Investigation of Quantitative Relationship Between Adsorbed Amount of Solute and Solvent Concentration at Relatively High Solute Concentration by Frontal Analysis in RPLC

WANG, Yan[a] **(王彦)** **GENG, Xin-Du**[*,a] **(耿信笃)** **ZEBOLSKY, Don M.**[b]

[a] *Institute of Modern Separation Science, Province Key Laboratory of Modern Separation Science, Northwest University, Xi'an, Shaanxi 710069, China*

[b] *Department of Chemistry, Creighton University, Omaha 68178-0104, USA*

In previous paper a new adsorption isotherm which relates the amount of solute absorbed to the solvent concentration is proposed and simplified, and it only can be used at lower solute concentration. In this article the scope of the new adsorption isotherm is extended and the expressions with three and four parameters are obtained. The equations with multi-parameters are valid when the adsorbed amounts are larger and show non-linear logarithmic relationships. Tests with a homologue of aromatic alcohols by frontal analysis in reversed phase liquid chromatography demonstrate that the experimental results fit those equations well. In addition, the predicted values by the multi-parameters were found to fit the experimental values well also. The parameters have physical meaning only for the two-parameter equation for the aromatic alcohols.

Keywords solid-liquid adsorption, solvent concentration, stoichiometric displacement, adsorption isotherm, reversed phase liquid chromatography, frontal analysis, phenyl alcohol

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, affect solute adsorption in a liquid-solid system.[1] Among them solvent effects are of significance. Dispersions of silica are stabilized by ethanol. It is reported that solvent film thickness is greatest in mixtures of 50 percent ethanol with water.[2] The repulsion between dispersed particles is above the effects from the double layer and van der Waals forces[3] and is attributed to structured solvent in the film.[2] Langmuir's equation[4] is very popular but does not describe the solvent effects. The extended Langmuir isotherm reported by Pineiro *et al*.[5] utilizes volume fractions but did not use the volume of the solvent as a variable. Geng *et al*.[6] considered all kinds of interaction among solute, solvent and absorbent, and derived another extended Langmuir equation, which elucidates the effects of solvent concentration on the adsorbed amount in a liquid-solid systems. But it is very complex.

In the stoichiometric displacement theory for adsorption (SDT-A)[7] intermolecular interactions among adsorbent, solute and solvent are included. It has been proved to be an effective quantitative adsorption model in liquid-solid systems.[7,8] In the previous paper,[9] the SDT-A model was used to derive a new adsorption isotherm that makes the relationship between adsorption amount and the solvent concentration explicit. The obtained equation was 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 the solute and the active sites on the adsorbent. In this article, the equation with three and four parameters, valid for high concentrations of solute, will be firstly derived. The equation will be tested with data from reversed phase liquid chromatography (RPLC) and frontal analysis (FA) on a homologue of phenyl alcohols in a mixed solvent of methanol and water.

Theory

In the previous paper,[9] a new adsorption isotherm which relates the amount of solute absorbed to the solvent concentration was derived, based on Geng and Shi's SDT-A.[7] The expression of the adsorption isotherm is,

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

where P is a constant, $P = K_a \cdot c_m \cdot a_{SD}{}^n$. K_a is the general thermodynamic equilibrium constant of the stoichiometric displacement process for solute displacing solvent, c_s is

* E-mail: xdgeng@nwu.edu.cn

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the solute concentration adsorbed on the adsorbent, c_m denotes the solute concentration in bulk solution, Z represents the total moles of the solvent released or adsorbed for one mole of 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 in the adsorbent side between one mole of solute and adsorbent, a_{SD} is the total number of active sites on the adsorbent surface, a_D stands for the solvent activity in the bulk solution. Concentrations are often used when activities are unknown.

Eq. (1) shows the functional relationship between the adsorbed amount and solvent concentration. Because Eq. (1) 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. Approximations of Eq. (1) in three ways are as following.

c_s is very small, c_s/a_{SD} approximates zero

Inserting Eq. (2),

$$\ln\left(1 - \frac{c_s}{a_{SD}}\right) = 0 \tag{2}$$

into Eq. (1), then we obtain,

$$\ln c_s = \ln P - Z\ln a_D \tag{3}$$

Eq. (3) shows a straight line. By plotting $\ln c_s$ versus $\ln a_D$, $-Z$ is the slope of the straight line and $\ln P$ is its intercept. In the previous paper,[9] the Eq. (1) was simplified into Eq. (3), which is validated at very low solute concentration.

Rewriting Eq. (3) as:

$$\ln a_D = A_{20} + A_{21}\ln c_s \tag{4}$$

We have $A_{20} = (1/Z)\ln P$ and $A_{21} = -1/Z$. Eq. (4) is an approximate equation containing two parameters A_{20} and A_{21}.

c_s is small, but c_s/a_{SD} is too large to neglect

Extending Eq. (1) by Taylor's rule, and taking the first term of a Taylor Expansion,

$$\ln\left(1 - \frac{c_s}{a_{SD}}\right) = -\frac{c_s}{a_{SD}} \tag{5}$$

Eq. (1) can be converted as:

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

Simplifying Eq. (6), it can also be expressed as

$$\ln a_D = \frac{1}{Z}\ln P - \frac{1}{Z}\ln c_s - \frac{n}{Z\cdot a_{SD}}c_s \tag{7}$$

$$\ln a_D = A_{30} + A_{31}\ln c_s + A_{32}c_s \tag{8}$$

where $A_{30} = (1/Z)\ln P$, $A_{31} = -1/Z$, and $A_{32} = -n/(Z\cdot a_{SD})$. Eq. (8) is an approximate equation containing three parameters A_{30}, A_{31} and A_{32}.

In order to express the relationship between the adsorbed amount and solvent concentration more accurately, the first two terms of the Taylor Expansion were taken,

$$\ln\left(1 - \frac{c_s}{a_{SD}}\right) = -\frac{c_s}{a_{SD}} - \frac{1}{2}\left(\frac{c_s}{a_{SD}}\right)^2 \tag{9}$$

Eq. (1) can be evolved as,

$$\ln a_D = \frac{1}{Z}\ln P - \frac{1}{Z}\ln c_s - \frac{n}{Z\cdot a_{SD}}c_s - \frac{n}{2Z\cdot a_{SD}^2}c_s^2 \tag{10}$$

or,

$$\ln a_D = A_{40} + A_{41}\ln c_s + A_{42}c_s + A_{43}c_s^2 \tag{11}$$

where, $A_{40} = (1/Z)\ln P$, $A_{41} = -1/Z$, $A_{42} = -n/(Z\cdot a_{SD})$ and $A_{43} = -n/(2Z\cdot a_{SD}^2)$. Eq. (11) is an approximate equation containing four parameters A_{40}, A_{41}, A_{42} and A_{43}.

A fundamental function, Eq. (1), obtained above to express the relationship between the absorbed amount and solvent concentration is really a complex equation. It may be simplified by different assumptions to get approximate solutions. Three equations containing two, three and four parameters approximating this quantitative relationship were obtained.

Experimental

Equipment and reagents

An LC-6A liquid chromatograph (Shimadzu Corporation, Japan) was used, consisting of two pumps (LC-6A), a variable-wavelength UV-visible 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 × 1 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 ℃.

Phenethyl alcohol, 3-phenyl-1-propanol, 4-phenyl-1-butanol, 5-phenyl-1-pentanol and 6-phenyl-1-hexanol were purchased from Sigma Co. (St. Louis, MO, USA). The 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.

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 analysis as described by Horvath and his co-workers.[10,11] Frontal elution allows adsorption data to be obtained quickly, conveniently and reliably.[10] When the equilibrium concentration of solute in mobile phase was $c_{m,i}$, the concentration of solute adsorbed on the stationary phase $c_{s,i}$ was calculated as

$$c_{s,i} = c_{s,i-1} + (c_{m,i} - c_{m,i-1})(V_R - V_o)/m \quad (11)$$

where $c_{m,i}$ and $c_{m,i-1}$ are two different equilibrium concentrations of solute in mobile phase, $c_{s,i-1}$ 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 the frontal retention volume, V_o 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.

Results and discussion

In order to test the equations containing three and four parameters, firstly the parameters and correlation coefficients of these equations must be obtained by non-linear regression. A high correlation coefficient is assurance of the reliability of the equation. Accurate parameters would lead to a better coincidence between experiment and predicted results.

Parameters of multi-parameter equations

The two-parameter equation would be expected to fit for the condition that the solute concentration is very low. With three and four-parameter equations solute concentrations could be larger than those fit with two parameters. In this experimental part, the solute concentration was 7.5 times of that of the fit of the two-parameter equation shown in previous paper.[9]

In addition, from the process of derivation of these three equations it could be found out that the two-parameter equation is the simplest one, the three-parameter equation is more complex, and the four-parameter one is the most complex. So the four-parameter equation will predict the best.

Table 1 indicates the parameters 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 and relatively high solute concentration. In Table 1, it can be found that both Z and ln P increase regularly with the chain length of the homologue.[12] This implies that the chain participates in binding to the solid. If only the alcohol group contacted the solid on end Z values would be expected to be about the same for all the solutes. However, all Z values are less but ln P values are greater at high concentration than at low concentration. The increase in concentration would double all ln P values if the equilibrium constants were the same but the ln P values increase by more than that. When solute concentration is low, each solute molecule can displace more solvent molecules than that when it is high. That is the meaning of the lower Z values at higher solute concentrations. It is reasonable at the higher concentrations that some solute molecules can not contact adsorbent, because they interact with other solute molecules. Because of this, the density of the solute in the adsorbent surface would increase. The physical meaning of the higher values of ln P includes a higher equilibrium constant, a higher affinity of solute for the adsorbent. There is a greater adsorption of solute by adsorbent at the higher concentration.

Table 2 lists the parameters from in three or four-parameter equations using non-linear correlation regression at relatively high concentration. For convenience to compare the results, parameters obtained from the two-parameter equation using linear correlation regression are listed at the same time. It is shown that the correlation coefficients of these three equations for five solutes were all above 0.97. So each of the three equations could predict the experimental results. The correlation coefficients of the three and four-parameter equations for each solute are all above 0.99. In addition, those of the four-parameter equation are better than those with three parameters. This shows that with the increasing of the number of parameters, the accuracy of the equation for prediction appears better. In Table 2, at least 6 digits are needed during calculating the parameters of the three equations in order to calculate the adsorbed amounts of solute within experimental precision.[13]

The parameters A_{31} of Eq. (8) and A_{41} of Eq. (11), are also $-1/Z$. As such they must be negative. The SDT predicts all parameters negative but the intercepts. The positive parameters in Table 2 provide better fits mathematically, but only the linear fits are valid to interpret the parameters physically.[14]

Table 1 Parameters obtained from the plotting of ln c_s versus ln a_D at low and high concentrations

Homologue	ln P		Z	
	Low concentration	High concentration	Low concentration	High concentration
Phenethyl alcohol	0.694	3.25	0.551	0.54
3-Phenyl-1-propanol	1.57	4.45	1.22	0.85
4-Phenyl-1-butanol	2.33	6.16	1.88	1.46
5-Phenyl-1-pentanol	3.74	9.20	3.05	2.58
6-Phenyl-1-hexanol	5.46	13.85	4.60	4.31

Table 2 Parameters and correlation coefficients obtained from equations with two, three or four-parameters, respectively ($c_m = 0.75$ mg/mL)[a]

Parameter and coefficient	Phenethyl alcohol	3-Phenyl-1-propanol	4-Phenyl-1-butanol	5-Phenyl-1-pentanol	6-Phenyl-1-hexanol
A_{20}	6.019837	5.236116	4.222896	3.564785	3.213911
$A_{21} = -1/Z$	-1.8583	-1.1733	-0.68652	-0.38694	-0.23217
R_{two}	0.9925	0.9747	0.9912	0.9747	0.9912
A_{30}	0.258447	0.235256	2.847476	2.454773	1.340899
$A_{31} = -1/Z$	1.379223	1.070097	-0.15265	0.070307	-0.20845
A_{32}	-0.19839	-0.08538	-0.01444	-0.01386	-0.001343
R_{three}	0.9987	0.9985	0.9944	0.9925	0.9964
A_{40}	13.19242	9.56061	1.825223	0.619822	3.085343
$A_{41} = -1/Z$	-8.67768	-4.33127	0.337249	1.02941	-0.20738
A_{42}	1.033112	0.333872	-0.04106	-0.07434	0.003032
A_{43}	-0.01859	-0.00389	0.000174	0.000441	-0.000044
R_{four}	0.9990	1.000	0.9944	0.9952	0.9964

[a] R_{two}, R_{three} and R_{four} denote the correlation coefficient of equations with two, three and four-parameters, respectively.

Comparison between experimental and calculated results obtained under the conditions of relatively large solute concentrations

In order to show the accuracy of fit of Eq. (4), Eq. (8) and Eq. (11) under the conditions of relatively larger solute concentrations, Table 3 shows the comparison between experimental and calculated results obtained from equations with two, three and four parameters at the higher concentration.

Table 3 shows the deviations between the experimental and calculated values of the absorbed amounts with the three equations are not significant. The largest deviation is 13%. Moreover, the relative average deviation of all five solutes is 4.49% for the equation with two parameters, 2.24% for the equation with three parameters, and 1.88% for the equation with four parameters. This elucidates that if the equation has more parameters, it usually fits the experimental data better, mathematically. However the equations with more parameters in this case cannot be used to interpret the data physically. It is well-known that polynomials of higher order may provide better fits but incorrect interpretations.[15] The SDT predicts that multiple parameters may improve the fit mathematically but cannot be used to interpret data physically. Only the two-parameter equation has physical meaning in this homologous series. Higher concentrations or another series are needed to find the ranges of concentration where the equations with more parameters might be valid physically.

Conclusion

A new adsorption isotherm that makes the concentration of the solvent explicit has been derived. With different assumptions, equations containing two, three or four parameters were derived. Because the truncation of the Taylor Expansion becomes less severe, isotherms were expected to become increasingly valid as solute concentration increases. When tested with experimental data, it was found that a series of phenyl alcohols all were fit by the equations, and that the length of the side chain of the phenyl alcohols was involved in the adsorption. As the number of parameters of fitting equation increased, the accuracy of the fit to the experiment improves, but the parameters are only physically meaningful for the two-parameter equation.

Table 3 Comparisons between experimental and calculated absorbed amounts of aromatic homologues under the conditions of relatively high solute concentration ($c_m = 0.75$ mg/mL)[a]

Solute	Methanol concentration	$c_{s,exp}$	$c_{s,two}$	$c_{s,three}$	$c_{s,four}$
Phenethyl alcohol	6%	20.3	20.8	20.3	20.3
	8%	18.0	17.8	18.0	18.1
	10%	16.3	15.8	16.1	16.1
	12%	14.2	14.3	14.4	14.3
	14%	13.0	13.2	12.9	13.0
3-Phenyl-1-propanol	10%	37.7	40.5	7.8	37.7
	16%	29.5	27.1	29.0	29.5
	20%	23.4	22.4	24.0	23.4
	25%	17.6	18.6	17.3	17.6
4-Phenyl-1-butanol	18%	52.6	54.3	52.7	52.8
	20%	47.3	46.6	46.7	46.6
	22%	39.6	40.5	41.4	41.3
	25%	36.1	33.6	34.5	34.6
	28%	28.2	28.5	28.6	28.7
	30%	25.3	25.8	25.2	25.1
5-Phenyl-1-pentanol	30%	54.5	58.3	53.6	54.8
	32%	47.4	49.4	48.5	47.6
	35%	41.3	39.2	41.2	40.2
	38%	32.4	31.6	34.3	34.3
	40%	27.1	23.5	24.2	25.6
	45%	18.3	20.4	19.1	19.1
6-Phenyl-1-hexanol	38%	64.6	69.9	65.7	65.4
	40%	58.3	56.1	56.1	56.5
	42%	45.4	45.4	47.4	47.2
	45%	36.0	32.8	34.6	34.4
	48%	25.0	25.6	25.9	25.6
	50%	20.7	21.4	20.3	20.5

[a] $c_{s,exp}$, experimental value of c_s; $c_{s,two}$, the calculated value of c_s with the equation of two parameters; $c_{s,three}$, the calculated value of c_s with the equation of three parameters; $c_{s,four}$, the calculated value of c_s with the equation of four parameters; all c_s values are in mg solute/g adsorbent.

References

1 Zhu, B. Y.; Zhao, Z. G. *Basis of Interface Chemistry*, Chemical Engineering Press, Beijing, **1996**, p. 237 (in Chinese).

2 Ren, J.; Song, S.; Lopez-Valdivieso, A.; Shen, J.; Lu, S. *J. Colloid Interface Sci.* **2001**, *238*, 279.

3 Verwey, E. J.; Overbeck, J. Th. G. *Theory of the Stability of Lyophobic Colloids*, Elsevier, Amsterdam, **1948**, p. 205.

4 Langmuir, I. *J. Am. Chem. Soc.* **1918**, *40*, 1361.

5 Pineiro, A.; Brocos, P.; Amigo, A.; Garcia-Fadrique, J.; Lemus, M. G. *Langmuir* **2001**, *17*, 4261.

6 Geng, X. D.; Wang, Y.; Yu, Q. M. *Acta Chim. Sinica* **2001**, *59*, 1847 (in Chinese).

7 Geng, X. D.; Shi, Y. L. *Sci. China, Ser. B: Chem.* **1989**, *32*(1), 571.

8 Zhao, F. S.; Shen, J. H. *Langmuir* **1995**, *11*, 1403.

9 Wang, Y.; Geng, X. D.; Zebolsky, D. M. *Thermochim. Acta* **2003**, *397*(1—2), 13—17.

10 Jacobson, J.; Frenz, J.; Horvath, C. *J. Chromatogr.* **1984**, *316*, 53.

11 Huang, J.; Horvath, C. *J. Chromatogr.* **1987**, *406*, 275.

12 Geng, X. D.; Zebolsky D. M. *J. Chem. Educ.* **2002**, *79*, 385.

13 Geng, X. D. *J. Northwest Univ.* **1991**, *21*(2), 25 (in Chinese).

14 Wang, Y; Geng, X. D. *Chin. J. Chromatogr.* **1999**, *17*(4), 326 (in Chinese).

15 Noggle, J. H. *Physical Chemistry on a Microcomputer*, Little, Brown and Co., Boston, **1985**, p. 90—92.

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