Calculation of sorption isotherms from the retention parameters in high-performance liquid chromatography

Sergei N. Lanin,* Mariya Yu. Ledenkova and Yuri S. Nikitin

Department of chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation.
Fax: +7 095 932 8846; e-mail: SNLanin@phys.chem.msu.ru

DOI: 10.1070/MC2000v010n01ABEH001191

A new rapid method for the calculation of sorption isotherms from the dependence of retention volumes on concentrations with the use of an equation in the form of virial expansion was suggested.

Recently, studies of sorption from solutions particularly at low concentrations are often carried out by HPLC. HPLC is a unique combination of a directly studied sorption system and a highly sensitive measuring instrument.

In chromatography, the calculation of sorption isotherms by the Glueckauf method[1,2] is commonly used. The disadvantages of this method are due to the fact that in real chromatography the conditions of ideal equilibrium chromatography with the instantaneous establishment of equilibrium are not always met; *i.e.*, the Glueckauf method does not take into account factors occurring in real chromatography, such as diffusion broadening of chromatographic zones and mass transfer dispersion process of sorbate between the mobile and stationary phases.[3–5]

Huber[6–7] has improved the Glueckauf method; he found that a curve drawn through peak tops approximates the elution curve for the case of ideal equilibrium chromatography. A near-equilibrium sorption isotherm can be calculated by the Glueckauf method. However, the necessity of the determination of chromatographic peak and adsorption areas in the Glueckauf and Huber methods complicates the calculation of sorption isotherms and introduces errors due to an inaccuracy of the determination of these areas.

The purpose of this work was to develop a new rapid method for the calculation of sorption isotherms from chromatographic data (retention values and chromatographic peak heights).

The normal-phase HPLC measurements were conducted on a Milikhrom-1 microcolumn chromatograph with a syringe pump (the mobile phase flow rate 2–600 μl min^{-1}) and a spectrophotometric UV detector (spectral range 190–360 nm). The sorbates (benzene, nitrobenzene and anisole) were injected into the chromatographic column with a needle by a stopped-flow technique. A steel column (120×2 mm) was packed with Silasorb-300 hydroxylated silica with a specific surface area of 300 m^2 g^{-1} and a particle diameter of ~5 μm (the adsorbent mass in the column $m = 0.2\pm0.005$ g). *n*-Hexane used as a mobile phase was dried with zeolite NaA (heated for 4 h at 450 °C) for 2–3 days. Experimental conditions: mobile phase flow rate $w = 100$ μl min^{-1}, room temperature, detection at 254 and 300 nm. The injected sample volume was 1–25 μl. The dead volume (V_0) was determined by measuring the elution time of a practically unsorbed substance, CCl_4. The corrected retention volume $V'_{\mathrm{R,g}}$ was determined by the equation $V'_{\mathrm{R,g}} = (V_{\mathrm{R}} - V_0)/m$.

It is known from the theory of equilibrium chromatography[4,8] that

$$V'_{\mathrm{R,g}} = \frac{\mathrm{d}a}{\mathrm{d}c} = v_{\mathrm{m}}\frac{\mathrm{d}a}{\mathrm{d}X_{\mathrm{s}}}\,, \qquad (1)$$

where $V'_{\mathrm{R,g}}$ is the corrected retention volume per gram of adsorbent, a is the Gibbs adsorption, v_{m} is the average mole volume of a binary solution of the mobile phase (*i.e.*, the mixture of a solvent and an adsorbate), c and X_{s} are the equilibrium concentration and the mole fraction of the sorbate, respectively, as determined from the calibration functions $c = f(h)$ or $X_{\mathrm{s}} = f(h)$, where h is the detector response. Usually, the detector response is directly proportional to the substance concentration $c = Kh$, where K is constant for a given adsorbate and a given detector sensitivity.

Table 1 Dependence of the retention volume of sorbate (V'_v) on equilibrium concentration (X_{s}).

Sorbate	Equation $V'_v = f(X_{\mathrm{s}})$	Correlation coefficient
Benzene	$V'_v = 4.518\times10^6X_{\mathrm{s}}^2 - 0.156\times10^6X_{\mathrm{s}} + 6500$	0.9958
	$V'_v = -1756.8\times10^6X_{\mathrm{s}}^3 + 37.782\times10^6X_{\mathrm{s}}^2 - 0.3514\times10^6X_{\mathrm{s}} + 6900$	0.9979
Anisole	$V'_v = 740.744\times10^7X_{\mathrm{s}}^2 - 516.166\times10^5X_{\mathrm{s}} + 113128$	0.9686
	$V'_v = -365.708\times10^{10}X_{\mathrm{s}}^3 + 294.654\times10^8X_{\mathrm{s}}^2 - 848.870\times10^5X_{\mathrm{s}} + 122196$	0.9921
Nitrobenzene	$V'_v = 513.328\times10^7X_{\mathrm{s}}^2 - 470.884\times10^5X_{\mathrm{s}} + 136561$	0.9685
	$V'_v = -171.672\times10^{10}X_{\mathrm{s}}^3 + 201.102\times10^8X_{\mathrm{s}}^2 - 838.488\times10^5X_{\mathrm{s}} + 159140$	0.9924

The sorption values for any type of isotherms can be calculated from the retention volumes by integrating equation (1). If the virial expansion equation is used for describing the retention volume $V'_{\mathrm{R,g}}$ as a function of the adsorbate mole fraction X_{s},

$$V'_v = V'_{\mathrm{R,g}}/v_{\mathrm{m}} = b_0 + b_1X_{\mathrm{s}} + b_2X_{\mathrm{s}}^2 + \ldots\,, \qquad (2)$$

then sorption can be calculated by the equation

$$a = b_0X_{\mathrm{s}} + b_1X_{\mathrm{s}}^2/2 + b_2X_{\mathrm{s}}^3/3 + \ldots + \mathrm{const} \qquad (3)$$

on the assumption that $X_{\mathrm{s}} \to 0$, the sorption $a \to 0$ and const $\to 0$ and equation (3) takes the form

$$a = c_0X_{\mathrm{s}} + c_1X_{\mathrm{s}}^2 + c_2X_{\mathrm{s}}^3 + \ldots\,, \qquad (4)$$

where b_i and c_i are the virial expansion coefficients.

Equation (4) is identical to an equation of sorption in the form of virial expansion, which is derived strictly by methods of statistical[9–11] and classic thermodynamics.[4] It can describe both convex and concave isotherms of sorption. Consequently, equation (2) derived easily from equation (4) can be considered theoretically valid, and it can be used for the calculation of isotherms of sorption.

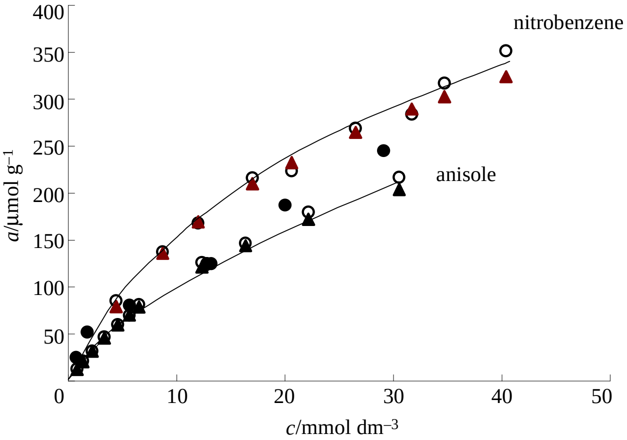

Figure 1 Adsorption isotherms of anisole and nitrobenzene from *n*-hexane on Silasorb-300 hydroxylated silica calculated (▲) by virial equation (3) of fourth degree, (○) by the Glueckauf method, (●) determined by the static adsorption method for anisole.

Table 2 Retention and sorption values of sorbates calculated by different methods.

	Corrected retention volume V'_R/μl	Equilibrium concentration of sorbate in the column c/mmol dm^{-3}	Calculated sorption a/μmol g^{-1}		
			the Glueckauf method	virial equation (3) of third degree	virial equation (3) of fourth degree
Anisole	3044	0.79	12.64	11.38	12.14
	2871	1.37	21.10	19.42	20.54
	2582	2.21	31.57	30.10	31.50
	2297	3.33	46.64	44.49	45.86
	2072	4.56	51.91	58.70	59.64
	1857	5.62	69.81	70.06	70.40
	1816	6.53	81.44	79.19	78.91
	1371	12.32	125.90	125.42	121.45
	1039	16.37	146.60	147.95	144.04
	824	22.15	179.55	170.97	171.93
	555	30.54	217.02	197.19	203.89
Nitrobenzene	3116	4.42	85.41	71.26	79.08
	2179	8.72	137.36	127.41	135.95
	1795	12.0	168.03	162.69	169.56
	1521	17.0	216.01	206.02	209.75
	1157	20.6	223.51	230.15	232.59
	1047	26.5	269.01	261.38	264.72
	863	31.7	283.93	283.03	289.61
	826	34.7	317.00	294.39	302.83
	669	40.4	351.48	315.73	324.0
Benzene	159	25.1	23.5	20.58	21.03
	152	40.9	36.1	32.83	33.26
	149	53.0	47.2	41.90	42.33
	145	64.6	57.2	50.37	50.83
	143	77.2	69.4	55.83	56.29

We obtained asymmetric chromatographic peaks of anisole and nitrobenzene with tailing edges, and the retention times significantly shortened with increasing sample volume. This is consistent with the type of sorption isotherm which is convex to the axis of sorption (Figure 1).

The dependence of the retention volume on the equilibrium sorbate concentration in the mobile phase (for all sorbates the retention decreased with increasing concentration) was processed by polynomials of second and third degrees [equation (2)]. The coefficients of equation (2) were calculated by the regression analysis method; next, the sorption isotherms were calculated using equation (3).

The sorption isotherms for anisole, nitrobenzene and benzene calculated by the Glueckauf method and by equation (3) using the coefficients of equation (2) (see Table 1) are presented in Figures 1 and 2. There is a good agreement between the values of sorption calculated by the Glueckauf method and from the retention volumes calculated by virial equation (3) (Table 2) and those obtained by the static sorption method (Figure 1).

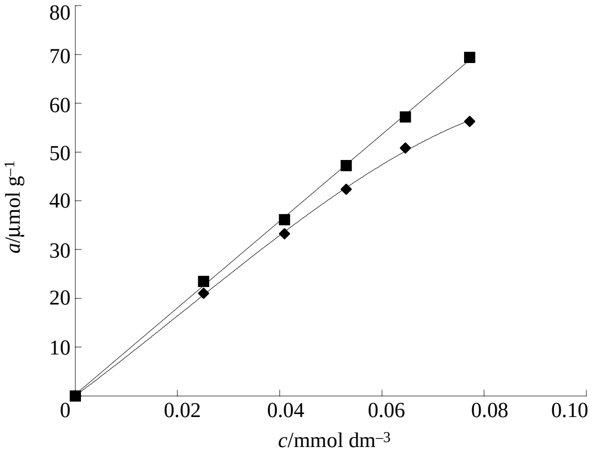

Figure 2 Adsorption isotherms of benzene from n-hexane on Silasorb-300 hydroxylated silica calculated by (◆) virial equation (3) of fourth degree and (■) the Glueckauf method.

Note that the sensitivity of the method suggested is higher than that of the Glueckauf method in calculations of slow-adsorbed substances, for example, the sorption isotherm of benzene. Table 2 indicates that the retention volumes decrease with increasing sample volumes; this corresponds to a convex isotherm. However, a linear sorption isotherm calculated by the Glueckauf method and inconsistent with experimental data (with the peak shape and changes in the retention time) was obtained. This can be explained by lower sensitivity of measurements of the chromatographic peak areas in comparison with the retention volumes.

Thus, the proposed method allows us to measure rapidly isotherms of sorption from a solution with a sufficient accuracy in the region of low concentrations. In this method of processing of chromatographic data, as well as in the Huber method,[7] the influence of diffusion broadening of chromatographic peaks is minimised (unlike the Glueckauf method).

This work was supported by the Russian Foundation for Basic Research (grant no. 98-03-32690).

References

1 E. Glueckauf, *J. Chem. Soc.*, 1947, 1302.
2 E. Glueckauf, *Disc. Faraday Soc.*, 1949, **7**, 199.
3 S. I. Zverev, O. G. Larionov and K. V. Chmutov, *Zh. Fiz. Khim.*, 1974, **48**, 1556 (*Russ. J. Phys. Chem.*, 1974, **48**, 916).
4 A. V. Kiselev, *Molekulyarnye vzaimodeistviya v adsorbtsii i khromatografii* (*Molecular Interactions in Adsorption and Chromatography*), Vysshaya Shkola, Moscow, 1986 (in Russian).
5 A. V. Kiselev and Ya. I. Yashin, *Gas-adsorption chromatography*, New York, Plenum Press, 1969.
6 J. F. K. Huber and A. I. M. Keulemans, in *Gas Chromatography*, ed. M. Van Swaay, Butterworth, London, 1962, p. 26.
7 J. F. K. Huber and R. G. Gerritse, *J. Chromatogr.*, 1971, **58**, 137.
8 F. Riedo and E. J. Kovats, *Chromatographia*, 1982, **239**, 1.
9 W. A. Steel and G. D. Halsey, Jr, *J. Chem. Phys*., 1954, **22**, 979.
10 W. A. Steel, in *The Solid–Gas Interface*, ed. E. A. Flood, Dekker, New York, 1967, vol. 1, p. 199.
11 R. A. Pierotti and H. E. Thomas, in *Surface and Colloid Science*, ed. E. Matijevic, Wiley Interscience, New York, 1971, vol. 4, p. 93.

Received: 15th July 1999; Com. 99/1519