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A FUNDAMENTAL EQUATION FOR DESCRIBING THE RELATIONSHIP BETWEEN THE COMPOSITION OF THE MULTICOMPONENT MOBILE PHASE AND CHROMATOGRAPHIC RETENTION

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Abstract

A fundamental equation for discribing the relationship between the composition of the multicomponent mobile phase (CMCMP) and chromatographic retention (CRV)

$$\ln k' = a + \sum_{i=1}^{n} b_i c_{B_i} + \sum_{i=1}^{n} c_i \ln c_{B_i},$$

is derived by using statistical thermodynamic method. The equation is proven by a ternary mobile phase experiment for 11 compounds. Based on this equation, we also obtain retention equations for weak dissociative solute.

I. Introduction

In liquid-solid chromatography (LSC), to derive a good relationship between the composition of the mobile phase and the retention value is still an interesting subject. Many researches on it have been made for binary mobile phase[1-5]. Recently, there is an emphasis on the use of multicomponent mobile phase for satisfactory separation[6]. Therefore, great attention is paid to the research on the relationship between the composition of the multicomponent mobile phase and retention value. Snyder reported the relationship between the composition of the mobile phase and solvent strength[7-8] so that it can predict the retention value of sample from the solvent strength. For binary solvent, Snyder's equation is:

$$\varepsilon_{ab} = \varepsilon_a + \frac{\log(N_b 10^{\alpha' n_b(\varepsilon_a - \varepsilon_b)} + 1 - N_b)}{\alpha' n_b}. \tag{1}$$

Eq. (1) can be rewritten as[8]

$$\varepsilon_{ab} = \varepsilon_a + \frac{\log(N_a/\theta_a)}{\alpha' n_b}. \tag{2}$$

In Eq. (1) and Eq. (2), ε_a and ε_b are solvent strength values (ε^0) for solvents A and B, n_b is the cross-sectional area of a molecule of B, N_a and N_b refer to the mole fractions in mobile phase for solvents A and B respectively, and θ_a is the mole fraction of A in the stationary phase. A similar equation was presented by

Snyder and Glajch for multicomponent mobile phase.

These equations can be used only for less polar solvents B but can not be used for more polar B solvents because of localization effect. Snyder and Glajch considered the effect of localization on the calculation of the solvent strength. They gave an expression to calculate the localization function as an approximation for calculating ε^0 value. However, it is only an empirical expression.

Based on the solubility parameter theory, Schoenmakers presented an equation for describing the relationship between the composition of the ternary mobile phase and the capacity factor of sample in reversed phase liquid chromatography (RPLC)[9]

$$\ln k_i' = A_1\varphi_1^2 + A_2\varphi_2^2 + B_1\varphi_1 + B_2\varphi_2 + C + D\varphi_1\varphi_2, \tag{3}$$

where, φ_1 and φ_2 refer to the volume fractions of two organic modifers in mobile phase respectively, k_i' is the capacity factor of solute i, A_1, A_2, B_1, B_2, C and D all are constants which relate to sample and stationary phase. Eq. (3) gives a more accurate description of variation of retention with composition in certain concentration range in ternary RPLC system. However, when mobile phases of high water content ($\varphi_1 + \varphi_2 \leqslant 0.1$) are used, Eq. (3) is insufficient [9,10], it can only be used in a limited concentration range.

In this paper, we theoretically derive a fundamental equation for describing the relationship between the composition of the multicomponent mobile phase and sample capacity factor by using statistical thermodynamic method[11]. Our experimental results prove that the fundamental equation can predict the retention value accurately in wide concentration range. In addition, retention equations are given for weak dissociative solute by using the equilibrium principle of weak dissociative solute and chemical dynamic method.

II. The Derivation of Chromatographic Retention Equation for Non-dissociative Solution System

Consider an isolated system which has no material exchange with outside circumstance. The system contains the solute A, solvents B_1, B_2, $\cdots$, B_n and adsorbent S

In the system, the total partition function Q is

$$Q = (T_A \cdot J_A)^{N_A} \cdot \prod_{i=1}^{n} (T_{B_i} \cdot J_{B_i})^{N_{B_i}} \cdot \Omega, \tag{4}$$

where T_A, T_{B_i} are the translational partition functions of the solute A and solvent B_i, J_A, J_{B_i} are the internal partition functions respectively. As

$$N_A \ll N_{B_1}, N_{B_2}, \cdots, N_{B_n},$$

the interaction between solute molecule A as well as between molecule A and solvent molecules B_i can be neglected. The configuration partition function, Ω, can be expressed as:

$$Q = \frac{1}{N_{\mathrm{A}}!\prod_{i=1}^{n} N_{\mathrm{B}_i}!}\int\cdots\int e^{-\frac{1}{kT}[\chi_{\mathrm{A}}N_{\mathrm{A}}+\sum_{i=1}^{n}(\chi_{\mathrm{B}_i}N_{\mathrm{B}_i})]}\cdot(d\omega_{\mathrm{A}})^{N_{\mathrm{A}}}\cdot\prod_{i=1}^{n}(d\omega_{\mathrm{B}_i})^{N_{\mathrm{B}_i}}, \tag{5}$$

where χ refers to the potential of the molecule in the solution. According to the smoothed potential model, we can obtain:

$$Q = \frac{1}{N_{\mathrm{A}}!\prod_{i=1}^{n} N_{\mathrm{B}_i}!} e^{-\frac{1}{kT}[\chi_{\mathrm{A}}N_{\mathrm{A}}+\sum_{i=1}^{n}(\chi_{\mathrm{B}_i}N_{\mathrm{B}_i})]}\cdot V_0^{(N_{\mathrm{A}}+\sum_{i=1}^{n}N_{\mathrm{B}_i})}, \tag{6}$$

where $V_0 = N_{\mathrm{A}}V_{\mathrm{A}} + \sum_{i=1}^{n} N_{\mathrm{B}_i}V_{\mathrm{B}_i}$ is the total volume of solution in the system and V_{A}, V_{B_i} are the volumes of individual molecule in the liquid phase.

The Helmholze function of solution is:

$$\begin{aligned} F &= -RT\ln Q \\ &= -RT\Big\{-\ln N_{\mathrm{A}}! - \sum_{i=1}^{n}\ln N_{\mathrm{B}_i}! - \frac{1}{kT}\Big[\chi_{\mathrm{A}}N_{\mathrm{A}} + \sum_{i=1}^{n}(\chi_{\mathrm{B}_i}N_{\mathrm{B}_i})\Big] \\ &\quad + \Big(N_{\mathrm{A}} + \sum_{i=1}^{n}N_{\mathrm{B}_i}\Big)\ln V_0 + N_{\mathrm{A}}\ln(J_{\mathrm{A}}\cdot T_{\mathrm{A}}) + \sum_{i=1}^{n}[N_{\mathrm{B}_i}\ln(T_{\mathrm{B}_i}J_{\mathrm{B}_i})]\Big\}. \end{aligned} \tag{7}$$

Therefore, the chemical potential of solute A in the solution is:

$$\begin{aligned} \mu_{\mathrm{A}} = \frac{\partial F}{\partial N_{\mathrm{A}}}\Big|_{T,V} &= -RT\Big\{-\ln N_{\mathrm{A}} - \sum_{i=1}^{n}\frac{\partial N_{\mathrm{B}_i}}{\partial N_{\mathrm{A}}}\ln N_{\mathrm{B}_i} - \frac{1}{kT}\Big(\chi_{\mathrm{A}} + \sum_{i=1}^{n}\chi_{\mathrm{B}}\frac{\partial N_{\mathrm{B}_i}}{\partial N_{\mathrm{A}}}\Big) \\ &\quad + \Big(1 + \sum_{i=1}^{n}\frac{\partial N_{\mathrm{B}_i}}{\partial N_{\mathrm{A}}}\Big)\ln V_0 + \ln(J_{\mathrm{A}}\cdot T_{\mathrm{A}}) + \sum_{i=1}^{n}\Big[\frac{\partial N_{\mathrm{B}_i}}{\partial N_{\mathrm{A}}}\ln(T_{\mathrm{B}_i}\cdot J_{\mathrm{B}_i})\Big]\Big\}. \end{aligned} \tag{8}$$

The numbers of adsorbed molecules A, B_1, $\cdots$, B_n which have potential $\chi^{\mathrm{a}}_{\mathrm{A}}$, $\chi^{\mathrm{a}}_{\mathrm{B}_1}, \cdots, \chi^{\mathrm{a}}_{\mathrm{B}_n}$ denote $N^{\mathrm{a}}_{\mathrm{A}}$, $N^{\mathrm{a}}_{\mathrm{B}_1}, \cdots, N^{\mathrm{a}}_{\mathrm{B}_n}$. According to the ideal localized monolayers model, the partition function of the adsorbent sunface is:

$$Q^{\mathrm{a}} = \frac{N_{\mathrm{S}}}{N^{\mathrm{a}}_{\mathrm{A}}!\prod_{i=1}^{n}N^{\mathrm{a}}_{\mathrm{B}_i}!} e^{-\frac{1}{kT}[\chi^{\mathrm{a}}_{\mathrm{A}}N^{\mathrm{a}}_{\mathrm{A}}+\sum_{i=1}^{n}(\chi^{\mathrm{a}}_{\mathrm{B}_i}N^{\mathrm{a}}_{\mathrm{B}_i})]}\cdot(J^{\mathrm{a}}_{\mathrm{A}})^{N^{\mathrm{a}}_{\mathrm{A}}}\cdot\prod_{i=1}^{n}(J^{\mathrm{a}}_{\mathrm{B}_i})^{N^{\mathrm{a}}_{\mathrm{B}_i}}, \tag{9}$$

where $N_{\mathrm{S}} = N^{\mathrm{a}}_{\mathrm{A}} + \sum_{i=1}^{n} N^{\mathrm{a}}_{\mathrm{B}_i}$ refers to the number of the adsorbed molecule on the adsorbent surface. The Helmholze function of adsorbent surface can be written as follows:

$$\begin{aligned} F^{\mathrm{a}} &= -RT\ln Q^{\mathrm{a}} \\ &= -RT\Big\{\ln N_{\mathrm{S}}! - \ln N^{\mathrm{a}}_{\mathrm{A}}! - \sum_{i=1}^{n}\ln N^{\mathrm{a}}_{\mathrm{B}_i}! - \frac{1}{kT}\Big[\chi^{\mathrm{a}}_{\mathrm{A}}N^{\mathrm{a}}_{\mathrm{A}} + \sum_{i=1}^{n}(\chi^{\mathrm{a}}_{\mathrm{B}_i}N^{\mathrm{a}}_{\mathrm{B}_i})\Big] \end{aligned}$$

$$+ N_{\mathrm{A}}^{\mathrm{a}} \ln J_{\mathrm{A}}^{\mathrm{a}} + \sum_{i=1}^{n} N_{\mathrm{B}_i}^{\mathrm{a}} \ln J_{\mathrm{B}_i}^{\mathrm{a}}. \tag{10}$$

The chemical potantial of solute A on the adsorbent surface therefore can be obtained

$$\mu_{\mathrm{A}}^{\mathrm{a}} = -RT \left\{ \left(1 + \sum_{i=1}^{n} \frac{\partial N_{\mathrm{B}_i}^{\mathrm{a}}}{\partial N_{\mathrm{A}}^{\mathrm{a}}}\right) \ln N_{\mathrm{S}} - \ln N_{\mathrm{A}}^{\mathrm{a}} - \sum_{i=1}^{n} \left(\frac{\partial N_{\mathrm{B}_i}^{\mathrm{a}}}{\partial N_{\mathrm{A}}^{\mathrm{a}}} \ln N_{\mathrm{B}_i}^{\mathrm{a}}\right) \right.$$

$$\left. - \frac{1}{kT} \left[\chi_{\mathrm{A}}^{\mathrm{a}} + \sum_{i=1}^{n} \left(\frac{\partial N_{\mathrm{B}_i}^{\mathrm{a}}}{\partial N_{\mathrm{A}}^{\mathrm{a}}} \chi_{\mathrm{B}_i}^{\mathrm{a}}\right)\right] + \ln J_{\mathrm{A}}^{\mathrm{a}} + \sum_{i=1}^{n} \left(\frac{\partial N_{\mathrm{B}_i}^{\mathrm{a}}}{\partial N_{\mathrm{A}}^{\mathrm{a}}} \ln J_{\mathrm{B}_i}^{\mathrm{a}}\right) \right\}. \tag{11}$$

Because of isolated system, it has no material exchange with outside circumstance, therefore

$$\partial N_{\mathrm{A}}^{\mathrm{a}} = -\partial N_{\mathrm{A}}, \tag{12}$$

$$\partial N_{\mathrm{B}_i}^{\mathrm{a}} = -\partial N_{\mathrm{B}_i}, \tag{13}$$

then

$$\frac{\partial N_{\mathrm{B}_i}^{\mathrm{a}}}{\partial N_{\mathrm{A}}^{\mathrm{a}}} = \frac{\partial N_{\mathrm{B}_i}}{\partial N_{\mathrm{A}}}. \tag{14}$$

Substituting Eq. (14) into Eq. (11), we obtain

$$\mu_{\mathrm{A}}^{\mathrm{a}} = -RT \left\{ \left(1 + \sum_{i=1}^{n} \frac{\partial N_{\mathrm{B}_i}}{\partial N_{\mathrm{A}}}\right) \ln N_{\mathrm{S}} - \ln N_{\mathrm{A}}^{\mathrm{a}} - \sum_{i=1}^{n} \left(\frac{\partial N_{\mathrm{B}_i}}{\partial N_{\mathrm{A}}} \ln N_{\mathrm{B}_i}^{\mathrm{a}}\right) \right.$$

$$\left. - \frac{1}{kT} \left[\chi_{\mathrm{A}}^{\mathrm{a}} + \sum_{i=1}^{n} \left(\frac{\partial N_{\mathrm{B}_i}}{\partial N_{\mathrm{A}}} \chi_{\mathrm{B}_i}^{\mathrm{a}}\right)\right] + \ln J_{\mathrm{A}}^{\mathrm{a}} + \sum_{i=1}^{n} \left(\frac{\partial N_{\mathrm{B}_i}}{\partial N_{\mathrm{A}}} \ln J_{\mathrm{B}_i}^{\mathrm{a}}\right) \right\}. \tag{15}$$

Both chemical potentials of solute A in the solution and on the adsorbent surface are equal at equilibrium. We obtain

$$\ln k' = \ln \frac{N_{\mathrm{A}}^{\mathrm{a}}}{N_{\mathrm{A}}} = \sum_{i=1}^{n} \left(\frac{\partial N_{\mathrm{B}_i}}{\partial N_{\mathrm{A}}} \ln \frac{N_{\mathrm{B}_i}}{N_{\mathrm{B}_i}^{\mathrm{a}}}\right) + \left(1 + \sum_{i=1}^{n} \frac{\partial N_{\mathrm{B}_i}}{\partial N_{\mathrm{A}}}\right) \ln \frac{N_{\mathrm{S}}}{V_0} + \ln \left(\frac{J_{\mathrm{A}}^{\mathrm{a}}}{T_{\mathrm{A}} \cdot J_{\mathrm{A}}}\right)$$

$$+ \sum_{i=1}^{n} \left[\frac{\partial N_{\mathrm{B}_i}}{\partial N_{\mathrm{A}}} \ln \left(\frac{J_{\mathrm{B}_i}^{\mathrm{a}}}{T_{\mathrm{B}_i} J_{\mathrm{B}_i}}\right)\right] + \frac{1}{kT} \left\{\chi_{\mathrm{A}} - \chi_{\mathrm{A}}^{\mathrm{a}} + \sum_{i=1}^{n} \left[\frac{\partial N_{\mathrm{B}_i}}{\partial N_{\mathrm{A}}} (\chi_{\mathrm{B}_i} - \chi_{\mathrm{B}_i}^{\mathrm{a}})\right]\right\}\Big\}. \tag{16}$$

The potential of molecule A in the solution, χ_{A}, includes the Van der Waals interraction energy and hydrogen bond energy involved the molecule A, therefore, the χ_{A} can be written as

$$\chi_{\mathrm{A}} = \sum_{i=1}^{n} Z_{\mathrm{AB}_i} E_{\mathrm{AB}_i} + E_{\mathrm{AH}}, \tag{17}$$

where E_{AH} is the hydrogen bond energy of molecule A, E_{AB_i} refers to the Van der Waals energy of the each pair of adjacent molecules A-B_i, Z_{AB_i} is the number of molecule B_i surrounding molecule A.

If we think the meeting each other of the molecules as a random process, the number of molecule B_i surrounding molecule A is proportional to the concentration of solvent B_i in the solution, that is

$$Z_{AB_i} = K_{AB_i} \cdot c_{B_i}, \tag{18}$$

where K_{AB_i} is a constant relating to molecule size.

Substituting Eq. (18) into Eq. (17), we obtain

$$\chi_A = \sum_{i=1}^{n} K_{AB_i} E_{AB_i} c_{B_i} + E_{AH}. \tag{19}$$

In the same way, we can write the potential energy of an adsorbed molecule A as follows:

$$\chi_A^a = \sum_{i=1}^{n} K_{AB_i}^a E_{AB_i} c_{B_i} + E_A^a, \tag{20}$$

where E_A^a is the adsorption energy of molecule A (If there is hydrogen bond between the adsorbed molecule A and solvent molecule, the term E_A^a also includes the hydrogen bond energy).

Therefore,

$$\chi_A - \chi_A^a = \sum_{i=1}^{n} (K_{AB_i} - K_{AB_i}^a) E_{AB_i} c_{B_i} + E_{AH} - E_A^a \tag{21}$$

and

$$\chi_{B_i} - \chi_{B_i}^a = \sum_{j=1}^{n} (K_{B_iB_j} - K_{B_iB_j}^a) E_{B_iB_j} c_{B_j} + E_{B_iH} - E_{B_i}^a. \tag{22}$$

We used Langmuir adsorption isotherm for multicomponent adsorption and obtained an equation for describing the relationship between the composition and retention[12]

$$\ln k' = a' + b' \ln\left(1 + \sum_{i=1}^{n} k_i c_{B_i}\right) + \sum_{i=1}^{n} c_i' c_{B_i} \tag{23}$$

where a', b', k_i and c_i' are constants.

Eq. (23) was proven by Dai Chaozheng and Chen Bailin with a ternary mobile phase experiment[13]. However, it is difficult to obtain the constants in the Eq. (23) from experimental data. On the other hand, under the liquid chromatography condition, Freundlish isotherm is better than Langmuir's for multicomponent adsorption, by using Freundlish isotherm,

$$N_{B_i}^a = N_S k_i c_{B_i}^{1/n_i}, \tag{24}$$

where k_i and n_i are constants and

$$c_{B_i} = \frac{V_{B_i}}{V_0} N_{B_i}. \tag{25}$$

We obtain

$$\frac{N_{B_i}^a}{N_{B_i}} = N_S k_i c_{B_i}^{\frac{1}{n_i}-1} \cdot \frac{V_{B_i}}{V_0}. \tag{26}$$

Substituting Eqs. (21), (22), (26) into Eq. (16), the fundamental equation of retention of non-dissociative solute in the multicomponent mobile phase system of LSC can be derived as

$$\begin{aligned}\ln k' = {} & \ln \frac{N_S}{V_S} + \ln \frac{V_S}{V_0} + \sum_{i=1}^{n} \left[\frac{\partial N_{B_i}}{\partial N_A} \ln\left(\frac{J^a_{B_i}}{T_{B_i} J_{B_i} k_i V_{B_i}}\right)\right] + \ln\left(\frac{J^a_A}{T_A J_A}\right) \\ & + \frac{1}{kT}\left[E_{AH} - E^a_A + \sum_{i=1}^{n} \frac{\partial N_{B_i}}{\partial N_A}(E_{B_iH} - E^a_{B_i})\right] \\ & + \sum_{i=1}^{n}\left[\frac{\partial N_{B_i}}{\partial N_A}\left(1 - \frac{1}{n_i}\right)\ln c_{B_i}\right] \\ & + \frac{1}{kT}\sum_{i=1}^{n}\left\{(K_{AB_i} - K^a_{AB_i})E_{AB_i} + \sum_{j=1}^{n}\left[\frac{\partial N_{B_j}}{\partial N_A}(K_{B_jB_i} - K^a_{B_jB_i})E_{B_iB_j}\right]\right\} c_{B_i} \\ = {} & a + \sum_{i=1}^{n} c_i \ln c_{B_i} + \sum_{i=1}^{n} b_i c_{B_i}, \end{aligned} \tag{27}$$

where V_S is the volume of the absorbent,

$$\begin{aligned} a = {} & \ln \frac{N_S}{V_S} + \ln \frac{V_S}{V_0} + \sum_{i=1}^{n} \left[\frac{\partial N_{B_i}}{\partial N_A} \ln\left(\frac{J^a_{B_i}}{T_{B_i} J_{B_i} k_i V_{B_i}}\right)\right] + \ln\left(\frac{J^a_A}{T_A J_A}\right) \\ & + \frac{1}{kT}\left[E_{AH} - E^a_A + \sum_{i=1}^{n} \frac{\partial N_{B_i}}{\partial N_A}(E_{B_iH} - E^a_{B_i})\right], \end{aligned} \tag{27-1}$$

$$b_i = \frac{1}{kT}\left\{(K_{AB_i} - K^a_{AB_i})E_{AB_i} + \sum_{j=1}^{n}\left[\frac{\partial N_{B_j}}{\partial N_A}(K_{B_jB_i} - K^a_{B_jB_i})E_{B_iB_j}\right]\right\}, \tag{27-2}$$

$$c_i = \frac{\partial N_{B_i}}{\partial N_A}\left(1 - \frac{1}{n_i}\right). \tag{27-3}$$

It should point out that in the Eq. (27), $\ln c_{B_i} \to -\infty$ when $c_{B_i} \to 0$, but when $c_{B_i} = 0$, the constant $c_i = \frac{\partial N_{B_i}}{\partial N_A}\left(1 - \frac{1}{n_i}\right)$ must be zero because $N_{B_i} = 0$. So the term $c_i \ln c_{B_i} = 0$ when $c_{B_i} \to 0$. it is easy to find constants a, b_i, and c_i from experimental data.

We prove Eq. (27) by using ternary mobile phase (hexane, ether and dichloromethane) for 11 solutes. In the experiment, the high performance liquid chromatograph LC-Series 4 (made in PERKIN-ELMER Company in U. S) is used, chromatographic column packed with 5μ silica is installed. Data processing is carried out on the Data Station 3600.

For ternary mobile phase, the Eq. (27) can be written as

$$\ln k' = a + b_1 c_{B_1} + b_2 c_{B_2} + c_1 \ln c_{B_1} + c_2 \ln c_{B_2}. \tag{28}$$

In the Table 1, the k' values calculated form Eq. (28) and those from the experiment are listed. There is a better coincide with both k' values in the wide concertration range. In the Table 2, we give the constants a, b_1, b_2, c_1 and c_2

Table 1

The Experimental k' and Calculated k' for 4 Solutes at 35 Concentration Points of Ternary Mobile Phase

Concentration		Anthracene		Benzonitrile		Nitrobenzene		Benzyl Alcohol	
c_{B_1}	c_{B_2}	k'_e	k'_c	k'_e	k'_c	k'_e	k'_c	k'_e	k'_c
0.002	0.01	0.66	0.60	13.45	11.65	4.05	3.18	19.35	16.38
0.002	0.05	0.46	0.51	8.68	7.83	2.55	2.32	13.11	11.89
0.002	0.1	0.36	0.40	6.64	6.07	2.00	1.81	10.17	9.71
0.002	0.2	0.22	0.25	3.15	4.14	1.16	1.20	5.52	7.21
0.002	0.3	0.16	0.15	2.26	2.98	0.83	0.82	4.04	5.58
0.002	0.7	0.04	0.02	0.84	0.93	0.32	0.19	1.74	2.26
0.004	0.01	0.48	0.47	8.71	7.65	2.64	2.40	12.65	10.43
0.004	0.05	0.36	0.40	5.74	5.14	1.79	1.75	9.12	7.57
0.004	0.1	0.29	0.31	4.51	3.98	1.41	1.36	7.29	6.18
0.004	0.2	0.19	0.19	2.85	2.72	0.91	0.90	4.59	4.59
0.004	0.3	0.13	0.12	1.76	1.96	0.68	0.62	3.52	3.55
0.004	0.7	0.01	0.02	0.59	0.61	0.04	0.14	1.44	1.44
0.01	0.01	0.34	0.34	4.37	4.37	1.60	1.65	6.16	5.73
0.01	0.05	0.26	0.29	3.23	2.94	1.14	1.21	4.92	4.16
0.01	0.1	0.20	0.23	2.20	2.28	0.84	0.94	3.53	3.40
0.01	0.2	0.15	0.14	1.55	1.56	0.59	0.62	2.43	2.52
0.01	0.3	0.10	0.09	1.14	1.12	0.44	0.42	1.98	1.95
0.01	0.7	0.01	0.01	0.40	0.35	0.15	0.10	0.80	0.79
0.1	0.01	0.16	0.15	0.89	1.02	0.59	0.61	0.95	1.22
0.1	0.05	0.14	0.13	0.70	0.69	0.48	0.45	0.82	0.89
0.1	0.1	0.09	0.10	0.49	0.53	0.30	0.35	0.66	0.72
0.1	0.2	0.06	0.06	0.34	0.36	0.21	0.23	0.48	0.54
0.1	0.3	0.04	0.04	0.22	0.26	0.13	0.16	0.39	0.42
0.1	0.7	0.00	0.00	0.08	0.08	0.04	0.04	0.19	0.17
0.3	0.01	0.11	0.10	0.43	0.46	0.33	0.34	0.46	0.54
0.3	0.05	0.10	0.08	0.34	0.31	0.27	0.25	0.39	0.39
0.3	0.1	0.08	0.07	0.25	0.24	0.21	0.20	0.36	0.32
0.3	0.2	0.04	0.04	0.17	0.16	0.14	0.13	0.24	0.24
0.3	0.3	0.03	0.03	0.11	0.12	0.08	0.09	0.19	0.18
0.3	0.7	0.00	0.00	0.04	0.04	0.03	0.02	0.10	0.07
0.6	0.01	0.06	0.07	0.19	0.25	0.17	0.21	0.23	0.29
0.6	0.1	0.03	0.05	0.15	0.13	0.12	0.12	0.17	0.17
0.6	0.2	0.03	0.03	0.10	0.09	0.09	0.08	0.14	0.12
0.6	0.3	0.02	0.02	0.07	0.06	0.06	0.05	0.12	0.10
0.9	0.05	0.05	0.05	0.10	0.11	0.09	0.11	0.13	0.14

Note: c_{B_1}——the concentration of ether,
c_{B_2}——the concentration of dichloromethane,
k'_e——experimental k',
k'_c——calculated k'.

that are calculated from experimental data. The average deviations of experimental k' from the calculated k', $\Delta=\frac{1}{N}\sum_{i=1}^{N}[(k'_e)_i-(k'_c)_i]$ are also listed in Table 2.

Table 2

The Constants in Eq. (28) and Average Deviations of Experimental k' From the Calculated k' for 11 Solutes

Solutes \ Constants	a	b_1	b_2	c_1	c_2	N	Δ
Fluoranthene	−2.38	−0.50	−3.55	−0.28	−0.074	35	0.0081
O-Nitrotoluene	−2.68	−0.34	−2.71	−0.50	−0.16	35	−0.0065
p-Nitrotoluene	−2.81	−0.42	−2.67	−0.55	−0.18	35	0.0025
O-Nitrochlorobenzene	−1.65	−0.76	−2.89	−0.32	−0.25	35	0.031
P-Nitrochlorobenzene	−2.97	−1.38	−2.23	−0.51	−0.18	35	0.025
Propyl Benzoate	−3.18	−0.64	−2.29	−0.80	−0.14	34	0.027
Methyl Phenyl Ketone	−1.61	−0.61	−2.11	−0.73	−0.11	30	0.10
Anthracene	−2.56	−0.21	−4.89	−0.35	0.015	35	−0.0043
Benzonitrile	−2.13	−0.65	−2.54	−0.61	−0.18	35	0.094
Nitrobenzene	−1.83	−0.69	−3.38	−0.40	−0.11	35	0.040
Benzyl Alcohol	−1.92	−0.54	−1.94	−0.65	−0.15	35	0.18

Note: $\Delta = \frac{1}{N}\sum_{i=1}^{N}[(k'_e)_i - (k'_c)_i]$.

N——The number of experimental datapoints.

III. A Fundamental Retention Equation for Weak Dissociative Solute

Let solute H_2A be a weak acid, the dissociation equilibriums would exist in the mobile phase:

$$H_2A^m \xrightleftharpoons{K_1} HA^{-m} + H^+, \tag{29}$$

$$HA^{-m} \xrightleftharpoons{K_2} A^{=m} + H^+. \tag{30}$$

On the adsorbent surface, there are the equilibriums

$$H_2A^m \xrightleftharpoons{K_3} H_2A^a, \tag{31}$$

$$H_2A^a \xrightleftharpoons{K_4} HA^{-a} + H^+, \tag{32}$$

$$HA^{-a} \xrightleftharpoons{K_5} HA^{-m}. \tag{33}$$

The superscript "a" stands for the adsorption, "m" for the mobile phase, capital K represents equilibrium constant. When equilibriums between the mobile phase and adsorbent surface are established, we can write following expressions for Equilibriums (29) to (32)

$$K_1 = \frac{[HA^{-m}][H^+]}{[H_2A^m]}, \tag{34}$$

$$K_2 = \frac{[A^{=m}][H^+]}{[HA^{-m}]}, \tag{35}$$

$$K_3 = \frac{[\mathrm{H_2A^a}]}{[\mathrm{H_2A^m}]}, \tag{36}$$

$$K_4 = \frac{[\mathrm{HA^{-a}}][\mathrm{H^+}]}{[\mathrm{H_2A^a}]}. \tag{37}$$

The mass distribution ratio α of solute H_2A between the mobile phase and stationary phase is

$$\alpha = \frac{[\mathrm{H_2A^a}] + [\mathrm{HA^{-a}}]}{[\mathrm{H_2A^m}] + [\mathrm{HA^{-m}}] + [\mathrm{A^{=m}}]}. \tag{38}$$

From the Eq. (34) to Eq. (37), we obtain

$$\alpha = K_3 \frac{1 + K_4/[\mathrm{H^+}]}{1 + K_1/[\mathrm{H^+}] + K_1K_2/[\mathrm{H^+}]^2}, \tag{39}$$

where

$$K_4/[\mathrm{H^+}] = [\mathrm{HA^{-a}}]/[\mathrm{H_2A^a}]. \tag{40}$$

For non-ion-exchangeable stationary phase, the adsorption of ion HA^- is much smaller than that of molecule H_2A, then $K_4/[H^+] \ll 1$, Eq. (39) can be written as

$$\alpha = K_3 \frac{1}{1 + K_1/[\mathrm{H^+}] + K_1K_2/[\mathrm{H^+}]^2}. \tag{41}$$

Therefore the logarithm of the capacity factor can be expressed as

$$\begin{aligned}\ln k'_{\mathrm{acid}} &= \ln\left(\alpha \frac{V_S}{V_0}\right) = \ln\left(K_3 \frac{V_S}{V_0}\right) - \ln(1 + K_1/[\mathrm{H^+}] + K_1K_2/[\mathrm{H^+}]^2) \\ &= \ln k' - \ln(1 + K_1/[\mathrm{H^+}] + K_1K_2/[\mathrm{H^+}]^2),\end{aligned} \tag{42}$$

where V_S/V_0 refers to the phase ratio. Substituting Eq. (27) into Eq. (42), the retention equation of weak acid can be obtained

$$\ln k'_{\mathrm{acid}} = a + \sum_{i=1}^{n} b_i c_{\mathrm{B}_i} + \sum_{i=1}^{n} c_i \ln c_{\mathrm{B}_i} - \ln(1 + K_1/[\mathrm{H^+}] + K_1K_2/[\mathrm{H^+}]^2). \tag{43}$$

For monoacid, K_2 is equal to zero, then,

$$\ln k'_{\mathrm{acid}} = a + \sum_{i=1}^{n} b_i c_{\mathrm{B}_i} + \sum_{i=1}^{n} c_i \ln c_{\mathrm{B}_i} - \ln\left(1 + \frac{K_1}{[\mathrm{H^+}]}\right). \tag{44}$$

With similar method, the same expressions can be derived for a weak organic base and amphoteric compound, the results are as follows:

$$\begin{aligned}\ln k'_{\mathrm{base}} = a &+ \sum_{i=1}^{n} b_i c_{\mathrm{B}_i} + \sum_{i=1}^{n} c_i \ln c_{\mathrm{B}_i} - \ln(1 + 10^{14}K_1[\mathrm{H^+}] \\ &+ 10^{28}K_1K_2[\mathrm{H^+}]^2),\end{aligned} \tag{45}$$

$$\ln k'_{\mathrm{am}} = a + \sum_{i=1}^{n} b_i c_{\mathrm{B}_i} + \sum_{i=1}^{n} c_i \ln c_{\mathrm{B}_i} - \ln\left(1 + \frac{K_a}{[\mathrm{H^+}]} + 10^{14}K_b[\mathrm{H^+}]\right). \tag{46}$$

The validity of Eq. (43) to Eq. (46) was proven by the experimental results[14].

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