of $\log Pa$ vs. $\log \alpha_{\mathrm{PDm}}$ by Eq. (19) must be required. It is vital for obtaining the reliability of the βa and q/z to precisely determine the solute activity partition coefficient, Pa, and the corresponding concentration in bulk phase, C_1^l (or α_{PDm}).

The Pa values calculated with Eqs. (14)–(18) for the initial isotherm of the system [8], ethanol(1)–water(2)/GraphonII, in various dilute concentrations at 298 K were listed in Table 1. The more parameters used here should be required to obtain more accurate calculations later. Table 1 indicates that the Pa values decreases with the increase in C_1^l. The same calculations under various temperatures (308 to 348 K) were also done and the obtained results (not listed here) were very similar to that at 298 K. In Table 2, it is obvious that the two typical adsorption parameters, q/Z and βa, of the SDM-A from the plot of $\log Pa$ vs. $\log(C_1^l/\mathrm{mol{\cdot}dm^{-3}})$ have a satisfactory reliability with the linear correlation coefficients from -0.9957 to -0.9994 for the corresponding six temperatures.

3.2. Fractions of Gibbs free energy changes, $\Delta G_{(\beta a)}$ and $\Delta G_{(q/Z,PDm)}$

The calculated $\Delta G_{(Pa)}$ and their two fractions, $\Delta G_{(\beta a)}$ and $\Delta G_{(q/Z,\mathrm{PDm})}$, varying with T and C_1^l were listed in Table 3. When temperature is fixed, the change in the adsorption Gibbs (affinity) free energy of the solute, $\Delta G_{(\beta a)}$, is a constant. The values of $\Delta G_{(\beta a)}$ in the range of 298 K to 348 K are all great with negative sign. This deeply implies that $\Delta G_{(\beta a)}$ is

Table 1
The calculation of adsorption equilibrium partition coefficients Pa for ethanol of the ethanol(1)–water(2)/Graphon II system [(a)] at 298 K [(b)]

X_1	$n_0\Delta x_1/m$	C_1^l	$10^3 n_1^s$	$10^3 n_2^s$	C_1^s	Pa
	10^{-4} mol g^{-1}	mol dm^{-3}	mol g^{-1}	mol g^{-1}	mol dm^{-3}	
0.022	4.343	1.150	0.4654	0.9498	10.30	8.956
0.029	6.646	1.494	0.5035	0.8364	11.09	7.423
0.051	4.776	2.510	0.5420	0.7213	11.88	4.733
0.106	4.607	4.686	0.5855	0.5917	12.77	2.725
0.145	4.128	5.979	0.5839	0.5963	12.73	2.129

[(a)] The initial adsorption data in the left two colums were taken from the literature [8].

[(b)] The other parameters for the calculations used to Eqs. (14)–(18) are as following: $A_1 = 17.9$ Å^2 molecule^{-1} [6], i.e. 10779 m^2 mol^{-1}, $A_2 = 6.0$ Å^2 molecule^{-1}, i.e. 36132.3 m^2 mol^{-1}(calculated from the diameter of water molecule [9]), $A = 84.5$ m^2 g^{-1} [8], $\rho_1 = 0.78524$ kg dm^{-3} (298 K) [10] and $\rho_2 = 0.99707$ kg dm^{-3} (298 K) [10].

Table 2
The linear parameters by plot of log*Pa* vs. log(C_1'/mol dm^{-3}) for the ethanol(1)-water(2)/Graphon II system [(a)]

T/K	*r*	−slope(or *q*/*Z*)	intercept(or *βa*)
298	−0.9994	0.873	1.02
308	−0.9991	0.869	1.01
318	−0.9988	0.863	0.998
328	−0.9985	0.857	0.990
338	−0.9975	0.850	0.981
348	−0.9957	0.841	0.970

(a) The values of C_1' are as same as that in Table 1.

the "driving force" for the spontaneous process in the traditional adsorption one. It is because that although the values of the desorption Gibbs free energy changes, $\Delta G(q/z,\mathrm{PDm})$, may be positive under the condition of the C_1', varying at a fixed temperature, the $\Delta G_{(Pa)}$ (the parenthetic data listed in Table 3) are still negative. The fact that the values of $\Delta G_{(q/Z,\mathrm{PDm})}$ are positive, shows that the desorption of the solvent molcules from the adsorbent is not spontaneous process alone. The occurrence of the displacement of the solvent molecules by the solute molecules should be attributed to the called "driving force" mentioned above. The trend for both of the increase in the $\Delta G_{(q/Z,\mathrm{PDm})}$ and the decrease in the negative $\Delta G_{(Pa)}$ with C_1' increasing suggests the well known rule that the solute adsorption onto the adsorbent dominates over the displacement adsorption at the beginning of it, because of the preferential occupation of the active sites distributed on the adsorbent surface by the adsorbate molecules. With the increase in the surface coverage of the adsorbate molecules, the number of empty active sites decreases gradually, so does the adsorbate molecule affinity (adsorption) onto the adsorbent surface. And, on the contrary, the desorption of the solvent molecules from the adsorbent surface increases relatively, at last, the displacement adsorption reaching into equilibrium between the adsorption and desorption (stopping in the sight of macrograph).

The $\Delta G_{(\beta a)}$ values listed in Table 3 become more negative with increase of temperature. This indicates that the affinity of the adsorbate molecules onto the adsorbent is getting stronger. It may be explained that the activation energy of adsorption decreases with the increase in temperatures. On the contrary, as the equilibrium concentration of the adsobate in the bulk solution is fixed, the $\Delta G_{(q/Z,\mathrm{PDm})}$ values would

Table 3
The total Gibbs free energy changes $\Delta G_{(Pa)}$ and their fractions for the ethanol(1)-water(2)/Graphon II system

T/K	$\Delta G_{(q/Z,\mathrm{PDm})}$ and $\Delta G_{(Pa)}$ ^{a}/kJ mol^{-1}					$\Delta G_{(\beta a)}$ kJ mol^{-1}
	C_1'/mol dm^{-3}					
	1.15	1.49	2.51	4.69	5.98	
298	0.304	0.870	1.99	3.34	3.87	−5.80
	(−5.50)	(−4.93)	(−3.81)	(−2.46)	(−1.93)	
308	0.313	0.895	2.05	3.44	3.98	−5.95
	(−5.64)	(−5.06)	(−3.90)	(−2.51)	(−1.97)	
318	0.321	0.917	2.10	3.53	4.08	−6.08
	(−5.76)	(−5.16)	(−3.98)	(−2.55)	(−2.00)	
328	0.329	0.940	2.15	3.61	4.18	−6.22
	(−5.89)	(−5.28)	(−4.07)	(−2.61)	(−2.04)	
338	0.336	0.960	2.20	3.69	4.28	−6.35
	(−6.01)	(−5.39)	(−4.15)	(−2.66)	(−2.07)	
348	0.342	0.978	2.24	3.76	4.36	−6.47
	(−6.13)	(−5.49)	(−4.23)	(−2.71)	(−2.11)	
298∼	0.16 ^{b}	0.43 ^{b}	0.98 ^{b}	1.64 ^{b}		3.61 ^{b}
348 ^{b}	(3.77) ^{b}	(4.04) ^{b}	(4.59) ^{b}	(5.25) ^{b}		
	1.17 ^{c}	1.52 ^{c}	2.56 ^{c}	4.86 ^{c}		

(a) The data in parentheses represent the values of $\Delta G_{(Pa)}$, the sums of $\Delta G_{(\beta a)}$ and $\Delta G_{(q/Z,\ \mathrm{PDm})}$. (b) The corresponding results obtained by the literature [4]. (c) The values of C_1' calculated by the literature [4] with as the identically initial adsorption data as this paper.

Table 4
The total displacement adsorption enthalpy and entropy changes, $\Delta H_{(Pa)}$ and $\Delta S_{(Pa)}$, as well as their fractions within 298–348 K for the ethanol(1)–water(2)/Graphon II system

C'_1	$\Delta S_{(q/Z,\ \mathrm{PDm})}$	$\Delta H_{(q/Z,\mathrm{PDm})}$	$\Delta S_{(\beta a)}$	$\Delta H_{(\beta a)}$	$\Delta S_{(Pa)}$	$\Delta H_{(Pa)}$
mol dm^{-3}	J mol^{-1} k^{-1}	kJ mol^{-1}	J mol^{-1} k^{-1}	kJ mol^{-1}	J mol^{-1} k^{-1}	kJ mol^{-1}
1.15	−0.763	0.0776	13.4	−1.81	12.6	−1.73
1.49	−2.16	0.227	13.4	−1.81	11.2	−1.58
2.51	−5.00	0.506	13.4	−1.81	8.40	−1.30
4.69	−8.37	0.856	13.4	−1.81	5.03	−0.954
5.98	−9.86	0.939	13.4	−1.81	3.54	−0.871

increase with the increase in temperature, i.e. the required energy for the desorption of the solvent molecules from the adsorbent surface becomes greater. However, as far as the whole displacement adsorption process is concerned, the total Gibbs free energy, $\Delta G_{(Pa)}$, is still negative, so that the process could proceed well. All these indicate that the $\Delta G_{(Pa)}$ and its two fractions deduced in this paper can more successfully elucidate a lot of experimental facts.

It is important to pay attention to the advantage that the calculations of $\Delta G_{(\beta a)}$ and $\Delta G_{(q/Z,\mathrm{PDm})}$, as similar as that of $\Delta H_{(Pa)}$ and its fractions, $\Delta H_{(\beta a)}$ and $\Delta H_{(q/Z,\mathrm{PDm})}$, in the previous paper [5] and as that of $\Delta G_{(Pa)}$ [11], do not restrict to that how many experimental points must be required for the adsorption isotherms. As long as the calculations obey some resticted conditions (i.e. dilute solution and not too wide temperature range), any fractions in various concentrations and temperatures may be obtained according to Eqs. (1) and (2). This definitely indicates a significant advance for the calculation of adsorption thermodynamic functions in liquid–solid system.

In order to compare the calculated results of this paper with that of the literature [4] for the same system, the latter were simultaneously listed at the bottom of Table 3 also. It is clear that the calculations of the functions of Gibbs free energy in various temperatures were developed in this approach, and the result obtained in this paper is more meticulous and more accurate than that of the literature [4], because the positive $\Delta G_{(\beta a)}$ and $\Delta G_{(Pa)}$ values in latter seem to be contrary to the well-known experimental fact. The reason is that with the calculations of several adsorption parameters, C'_1, n^s_1, n^s_2 and C^s_1 in this study (as shown in Table 1), the solute activity partition coefficient Pa can be attained precisely.

3.3. *Fractions of enthalpy and entropy change*

The calculated fractions of the enthalpy and entropy changes and their individual sums, $\Delta H_{(Pa)}$ and $\Delta S_{(Pa)}$, in the range of 298–348 K for the foregoing system were listed in Table 4. The fractions of the desorption enthalpy and entropy changes, $\Delta H_{(q/Z,\mathrm{PDm})}$ and $\Delta S_{(q/Z,\ \mathrm{PDm})}$, in a fixed concentration and that of the adsorption ones, $\Delta H_{(\beta a)}$ and $\Delta S_{(\beta a)}$, are separately obtained from the intercept and slope by the linear plots, $\Delta G_{(q/Z,\mathrm{PDm})}$ and $\Delta G_{(\beta a)}$ (in Table 3) separately vs. T by Eqs. (6) and (5), respectively. It is seen that all of these linear relationships, as shown in Fig. 1, are

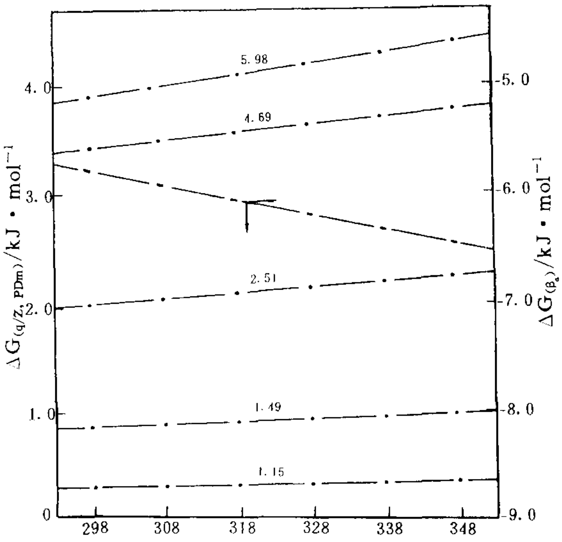

Fig. 1. The linear relationships between $\Delta G_{(\beta a)}$, $\Delta G_{(q/Z,\ \mathrm{PDm})}$ and T for the ethanol(1)–water(2)/Graphon II system. The lines marked by digits, which indicate the ethanol concentrations C'_1/mol dm^{-}3, represent the relationships between $\Delta G_{(q/Z,\ \mathrm{PDm})}$ and T.

satisfactory. This demonstrates that, on the one hand, Eqs. (5) and (6) are linear equations for temperature T, and with this it is easy to deduce the idea pointed out in the previous paper [11]. That is a good linear relationship between the general (total) adsorption Gibbs free energy change $\Delta G_{(Pa)}$ and Texists under the foregoing conditions. On the other hand, the accurate linear relationships suggest that the all mentioned fractions of thermodynamic function changes obtained in this paper are very reliable.

Table 4 shows that within 298–348 K, the values of the $\Delta H_{(\beta a)}$ (or $\Delta H^0{}_{(Pa)}$) are negative and that the values of the $\Delta H_{(q/Z,\ \mathrm{PDm})}$ under various concentrations C_1' are all positive and increasing with the increase in the C_1'. This rule agrees entirely with the recently reported results of the adsorption enthalpy changes for the three systems, *n*-Heptane–EtOH/Graphon I (282–333 K), EtOH–Water/Graphon II (298–338 K) and Cyanine dye-DMF/AgBr(298 K) [5]. This proves again the well-known rules that the adsorbate affinity acting onto the adsorbent is exothermic while the solvent desorption from the adsorbent is endothermic, and latter increases with the increase in C_1'. Moreover, the total displacement adsorption enthalpy $\Delta H_{(Pa)}$, i.e. the sum of $\Delta H_{(\beta a)}$ and $\Delta H_{(q/Z,\ \mathrm{PDm})}$, is a less absolute value than $\Delta H_{(\beta a)}$, and the negative values of the $\Delta H_{(Pa)}$ decrease with the increase of the C_1'. This conforms well with the standpoint reported recently [5,11] that the traditionally general adsorption is exothermic and that the extremely high active sites on the adsorbent surface are prior to be occupied, if the adsobate is in a lower concentration in the bulk solution [5].

We can not obtain a general rule for either the total entropy changes $\Delta S_{(Pa)}$ or their fractions depending on the solute concentration and temperature, because of their complexity. Since the values of $\Delta S_{(Pa)}$ for a given adsorption system may be positive or negative [12], the action of the adsorption affinity should be attributed to either the "enthalpy driving" (the value of $\Delta S_{(\beta a)}$ may be negative or less positive) or the "entropy driving" (that must be much larger positive value). The entropy change of adsorption affinity $\Delta S_{(\beta a)}$ for ethanol onto the Graphon II surface, as shown in Table 4, equals to 13.4 J mol^{-1} K^{-1}(entropy increase), and the desorption entropy changes $\Delta S_{(q/Z,\ \mathrm{PDm})}$ of water from the Graphon II surface under various concentrations of bulk solution are all negative (entropy decrease), and the values of negative $\Delta S_{(q/Z,\mathrm{PDm})}$ increase with increase of C_1' (entropy decrease becomes more intensive). However, the corresponding general entropy changes of the displacement adsorption $\Delta S_{(Pa)}$ are all positive and decrease with the increase in C_1'. Because the factors effecting on those changes mentioned above should include the entropy from the changes in the configuration due to its localized adsorption, the possibly existed both surface vibration entropy due to the mobile adsorption and the contributions from a loss in rotational entropy on adsorption, and from the changes in the adsorbent structure following adsorption [13], we can not attempt to explicate briefly the displacement adsorption entropy and its two fractions. In spite of this, it is obvious for the system (298–348 K) used in this paper that the negative $\Delta H_{(\beta a)}$ to be 1.81 kJ mol^{-1} listed in Table 4 is much less than that of the negative $\Delta G_{(\beta a)}$ ranging from 5.80 to 6.47 kJ mol^{-1} in various C_1' shown in Table 3, and therefore the system belongs to entropy driving.

4. Conclusion

Based on the equations presented in the paper, the calculations of the adsorbate affinity Gibbs free energy of an adsobate onto an adsobent, $\Delta G_{(\beta a)}$, and that of a solvent desorption from the adsorbent, $\Delta G_{(q/Z,\ \mathrm{PDm})}$, can be accomplished under various adsorbate concentration in bulk solution and different temperatures (within proposed condition). These equations can be used for estimating ΔG of displacement adsorption beyond the traditional restriction of standard state and for developing the calculations of literature [4]. It was discovered that the values of $\Delta G_{(\beta a)}$ in any equilibrium activity of the solute, α_{PDm}, and that of $\Delta G_{(q/Z,\mathrm{PDm})}$ at an identical α_{PDm} are both linear functions with temperature; at a same temperature, $\Delta G_{(\beta a)}$ is a constant while the variation of $\Delta G_{(q/Z,\mathrm{PDm})}$ with the logarithms of α_{PDm} shows a linear relationship. The corresponding fractions of the changes in the both enthalpy and entropy may be obtained by the plots of $\Delta G_{(\beta a)}$ and $\Delta G_{(q/Z,\ \mathrm{PDm})}$ vs. T, respectively. The rules for the fractions of all thermodynamic functions calculated in this paper are all good, and the elucidation of them is rather satisfactory except the entropy fractions for its more complexity.

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