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A quantitative relationship between the affinity of component to adsorbent in liquid–solid system, β_a, and composition of bulk solution

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Abstract

Based on the stoichiometric displacement theory for adsorption (SDT-A) of solute, an equation expressing the linear relationship between the affinity of component to adsorbent, β_a, and the logarithm of the molar concentration of solvent in the bulk solution, $\log a_D$, was derived. The derived equation was tested by the derivatives of benzene under different methanol concentrations by frontal analysis (FA) of reversed-phase liquid chromatography (RPLC). A satisfactory result was obtained. Moreover, the n and q terms' values (moles of the solvent separately released from the adsorbent and solute, respectively, as 1 mol of solute is adsorbed) which are summed in the stoichiometric parameter Z ($Z = n + q$), are very useful but hard to obtain only by RPLC alone. However, both were obtained from this relationship and tested with the presented method. It was also examined by the combination of the SDT-A with stoichiometric displacement theory for retention (SDT-R). Both n and q were further validated to follow the homologue rule. More solvent was released by adsorbent than by solute ($n > q$) and the fraction of solvent released by the adsorbent increased when the group attached to benzene was nonpolar.

Keywords: Stoichiometric displacement theory; Adsorption affinity energy; Fractions of stoichiometric displacement parameter; Bulk composition; Homologue rule

1. Introduction

The adsorption mechanisms of liquid–solid systems are more complex than that in gas–solid systems. Because in liquid–solid systems, in addition to the complexity of solid structure and surface characteristics, the adsorption mechanisms are also related to the interactions between solutes and solvents in solutions. In practice, the theoretical models derived for gas–solid adsorption have been empirically used to explain liquid–solid adsorption. However, as these equations were originally derived only for gas–solid adsorption systems, they have not been related to the strong interactions that exist among the solute, solvent and solid adsorbent in a liquid–solid adsorption process [1]. So a model describing the quantitative relationship should include three main variable amounts, that is the solute, solvent, and adsorbed amount of solute under the condition of a given adsorbent in the liquid–solid systems. Generally, the effects of solvent on the adsorption isotherm are not included in a liquid–solid adsorption model. For example, Langmuir's equation [2] is very popular but does not describe solvent effects.

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The extended Langmuir isotherm reported by Pineiro et al., utilized volume fractions but did not use the volume of the solvent as a variable [3]. Geng et al., considered all the kinds of interaction among solute, solvent, and absorbent, and derived another extended Langmuir equation [4], which elucidates the effects of solvent concentration on the adsorbed amount in liquid–solid systems. But it is very complex. In a previous paper [5], a new adsorption isotherm that relates the amount of solute adsorbed to the solvent concentration was proposed, but it was required that the concentration of solute be kept constant.

The parameter, β_a of stoichiometric displacement theory for adsorption (SDT-A) [6], denoting the affinity of component to adsorbent, is dependent on the properties of solute and solvent, but independent of the concentration of solute. Furthermore, from the definition of β_a, we may speculate that the β_a value would be influenced by the solvent concentration. This result has been experimentally found by Bian and Geng [7] from the adsorption of protein on hydrophobic interface in an aqueous salt solution. But the theoretical derivation was not given. In this article, based on SDT-A, an equation expressing the relationship between β_a, and the concentration of solvent in the bulk solution, is first derived. The derived equation was tested by the derivatives of benzene under different methanol concentrations by frontal analysis (FA) and usual high-performance reversed-phase liquid chromatography (RPLC).

In addition, the stoichiometric parameter Z of the SDT is a very useful parameter employed in many fields [8–10], such as a new characterization parameter for changes in the molecular conformation of proteins [11,12], the molecular structure of solute, the characters of the displacing agent in mobile phase and stationary phase used, and the separation selectivity of solutes in RPLC [13,14]. The parameter Z consists of two parts, n and q (moles of the solvent separately released from the adsorbent and solute, respectively, as 1 mol solute is adsorbed). If the two parts can be measured separately, it will be very useful to understand intensively the adsorption process of solute at the interface of solid–liquid in detail. But the exact values of n and q have not been obtained only by RPLC alone. In this article, n and q will be measured by using the quantitative relationship between β_a and the concentration of solvent in the bulk solution.

2. Theory

2.1. Theoretical basis of measuring β_a

The expression of SDT-A [6] is,

$$\log a_{P\bar{L}_n D_{(m-q)}} = \beta_a + \frac{n}{Z} \log a_{PD_m} \tag{1}$$

where, $a_{P\bar{L}_n D_{(m-q)}}$ is the solute concentration adsorbed on the adsorbent, a_{PD_m} denotes the solute concentration in bulk solution, β_a, which is a measure of the affinity of the solute to the adsorbent, is a constant, n the moles of the solvent originally adsorbed on the contact surface between 1 mol of solute and the adsorbent, Z represents the total moles of the solvent released or adsorbed for 1 mol solute together with its corresponding contact area on the adsorbent surface during the adsorption or desorption process, $Z = n+q$, q is the released number of solvent molecules from the solute as 1 mol of the solute molecule is adsorbed to the adsorbent. All of β_a, n, Z, and q are constants for the given conditions.

Eq. (1) is the mathematical expression of the SDT-A. It may be described as the logarithm of the adsorbed amounts of solute to be proportional to the logarithm of the equilibrium concentration of solute in solution. The fact that the slope is always less than unity verifies that the ratio of the mole of solvent molecules desorbed from solvated adsorbent to the total moles of the desorbed solvent molecules from both the solvated solute and solvated adsorbent must be less than one.

Plotting $\log a_{P\bar{L}_n D_{(m-q)}}$ versus $\log a_{PD_m}$, a straight line with slope n/Z, and intercept β_a will be obtained.

2.2. Derivation of the relationship between β_a versus $\log a_D$

The definition of β_a is,

$$\beta_a = \log K_a + n \log K'_d \tag{2}$$

where K_a is the general thermodynamic equilibrium constant of the stoichiometric displacement process for solvated solute displacing solvent from both solute and adsorbent upon adsorption, K'_d the partition coefficient of solvent in liquid–solid phase, a_D stands for the solvent activity in the bulk solution, K_a is constant in the given conditions, and the physical meaning of n value was described above. Geng and Shi argued by analogy between the partition coefficients of solute and solvent in discovering the definition [6,15].

K'_d can be described as,

$$\log K'_d = \log \frac{\sum a_D(\text{adsorbent})}{\sum a_D(\text{bulk})} \quad (3)$$

Solvent exists in the two forms, $\bar{L}D$ (ligand–solvent complex) and $P\bar{L}_nD_{(m-q)}$ (ligand–solute–solvent complex) on the adsorbents. Solvent exists also in the two forms in the bulk solution, D (free solvent molecules) and PD_m (solute–solvent). Eq. (3) can be written as,

$$\log K'_d = \log \frac{a_{LD} + a_{P\bar{L}_nD_{(m-q)}}}{a_D + a_{PD_m}} \quad (4)$$

If the total number of active sites, where an active site is defined as a "mean active site (MAS)" [16] being able to interact and adsorb one solvent molecule under a given experimental condition on the adsorbent surface, is denoted by a_{SD}, then, from materials balance, a_{SD} equals the sum of $a_{LD} + a_{P\bar{L}_nD_{(m-q)}}$. For a given chromatographic system, a_{SD} is a constant. Compared with the total solvent, the solute quantity is so small that the fraction of D in a_{PD_m} in solution may be ignored, namely, $a_D \gg a_{PD_m}$, hence,

$$\log K'_d = \log a_{SD} - \log a_D \quad (5)$$

Inserting Eq. (5) into Eq. (2),

$$\beta_a = \log K_a + n \log a_{SD} - n \log a_D \quad (6)$$

$$\beta_a = \log K^* - n \log a_D \quad (7)$$

where $\log K^* = \log K_a + n \log a_{SD}$. When solute and the stationary phase are given, a_{SD} and n are both constants. So K^* is also a constant. By plotting β_a versus $\log a_D$, the slope of the resulting straight line is $-n$ and the corresponding intercept is $\log K^*$.

2.3. *Validation of the relationship between β_a versus $\log a_D$*

Two ways can be employed to test Eq. (7). First, the goodness of the linearity for the plot of β_a versus $\log a_D$ and the reasonability of β_a, can be proved by the linearity of Eq. (7) [6]. Second, the reasonability of the obtained slope, denoted with n_1 from the linear plot can be proved by another way as follows.

The expression of the stoichiometric displacement theory for retention (SDT-R) is [16]

$$\log k' = \log I - Z \log a_D \quad (8)$$

By a combination of two slopes, Z from the linear plot of $\log k'$ versus $\log a_D$ shown in Eq. (8) and n/Z from another linear plot of $\log a_{P\bar{L}_nD_{(m-q)}}$ versus $\log a_{PD_m}$ shown in Eq. (1) a second n value can be obtained. The obtained n value this other way is denoted with n_2. The coincidence between n_1 and n_2 with the two methods can indicate the validation of Eq. (7).

2.4. *The parts of Z*

The parameter Z is composed of two terms,

$$Z = n + q \quad (9)$$

The term n can be obtained from the linear plot of Eq. (7), β_a versus $\log a_D$, and similarly Z from Eq. (8). So the term q can be obtained simply from Eq. (9).

3. Experimental

3.1. *Equipment*

A LC-6A liquid chromatograph system (Shimadzu Corporation, Japan) was used in the experiments. Its accessories consisted of two pumps (LC-6A), a variable wavelength UV-visible detector (SPD-6AV), a controller system (SCL-6B), a chart recorder (Dahua Instrument Corporation, Shanghai, China), and a WMZK-01 temperature indicator/controller (Medical Instrument Factory, Shanghai, China). A RPLC column (50 mm × 2 mm) was slurry packed with Lichrosorb RP-18 packing with a granularity of 10 μm (Z. Merck Darmstadt Company, Germany). Another RPLC column (50 mm × 2 mm) was slurry packed with YWG-C_6H_5 packing with a granularity of 10 μm (The Second Chemical Reagent Company, Tianjin, China).

3.2. Reagents

HPLC grade phenethyl alcohol, 3-phenyl-1-propanol, 4-phenyl-1-butanol, 5-phenyl-1-pentanol, and 6-phenyl-1-hexanol were purchased from Sigma (St. Louis, MO, USA). Analytical grades of methanol and of xylene were from Xi'an Chemical Reagent Factory. Ethylbenzene was from Beijing Chemical Engineering Factory and of chemical grade. Chlorobenzene was from the Second Chemical Reagent Factory, Tianjin, and of analytical grade. All deionized water and mobile phase were degassed by using an ultrasonic de-gasser (KQ-250, Kunshan Detection Instrument Factory, Shanghai, China).

3.3. Method

3.3.1. Determination of adsorption isotherms of solute

The method for the determination of the adsorption isotherm used in this paper is the same as in a previous paper [5].

3.3.2. Determination of Z values of solute from usual RPLC

The values of the stoichiometric parameter Z were determined by Eq. (8). All retention data of solute were determined with isocratic elution. The concentration of each mobile phase was adjusted by mixing a methanol solution with a low concentration (A) and methanol solution with a high concentration (B) by using the controller in the chromatographic system. Before the injection of a sample solution, the column was equilibrated with 20 bed volumes of a new mobile phase. The range of the capacity factors for the solute was controlled within the range of $2 < k' < 7$ by adjusting the concentration of methanol in the mobile phase.

4. Results and discussions

4.1. Adsorption isotherms of aromatic alcohol homologue and derivatives of benzene

The adsorption isotherms of an aromatic alcohol homologue (phenethyl alcohol, 3-phenyl-1-propanol, 4-phenyl-1-butanol, 5-phenyl-1-pentanol, and 6-phenyl-1-hexanol) on Lichrosorb RP-18 and xylene, ethylbenzene, chlorobenzene on YWG-C_6H_5 were obtained under various methanol (solvent) concentrations. Plots of $\log a_{P\bar{L}_nD_{(m-q)}}$ versus $\log a_{PD_m}$ in accordance with Eq. (1) for the adsorption of aromatic alcohol homologue and derivatives of benzene under various methanol concentrations are shown in Fig. 1, with 5-phenyl-1-pentanol on Lichrosorb RP-18 taken as an example. The slope of the straight line is $-n/Z$ and the intercept is a constant β_a.

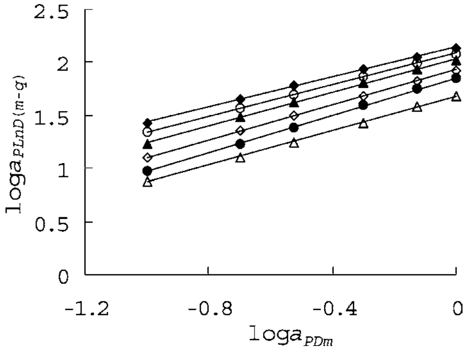

Fig. 1. The plotting of $\log a_{P\bar{L}_nD_{(m-q)}}$ vs. $\log a_{PD_m}$ of 5-phenyl-1-pentanol under the different methanol concentrations. Methanol concentration (v/v): (◆) 30%; (○) 32%; (▲) 35%; (◇) 38%; (●) 40%; (△) 45%.

The plots of $\log a_{P\bar{L}_nD_{(m-q)}}$ versus $\log a_{PD_m}$ all show excellent straight lines with the value of linear correlation coefficient, at least, higher than 0.99. So the adsorption behavior of all solutes under the given condition follows SDT-A well. The intercept, β_a, was also obtained from the plotting of $\log a_{P\bar{L}_nD_{(m-q)}}$ versus $\log a_{PD_m}$.

From the definition of n and Z, we know that the two values are constant for a given solute at the given conditions, independent of solvent concentration. So n/Z is also a constant at the different concentrations of solvent for a certain solute. This prediction is well validated from the six parallels in Fig. 1. The six parallels denote the slopes of these lines are the same, indicating n/Z to be the same for 5-phenyl-1-pentanol at different methanol concentrations. However, the intercept, namely β_a, is different for 5-phenyl-1-pentanol at the different methanol concentrations. Similar trends were also observed from the isotherms of the other aromatic alcohol homologue and derivatives of benzene.

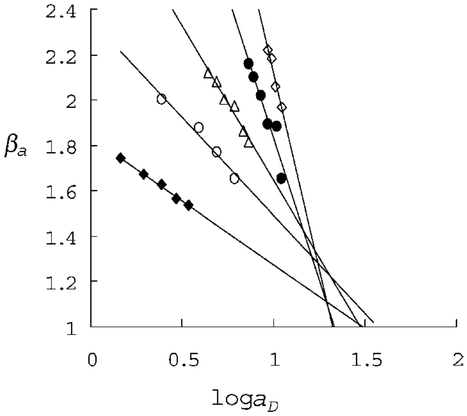

Fig. 2. Plot of β_a of the homologue of aromatic alcohols vs. $\log a_D$. (◆) Phenethyl alcohol; (○) 3-phenyl-1-propanol; (△) 4-phenyl-1-butanol; (●) 5-phenyl-1-pentanol; (◇) 6-phenyl-1-hexanol.

4.2. Validation of the relationship between β_a versus $\log a_D$

4.2.1. The relationship between the β_a of solute and concentration of solvent

The linear relationships between β_a, and the logarithm of the molar concentration of solvent in the bulk solution are shown in Fig. 2 with the aromatic alcohol homologue and Fig. 3 with derivatives of benzene compounds.

As Figs. 2 and 3 show, a linear relationship of β_a versus $\log a_D$ is generally valid. Furthermore, β_a was found to decrease with the increase of methanol concentration. This is because the stationary phase of the adsorption system is a reversed-phase chromatographic packing with strong non-polarity. The amount of the aromatic alcohol adsorbed should decrease with the increases of the methanol concentration. So β_a can be used to characterize the affinity of component to the adsorbent.

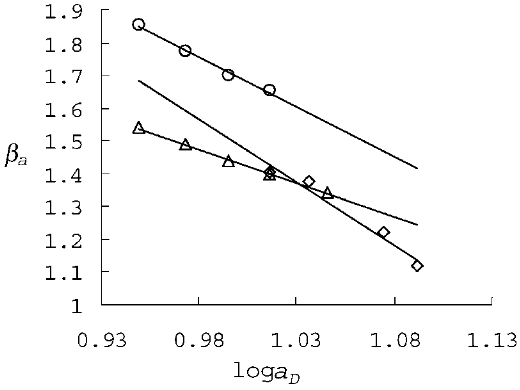

Fig. 3. Plot of β_a of the non-homologue vs. $\log a_D$. (◇) Dimethyl benzene; (△) chlorobenzene; (○) ethyl benzene.

In a gas–solid system, gas molecules are adsorbed as a result of the interactions with the bare surface of the solid. But in a liquid–solid system, the interactions also involve the solvent molecules. Molecules of the solute form complexes as a result of interaction with solvent molecules. At the same time, the solid surface is also solvated. As usually the solvent concentration is high, solvated sites still exist, even if the adsorption of solute has reached to a maximum value. Therefore, the adsorption of solute would be influenced by the kind and concentration of solvent. As Figs. 2 and 3 show, β_a can be employed to measure the effects of solvent concentration on the adsorption of solute.

4.2.2. Comparison between the value of *n* obtained from two methods

The terms *n* and *q* can be obtained from the present method (from Eqs. (7) and (9)) and another validated method from the combination of the SDT-A (Eq. (1)) and STA-R (Eqs. (8) and (9)). The *Z* value can be obtained from the linear plot of $\log k'$ of solutes versus $\log a_D$ by Eq. (8).

As shown in Figs. 4 and 5, the plots of $\log k'$ of aromatic alcohol homologue and non-homologue versus

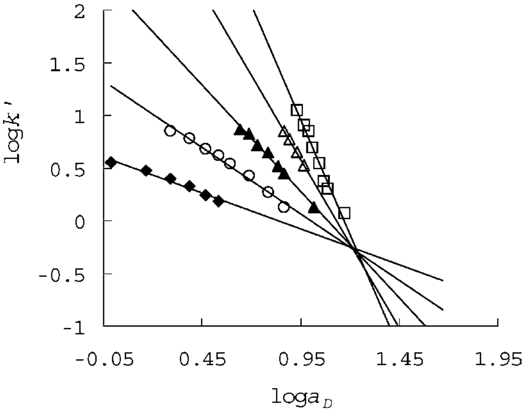

Fig. 4. The plot of $\log k'$ vs. $\log a_D$ of aromatic alcohols. (◆) Phenethyl alcohol; (○) 3-phenyl-1-propanol; (▲) 4-phenyl-1-butanol; (△) 5-phenyl-1-pentanol; (□) 6-phenyl-1-hexanol.

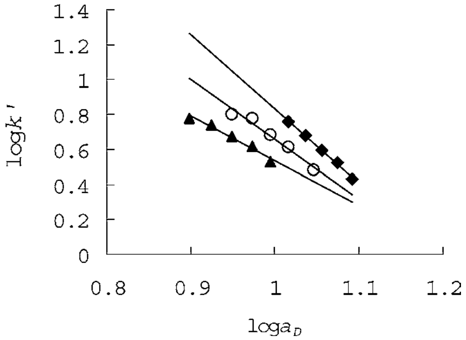

Fig. 5. The plot of $\log k'$ vs. $\log a_D$ of non-homologue. (◆) Dimethyl benzene; (○) ethyl benzene; (▲) chlorobenzene.

$\log a_D$ are linear. The parameters including the two sets of n and q obtained from the two methods are listed in Table 1. The term n_1 denotes the data from the adsorption isotherm by frontal analysis, while the term n_2 shows that from the combination between the retention data in usual RPLC and the adsorption one's. Both results coincide well. The average deviation is ±0.07 for both n and q. It is also shown that for all solutes, n values are always bigger than q. These results show the moles of the solvent released from the adsorbent are more than that released from the solute in the same process.

4.3. *The relationship of n and q value and carbon number N of the homologue*

The homologue rule is often used to validate the new retention mechanism and method in LC. So n and q were further investigated as to whether the homologue rule is followed. The linear correlation coefficient is above 0.97 from plotting of n and q values against carbon number N of aromatic alcohol homologue (not shown here). This explicated that the longer the carbon length of the homologue, the more active sites on the surface of absorbent are covered, the more molecules of solvent are displaced from solute and the surface of adsorbent.

Table 1
Comparison between the n and q value obtained from two methods

Solute	Z	n_1 [a]	n_2 [a]	q_1 [b]	q_2 [d]
Phenethyl alcohol[c]	0.68	0.55	0.56	0.13	0.12
3-Phenyl-1-propanol[c]	1.26	0.98	0.87	0.28	0.39
4-Phenyl-1-butanol[c]	2.02	1.48	1.37	0.54	0.65
5-Phenyl-1-pentanol[c]	3.20	2.53	2.40	0.67	0.80
6-Phenyl-1-hexanol[c]	4.35	3.39	3.47	0.96	0.88
Xylene[d]	4.26	3.35	3.80	0.91	0.46
Ethyl benzene[d]	3.41	3.06	3.05	0.35	0.36
Chlorobenzene[d]	2.63	2.23	2.05	0.40	0.58

[a] n_1 data is from SDT-A; n_2 data is from the combination of SDT-A and SDT-R.

[b] q_1 equals to $Z - n_1$; q_2 equals to $Z - n_2$.

[c] Absorbent used was Lichrosorb RP-18.

[d] Adsorbent used was YWG-C_6H_5.

It is interesting that the fraction of methanol released by the adsorbent when ethyl benzene adsorbs ($n/Z = 0.90$, $q/Z = 0.10$) is greater than that released by the adsorbent when phenethyl alcohol is adsorbed ($n/Z = 0.82$, $q/Z = 0.18$). This suggests that the latter with strong hydrophilicity enters the bonded phase layer (BPL) is shallower than the former. Thus the latter contacts to the BPL with a less surface area than that of the former. Thus, the n value from the latter is less than that from the former. On the contrary, the latter is more closed the mobile phase with more hydrophilicity with compared to the BPL, resulting to release more methanol, i.e. having greater q value than the former.

5. Conclusions

A new relationship between β_a and the solvent concentration has been derived. When tested with experimental data, it was found that the homologue of phenyl alcohols and derivatives of benzene all were fit by the derived equation in this paper. The parts of the stoichiometric parameter Z, n and q solvent molecules separately released from the solute and the surface of adsorbent during adsorption, respectively, were determined. They indicate that both n and q values obtained from the presented method agree with ones obtained from SDT-A and SDT-R of RPLC. Results suggest that more methanol is released by solid adsorbent than solute and that more methanol is released by the solid adsorbent when the group attached to benzene is nonpolar.

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