Quantitative relationship between adsorbed amount of solute and solvent composition

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Abstract

A new adsorption isotherm that relates the amount of solute adsorbed to the solvent concentration is proposed. The new equation is derived from Geng and Shi's stoichiometric displacement model for adsorption (SDM-A). The obtained equation may be simplified to an expression containing two parameters. The equation with two parameters, valid for low concentrations of solute, is a logarithmically linear relationship. The intercept contains a thermodynamic equilibrium constant of the solute displacing solvent from the adsorbent. The slope is the negative value of the stoichiometric displacement parameter (Z), the average total number of solvent molecules displaced from an active site on the adsorbent and from the solute. Tests with a homologous series of aromatic alcohols by frontal analysis in reversed phase liquid chromatography demonstrate that experimental results fit the equation well.
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1. Introduction

Many factors, including Traube's rule, temperature, solubility of solute, inorganic salt, the structure of adsorbent and the nature and concentration of the solvent, all affect solute adsorption in a liquid–solid system [1]. Solvent effects are of significance. Zavitsas [2] showed that deviations of colligative properties from the ideal can be explained by incorporating water of solvation into the solute, thus, removing it from bulk solvent. Dispersions of silica are better stabilized by ethanol than water; indeed, it is reported that solvent film thickness has a maximum at 50% ethanol when mixed with water [3]. The repulsion between dispersed

particles is over and above the effects from the double layer and van der Waals forces [4] and is attributed to structured solvent in the film [3]. Zajac et al. [5], demonstrated that vicinal water affects surface sites on various silica-based adsorbents. Langmuir's equation [6] is very popular but does not describe solvent effects. The extended Langmuir isotherm reported by Pineiro et al. [7], utilizes volume fractions but did not use the volume of the solvent as a variable. Geng et al. [8], considered all the kinds of interaction between the solute, solvent, and adsorbent, and derived another extended Langmuir equation, which can be used to calculate the solute adsorption under various solvent concentrations. The parameters in the derived equation were related to the stoichiometric displacement model (SDM) in reversed-phase liquid chromatography and they have exact physical meanings, but it is very

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complex. The solvent concentration influences the interactions between the solvent and the solute as well as the adsorption of solvent, and solute, by the adsorbent. In the SDM for adsorption (SDM-A) [9], intermolecular interactions among adsorbent, solute and solvent are included. It has been proved an effective quantitative adsorption model in liquid–solid systems [9,10]. New reviews introduce the recent development of the SDM for separation science [11] and for biotechnology [12].

First, the SDM-A model will be used to derive a new adsorption isotherm that makes the solvent concentration explicit. Then the equation will be simplified and it will be easy to use. Lastly, the equation will be tested with data from reversed phase liquid chromatography and frontal analysis on an homologous series of phenyl alcohols in a mixed solvent of methanol and water.

2. Theory

Suppose a solute adsorbs from a binary component solvent system consisting of water and an organic solvent. Water here is considered to be an eluent and only organic solvent is considered to have an effect on the solute adsorption. Equilibrium is assumed between solvated solute plus solvated adsorbent and adsorbed solute plus solvent displaced by both solute and adsorbent as a consequence of solute adsorption

$$PD_m + nLD = PD_{m-q}L_n + ZD \tag{1}$$

where PD_m is solvated solute, LD a solvated mean active site on the adsorbent, $PD_{m-q}L_n$ the adsorbed solute, D is the organic solvent, and $Z = n + q$ represents the amount of solvent displaced. When a stoichiometric displacement occurs between the solute and the organic solvent, the total thermodynamic equilibrium constant of the stoichiometric displacement process for solute displacing solvent is defined as [8]

$$K_a = \frac{C_s a_D^Z}{C_m a_{LD}^n} \tag{2}$$

where C_s is the solute concentration of $PD_{m-q}L_n$, the solute adsorbed on the adsorbent, C_m denotes the solute concentration of PD_m in bulk solution, 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, n is the moles of the solvent originally adsorbed on the contact surface of the solid adsorbent between one mole of adsorbed solute and adsorbent, a_D stands for the solvent activity in the bulk solution, and a_{LD} becomes the solvent activity adsorbed on the surface of adsorbent. When activities are unknown concentrations are often used.

Suppose the total number of active sites on the adsorbent surface is a_{SD}. When the solvent activity, a_D, is given, then a_{SD} can be expressed as

$$a_{SD} = a_{LD} + C_s \tag{3}$$

Replacing a_{LD} in Eq. (1) from Eq. (2) yields

$$K_a = \frac{C_s a_D^Z}{C_m (a_{SD} - C_s)^n} \quad \text{and}$$
$$C_s = \frac{K_a C_m (a_{SD} - C_s)^n}{a_D^Z} \tag{4}$$

Rearranging Eq. (4)

$$C_s = K_a C_m a_{SD}^n \left(1 - \frac{C_s}{a_{SD}}\right)^n a_D^{-Z} \tag{5}$$

where K_a, a_{SD}, and n are all constants. When C_m is kept constant also Eq. (5) can be written into the logarithmic form

$$\ln C_s = \ln P + n \ln \left(1 - \frac{C_s}{a_{SD}}\right) - Z \ln a_D \tag{6}$$

where P is a constant, $P = K_a C_m a_{SD}^n$. Eq. (6) shows the functional relationship between the adsorbed amount and solvent concentration. Since Eq. (6) is a non-linear equation and it is very difficult to obtain an exact analytical solution mathematically, some assumptions must be given to obtain their approximate solution.

While C_s is very small, C_s/a_{SD} is approximately zero. Inserting Eq. (7)

$$\ln \left(1 - \frac{C_s}{a_{SD}}\right) = 0 \tag{7}$$

into Eq. (6), we obtain

$$\ln C_s = \ln P - Z \ln a_D \tag{8}$$

Eq. (8) shows a straight line would be obtained by plotting $\ln C_s$ versus $\ln a_D$, so $-Z$ is the slope of the straight line and $\ln P$ is the intercept of it. Eq. (8) is an approximate equation containing two parameters Z and P.

3. Experimental

3.1. Equipment

An LC-6A liquid chromatograph (Shimadzu Corporation, Japan) was used, consisting of two pumps (LC-6A), a variable wavelength UV–VIS detector (SPD-6AV), a controller system (SCL-6B) and a recorder (Dahua Instrument Corporation, Shanghai). To carry out this experiment an RPLC column (50 mm long × 2 mm diameter) was packed with Lichrosorb RP-18 (granularity 10 μm, Z. Merck Darmstadt Company, Germany). A temperature indication controller (WMZK-01, Medical Instrument Factory, Shanghai) was employed to control column temperature to an accuracy of ±0.5 °C. The column temperature was controlled at 25 °C.

3.2. Reagents

Phenethyl alcohol, 3-phenyl-1-propanol, 4-phenyl-1-butanol, 5-phenyl-1-pentanol, and 6-phenyl-1-hexanol were purchased from Sigma. Methanol was from Xi'an Chemical Reagent Company (analytic-reagent grade). Water was deionized by a Barnsted E-pure cleaning water instrument (Barnsted Co. Ltd., USA). The mobile phase consisting of methanol and water was degassed by sonication by Ultrasonic Instrument (KQ-250, Gunshan Detector Instrument Factory, Shanghai) before being used. An octadecylsilane adsorbent was used on which methanol was preferentially adsorbed.

3.3. Experimental method

3.3.1. Determination of adsorption isotherms of aromatic alcohol homologues

All adsorption data were collected with a flow-rate of the mobile phase of 0.28 ml/min and the detection at 275 nm. The temperature of the column was adjusted by the temperature indication controller and an electric heater.

The method for the determination of the adsorption isotherm used in this paper was according to frontal elution as described by Horvath and co-workers [13,14]. Frontal elution allows adsorption data to be obtained quickly, conveniently and reliably [14]. When the equilibrium concentration of solute in mo-

bile phase was $C_{m,i}$, the concentration of solute adsorbed on the stationary phase $C_{s,i}$ was calculated as

$$C_{s,i} = \frac{C_{s,i-1} + (C_{m,i} - C_{m,i-1})(V_R - V_0)}{m} \quad (9)$$

where $C_{m,i}$ and $C_{m,i-1}$ are two different equilibrium concentrations of solute in mobile phase, $C_{s,i-1}$ is the concentration of solute adsorbed on the stationary phase when the equilibrium concentration of solute in the mobile phase is $C_{m,i-1}$, V_R is the frontal retention volume, V_0 the dead volume of the system including column hold-up volume, and m the mass of the packing in the column. The dead volume of the system was determined with $NaNO_2$ solution.

4. Results and discussion

In order to test Eq. (8), first the parameters and correlation coefficients of these equations must be obtained by linear regression. A high correlation coefficient is an assurance of the reliability of the equation. Accurate parameters would lead to a better coincidence between experiment and predicted result.

4.1. Linear relationship validation of two-parameter equation

Table 1 indicates the parameters and linear correlation coefficients obtained from the plotting of $\ln C_s$ versus $\ln a_D$ of aromatic alcohol homologues under the conditions of the very low solute concentration, C_m, of 0.10 mg of solute/ml of solution. From Table 1, it can be seen that a linear relationship of $\ln C_s$ versus $\ln a_D$ is generally valid for the range of solvent concentrations, a_D, and adsorbed amounts, C_s, shown in Table 2 and Fig. 1. The Z values are the total

Table 1
The parameters and the linear correlation coefficients, R, obtained from the plotting of $\ln C_s$ vs. $\ln a_D$

Homologue	$\ln P$	Z	R
Phenethyl alcohol	0.694	0.551	0.9808
3-Phenyl-1-propanol	1.57	1.22	0.9434
4-Phenyl-1-butanol	2.33	1.88	0.9977
5-Phenyl-1-pentanol	3.74	3.05	0.9981
6-Phenyl-1-hexanol	5.46	4.60	0.9880

$C_m = 0.10$ mg/ml.

Table 2
The comparison between experimental and calculated adsorbed amounts, C_s mg solute/g adsorbent, of aromatic homologues at low solute concentration

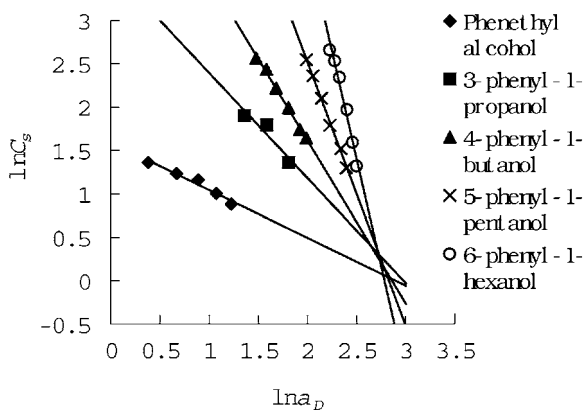| Solute	Methanol weight percent	Experimental C_s (mg/g)	Calculated C_s (mg/g)	Relative deviation (%)	Average relative deviation (%)
Phenethyl alcohol	6	3.90	4.00	2.5	2.42
	8	3.43	3.42	−0.3	
	10	3.20	3.02	−5.6	
	12	2.73	2.73	0	
	14	2.42	2.51	3.7	
3-Phenyl-1-propanol	16	6.70	7.05	5.2	7.0
	20	6.03	5.37	−10.9	
	25	3.90	4.09	4.9	
4-Phenyl-1-butanol	18	13.0	13.2	1.5	2.4
	20	11.4	10.8	−5.3	
	22	9.21	9.06	−1.6	
	25	7.33	7.13	−2.8	
	28	5.69	5.76	1.2	
	30	5.16	5.06	−1.9	
5-Phenyl-1-pentanol	30	12.8	12.6	−1.6	2.7
	32	10.7	10.4	−2.8	
	35	8.20	7.91	−3.5	
	38	5.98	6.15	2.8	
	40	4.58	4.32	−5.7	
	45	3.67	3.67	0	
6-Phenyl-1-hexanol	38	14.3	15.4	7.7	7.1
	40	13.6	12.2	−10.3	
	42	10.4	9.76	−6.1	
	45	7.18	6.86	−4.4	
	48	4.92	5.27	7.1	

$C_m = 0.10$ mg/ml.

Fig. 1. The plot of $\ln C_s$ vs. $\ln a_D$ of aromatic alcohol homologues, where C_s is expressed in mg solute/g adsorbent, and a_D expressed in mol/l.

number of solvent molecules released on adsorption [9]. They increase with the length of the carbon–hydrogen chain, thus, indicating that the chain participates in binding to solid [15].

In order to see clearly, the calculated values of adsorbed amounts obtained from Eq. (8) are compared with experimental values in Table 2.

As shown in Table 2, the largest relative deviation was 10.9%. Moreover, the largest relative average deviation of all five solutes at various experimental methanol concentrations is 7.1%. This elucidates that the calculated results fit experimental data well under such a very low concentration of solute, C_m, of 0.10 mg/ml. At a higher solute concentration, C_m, of 0.75 mg/ml calculated results fit experiment with correlation coefficients above 0.97, larger $\ln P$ values, slightly smaller Z values, and a largest relative deviation of 13% [16]. Adsorbed amounts of solute range

from 13 to 60 mg solute/g adsorbent at the higher solute concentration [16]. Methanol concentrations are the same.

In Fig. 1 an average convergence point (ACP) is shown at C_s of 1.2 mg/g and $\ln a_D$ of 2.90, where a_D is expressed in mol/l. Convergence occurs when displacing solvent activity approaches that when pure [17]. Pure methanol has ln (mol/l), 3.20. Geng and Regnier [17] report 3.32 and 3.45 for homologous series of *n*-alkyl phthalimides and *n*-carboxylic acids, respectively, in methanol–water. The fact that convergence solvent concentrations are close to the pure solvent indicates that extrapolation lines to higher methanol concentrations may be useful for predictive estimates of adsorption. The range of methanol concentrations displayed in Table 2 and Fig. 1 was based on optimum conditions for frontal analysis. One way to further validate the predictive validity of Eq. (8) over a larger range of solvent concentrations than displayed here would require Langmuir adsorption isotherms from equilibrium experiments traditional in physical chemistry laboratory courses [18] at each of several methanol concentrations using a hydrophobic solid adsorbent. Geng et al. [8], outline the procedure.

Empirical Freundlich isotherms may fit non-ideal adsorptions [19] when ideal Langmuir adsorptions are not adequate. Adamson [19] suggests site inequality, and two-dimensional interaction as possible causes. Solvent adsorption, such as observed here, may be another, and may be responsible for the reversal of Dubinin-type characteristic energies observed by Stoeckli et al. [20]. When adsorptions on different solids are fit from the gas phase, and compared with fits from aqueous solution, the characteristic energies vary in opposite directions [20].

5. Conclusion

A new adsorption isotherm that makes the activity of the solvent explicit has been derived and shown to be useful in its simplest form. The total number, Z, of solvent molecules released upon adsorption is a parameter obtained from best fits. When tested with experimental data, it was found that a series of phenyl alcohols all were fit by the equation, and that the lengths of the side chain of the phenyl alcohols were involved in the adsorption.

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