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USE OF THE AXIAL FILTER TO MEASURE LOW DISTRIBUTION COEFFICIENTS

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SUMMARY

Relationships have been derived for determining distribution coefficients in transients observable during axial filtration. Limitation of the technique with respect to film and particle diffusion are discussed. Results obtained by this technique have been compared with results obtained with batch equilibration, for Zn^{2+}/Na^{+} and Cd^{2+}/Na^{+} exchange on Dowex 50W. The axial filtration method should be particularly useful for measuring distribution coefficients with highly dispersed materials such as clays. Results are reported for the adsorption of Sr^{2+} on the sodium form of Wyoming montmorillonite over a wide ionic strength range. These results are in good agreement with literature data on the same system, obtained by batch equilibration and column-elution experiments.

INTRODUCTION

In dealing with equilibria in solid-liquid systems, very often one is interested in obtaining the distribution coefficient of a given species between the two phases. Many methods can be used for this purpose; basically they fall into two general categories: (i) batch equilibration ("shaking") experiments and (ii) column experiments. In the former type of experiments, a solution containing the adsorbate is shaken with a known amount of properly pretreated adsorbent until equilibrium is reached. The distribution coefficient can be evaluated when the liquid and the solid phases are analyzed for the adsorbate (direct experiment). Alternatively the amount of adsorbate on the solid phase can be evaluated by means of a difference experiment in which the liquid phase is analyzed for the adsorbate before and after equilibration. The batch method is convenient for evaluation of distribution coefficients (D) roughly between 10 and 10^3 l/kg (ref. 1). For values of D smaller than *ca.* 10 l/kg or greater than *ca.* 10^3 l/kg various column methods (elution, break-through, or preloaded column techniques) are often more suitable¹.

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To perform a batch equilibration the two phases must be separated, and to run a column experiment successfully, the column must have reasonably good hydraulic permeability. Both conditions are easily met with some adsorbents, such as synthetic ionic exchangers, even if they have small particle size. Many materials (especially natural materials) are made of very fine particles that have a tendency to disperse so that neither condition is easily met. Axial filtration² methods of measuring distribution coefficients can be adapted to measurements with such highly dispersible materials.

The axial filter

Fig. 1 shows a schematic illustration of the axial filter². In this system a cylindrical filter coaxially mounted in a cylindrical sleeve is rotated about its axis. A suspension of the adsorbent is pumped into this chamber and at a sufficiently low rotational speed the adsorbent can deposit as a thin layer on the filter; in this mode the axial filter will work as a very short multiplate column. At a moderately high rotational speed the adsorbent can be suspended and the axial filter will operate as a stirred-tank reactor³. When operated in either mode, the axial filter can be used to measure distribution coefficients. We shall mention a few experiments that might be done with the axial filter to get distribution coefficients spanning several orders of magnitude, and will focus attention on one of them which seems particularly useful in measurement of small distribution coefficients. We want to mention that, in general, the filter can be operated in two different ways for measurement of D : "steady state" and "transient" operation. The difference between the two operations is largely in the analysis of data rather than in the operation itself, so this further subdivision can be more a matter of convenience than of concept.

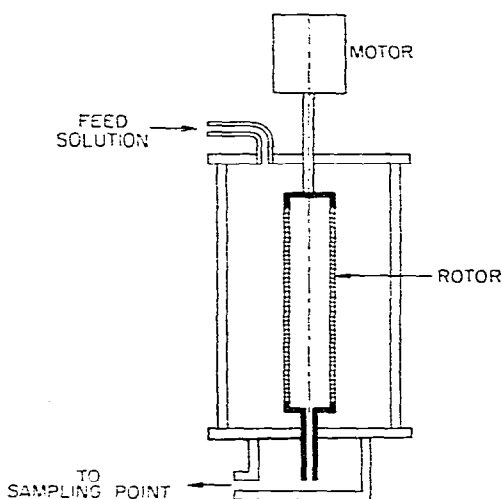


Fig. 1. Diagram of axial filter.

Steady state operation

In one experiment the axial filter might contain the adsorbent already loaded with the adsorbate. If we fill the cell with fresh solution (adsorbate-free) and

circulate the solution in a closed loop, the effluent will eventually contain the adsorbate at constant concentration equal to the equilibrium value for its partition between the solid and the liquid phases. The adsorbent can be collected on the surface of the filter or can be suspended in the liquid phase. In either case, the axial filter will operate essentially as a preloaded column¹. Distribution coefficients from very high to very low can be measured.

The closed loop operation, in addition, should be very useful whenever one is interested in studying the variation of the distribution coefficient with other parameters, like temperature, pH, loading. Obviously in the case of slow adsorption kinetics, a study of the rate of adsorption can be performed with closed loop operation. Alternatively the effluent instead of being recycled can be discharged and fresh solution can be continuously pumped into the cell. Provided the kinetics is favorable (and preferably when D is high), the axial filter, either with the adsorbent collected on the filter or dispersed in the cell, will still operate essentially as a preloaded column.

Mixed mode operation

Some experiments may have characteristics belonging to the "steady state" as well as to the "transient" operation, the distinction being essentially semantic. We will call the corresponding operation "breakthrough" operation because of the evident analogy with corresponding column operation. In this method the adsorbent might not contain the adsorbate. The axial filter could be operated as a column or as a stirred-tank reactor. If a solution containing the adsorbate is pumped into the cell, and the effluent collected and analyzed, a breakthrough curve can be obtained from which D can be extracted. Evidently the breakthrough will be sharper in the column operation than in the stirred-tank operation². With the "mixed mode" operation, distribution coefficients from small to moderately high can be obtained.

Transient operation

In this mode of operation for determining distribution coefficients, the axial filter might contain the adsorbent (not loaded with the adsorbate), either kept in suspension or collected on the surface of the filter. After filling the cell with a solution containing the adsorbate at concentration c_i , another solution, containing the adsorbate at different concentration, is continuously introduced into the cell and the effluent is collected and analyzed. From the transient, a "loading" curve can be constructed from which D can be extracted. Alternatively, if the axial filter contained the adsorbent already in equilibrium with the adsorbate, an "elution" curve can be constructed from the transient obtained by passing through the axial filter fresh (adsorbate-free) solution.

The present paper deals largely with a technique of transient analysis for determining distribution coefficients with the adsorbent uniformly suspended in the cell. The method seems particularly useful for measurement of small to intermediate-size distribution coefficients (i.e. values of D less than about 100 l/kg). After developing the pertinent equations and discussing the film and particle diffusion limitation of the technique, we shall illustrate the reliability of the method with several adsorption reactions involving organic ion exchangers and the clay montmorillonite. The latter was chosen because it represents the group of highly dispersible materials for which the technique seems particularly attractive.

Transient operation—mathematical model

Let V_c be the volume (l) of the chamber filled with a suspension containing an amount w (kg) of the adsorbent whose volume is V_{ads} ; $(V_c - V_{ads})$ liters is the volume of solution S_i in the chamber containing the adsorbate at concentration c_i . If we now pump into the cell another solution (the feed solution, S_f) whose composition is exactly the same as S_i except for the fact that it contains the adsorbate at concentration c_f , the concentration inside the cell (c) and on the adsorbent (\bar{c}) will vary as a function of the volume V of solution S_f passed through the filter, unless $c_i = c_f$. The mass balance when a volume dV of the solution inside the cell is displaced by an equal volume of solution S_f leads to the equation

$$c_f dV = (V_c - V_{ads}) dc + cdV + wd\bar{c} \quad (1)$$

if c is expressed in moles/l and \bar{c} in moles/kg adsorbent.

The functional dependence of \bar{c} on c is the adsorption isotherm. As far as eqn. 1 is concerned, any type of isotherm (e.g., Langmuir, ion-exchange, Freundlich, or complex) is suitable. At high dilution ($c \rightarrow 0$ and $\bar{c} \rightarrow 0$), the isotherm must become linear, where

$$\bar{c} = ac \quad (2)$$

and

$$d\bar{c} = adc \quad (2a)$$

In the present paper we shall restrict ourselves to consideration of linear isotherms only. In a forthcoming paper the effect of loading on the axial filter operation will be studied⁴. In the case of linear isotherms $a = D$ and eqn. 1 becomes

$$c_f dV = (V_c - V_{ads}) dc + cdV + wD dc \quad (3)$$

which can be rearranged to

$$(c_f - c)dV = V_E dc \quad (4)$$

where

$$V_E = V_c - V_{ads} + wD = V_c + w[D - V_{ads}/w] = V_c + w[D - V_{ex}/w - V_d/w] \quad (5)$$

In eqn. 5 we considered V_{ads} to be the sum of two terms: $V_{ads} = V_d + V_{ex}$; V_d/w is the specific volume of the dry adsorbent and is given by $1/\rho$, the reciprocal of the density of the material. V_{ex}/w is a hypothetical specific "exclusion" volume which takes into consideration that the concentration of adsorbate may be smaller within or near the particles of adsorbent than in the bulk solution. With ion

exchangers this term is related to the so-called Donnan effect and often referred to with "ion-exclusion" or "electrolyte exclusion." Although exclusion is generally not complete and can vary with distance from the particle, we shall assume that an equivalent volume V_{ex} , for which $c = 0$, can be identified to satisfy eqn. 5. However, it should be pointed out that the extent of exclusion, and hence V_{ex} , will almost surely vary with conditions such as supporting electrolyte concentration and type of adsorbate considered.

Upon separation of variables, followed by definite integration, eqn. 4 gives

$$-\ln \Phi = V/V_E \quad (6)$$

where

$$\Phi = (c_f - c)/(c_f - c_i) \quad (6a)$$

Thus the slope of a plot of $\ln \Phi$ vs. V yields V_E . When it is combined according to eqn. 5 with the cell volume V_c , the weight of adsorbent w , and $V_d/w = 1/\rho$, an apparent distribution coefficient $D_{obs} = (D - V_{ex}/w)$ may be obtained:

$$D_{obs} = \left(D - \frac{V_{ex}}{w} \right) = (V_E - V_c)/w + 1/\rho \quad (7)$$

Evaluation of the distribution coefficient D requires estimation of (V_{ex}/w) . This term, in many cases, cannot be obtained unambiguously since it corresponds to the (specific) solution volume from which the adsorbate of interest is essentially excluded. D_{obs} becomes essentially equal to the distribution coefficient D only when the specific exclusion volume (V_{ex}/w) is negligible compared with D . For organic ion exchangers, V_{ex} cannot be larger than the volume of the swollen beads which, for reasonably cross-linked materials, is of the order of 1 l/kg. With a highly dispersible material, such as montmorillonite, V_{ex}/w is difficult to establish with confidence.

Thus while the differences $(D - V_{ex}/w)$ can be established from the experimental data with good precision, computation of D requires additional assumptions regarding the value of V_{ex} . The corresponding uncertainty in D may become serious for low values of D and, indeed, incorrect assignment of V_{ex}/w may lead to apparent negative values of D . This difficulty in obtaining D occurs with most methods of determining D and is not a specific "weakness" of the axial filtration method.

Consider, for example, a batch equilibration experiment in which w kg of dry adsorbent are introduced into V_0 liters of solution with adsorbate concentration c_0 . The usual technique to evaluate an observed distribution coefficient D'_{obs} is to measure the final equilibrium concentration c and compute D'_{obs} from the solution volume, V_0 , the difference in concentration (before and after) and the weight of adsorbent by the relationship

$$D'_{obs} = V_0(c_0 - c)/wc \quad (8)$$

From a mass-balance we obtain

$$V_0c_0 = wc + (V_0 - V'_{ex})c \quad (9)$$

where, as before, \bar{c} is the amount of adsorbate per kg of dry adsorbent. The term $(V_o - V'_{ex})$ allows for the fact that, because of exclusion, the volume of solution with equilibrium concentration c , sampled from the clear supernatant, may be less than V_o by an assumed exclusion volume V'_{ex} .

After rearranging terms and setting $\bar{c} = cD$ eqn. 9 yields

$$V_o(c_o - c)/wc = D'_{obs} = (D - V'_{ex}/w) \quad (10)$$

The left hand term of eqn. 10 is identical (see eqn. 8) with the formula for calculating D'_{obs} from the experimental data in batch equilibrations. Formally D'_{obs} obtained from the batch equilibration is thus the same as D_{obs} obtained from axial filtration. In both, a specific exclusion volume term appears explicitly. While V_{ex}/w and V'_{ex}/w in the two types of experiments may be almost identical, it should be pointed out that they could differ because of, for example, differences in compaction of the beds during preparation (centrifugation) of clear supernatants for analysis.

In the derivation of eqn. 6 we assumed that both the injection point and the sampling point are immediately adjacent the cell. In a real experiment the injection point as well as the sampling points are outside and we should "correct" the results for a delay volume V_D to take into account the volume of tubings, fittings, valves, etc. Eqn. 6 then becomes

$$-\ln \Phi = (V - V_D)/V_E \quad (6b)$$

Let us now consider two limiting cases:

$c_i = 0, c_f \neq 0$ ("loading"). In this case $\Phi = 1 - c/c_f$; when the solution S_f is pumped into the axial filter the concentration of adsorbate inside the cell will increase (starting from 0) and will approach asymptotically the value c_f . The concentration profile will be an exponential curve characterized by a "volume constant" $(V_E)_{load}$ (see Fig. 2).

$c_i \neq 0, c_f = 0$ ("eluting"). In the case $\Phi = c/c_i$ and pumping the solution S_f into the axial filter, the concentration of the adsorbate will decrease exponentially (starting from the value c_i) and will approach asymptotically the value 0 with "volume constant" $(V_E)_{elut}$ (see Fig. 2).

When (i) D does not depend on c and (ii) film and particle diffusion⁵ take place in times short compared to the residence time of the adsorbate inside the chamber, $(V_E)_{load}$ and $(V_E)_{elut}$ should be the same. Point (i) can be controlled by working with small concentrations of the adsorbate and systems in the linear isotherm range; film and particle diffusion can be controlled, in principle, by proper choice of experimental conditions such as particle size, weight to volume ratios, stirring (rotational speed of the filter) and proper residence time (varied by varying the flow-rate of the solution).

Film and particle diffusion

In this section we shall give rough estimates of the half life time for film and particle diffusion, as it is evident that these processes play a fundamental role in the axial filtration experiment.

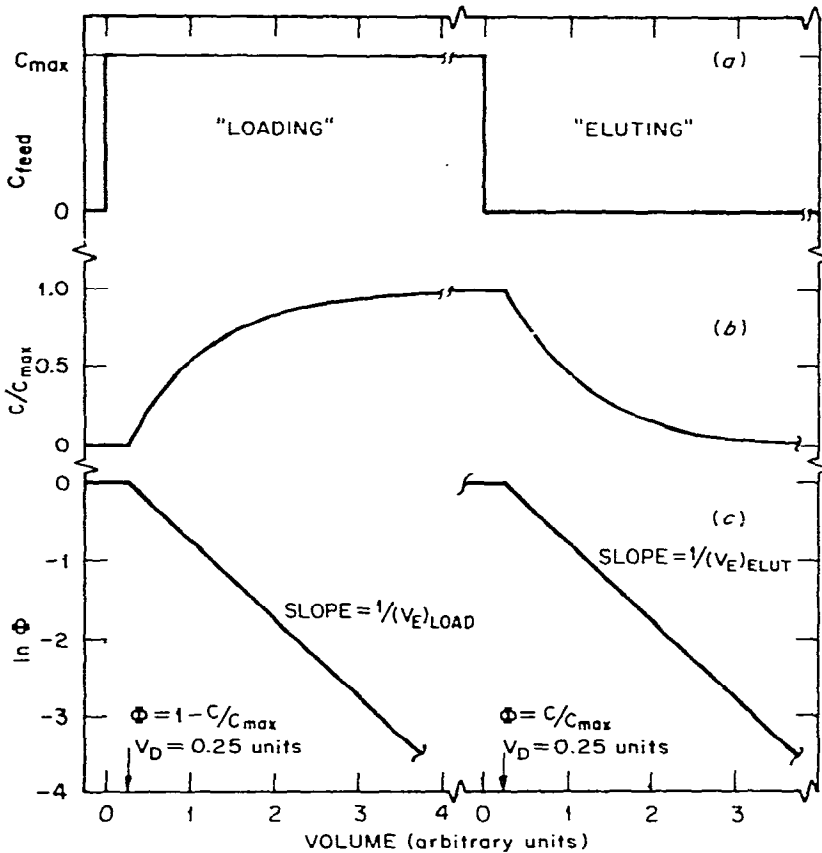


Fig. 2. Diagrammatic representation of "loading" and "eluting" transients in axial filter experiments.

Particle diffusion. In dealing with particle diffusion we will assume that the actual process can be described with sufficient precision by the equations derivable for isotopic exchange in the infinite solution volume approximation⁵. The rationale behind this is that in this application fresh and very dilute solution of the adsorbate is continuously passed through the axial filter and hence past the particles.

The solution of the differential equation for the particle diffusion process for spherical geometry, under the boundary conditions previously mentioned, leads to⁵

$$(t_{1/2})_{pd} = 3.0 \cdot 10^{-2} \cdot r^2/\bar{D} \quad (11)$$

where $(t_{1/2})_{pd}$ is the half life time for the particle diffusion process of the ion having diffusion coefficient \bar{D} (in the adsorbent) and r is the particle radius.

Fig. 3 shows $(t_{1/2})_{pd}$ as a function of the diffusion coefficient \bar{D} of the adsorbate for a few selected bead radii calculated according to eqn. 11. As can be seen, particle diffusion will not be the rate-determining step for the reaction, except for coarse mesh adsorbents and adsorbates with very small \bar{D} . For fine mesh organic exchangers (100–200 mesh, $r \approx 0.005$ cm) and a typical adsorbate with $\bar{D} \approx 10^{-6}$ cm²/sec, $(t_{1/2})_{pd}$ will be of the order of a second. With a dispersible clay with $r \approx 10^{-3}$ cm, $(t_{1/2})_{pd}$ will be in the millisecond range for \bar{D} of 10^{-5} to 10^{-6} cm²/sec.

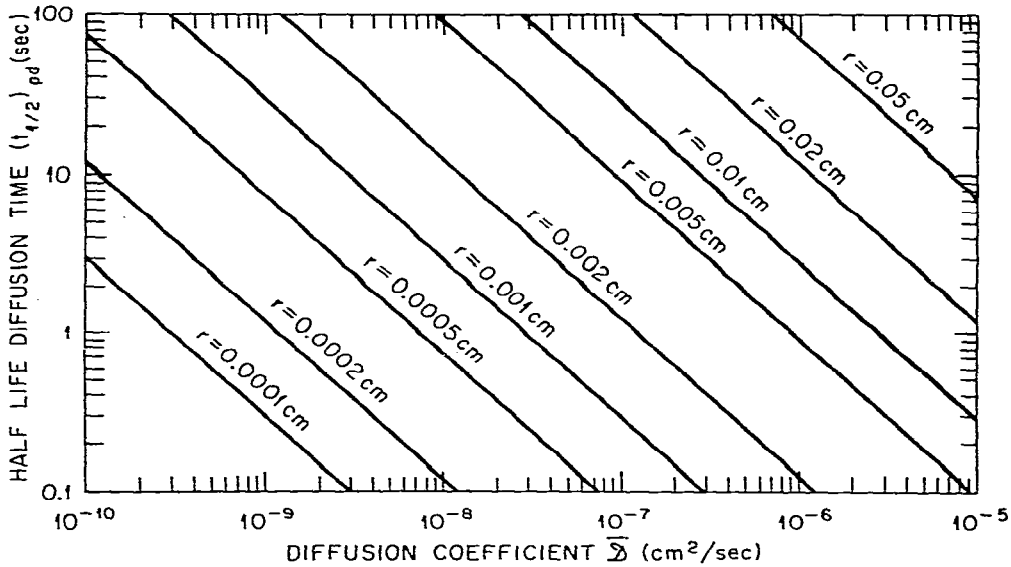


Fig. 3. Effect of radius and diffusion coefficients on particle diffusion.

Film diffusion. Intuition suggests that the film diffusion half life should be a function of the bead radius r , of the diffusion coefficient of the adsorbate in solution \mathcal{D} , of the film diffusion thickness δ , and of the concentrations \bar{c} and c of adsorbate in the adsorbent and in solution, respectively. In this case then, the use of the finite volume approximation⁵ should be a better way to calculate half life time $(t_{1/2})_{fd}$ for the film diffusion process. Under this condition, the solution of the differential equation for the film diffusion process leads to⁵

$$(t_{1/2})_{fd} = 0.23 \frac{r\delta}{\mathcal{D}} \bar{c}V/(\bar{c}\bar{V} + cV) \quad (12)$$

where V and \bar{V} are the volumes of the liquid and solid phases, respectively. Introducing into eqn. 12 the mass transfer coefficient $k_{mt} = \mathcal{D}/\delta$ and the distribution coefficient $D(D = \bar{c}/c)$ one obtains

$$(t_{1/2})_{fd} = 0.23 (r/k_{mt})/(\bar{V}/V + 1/D) \quad (13)$$

We have calculated $(t_{1/2})_{fd}$ as a function of D and of the solid to liquid ratio \bar{V}/V . Irizarry *et al.*³ obtained mass transfer data as a function of flow-rate, resin volume and size, temperature and rotational speed of the axial filter. From their results the value of $k_{mt} \approx 0.01$ cm/sec seems the most appropriate one for the systems we are dealing with in this paper. This value, together with $r = 0.005$ cm has been used in the calculations shown in Fig. 4.

The form of eqn. 13 is such that the influence of D on $(t_{1/2})_{fd}$ will be negligible when \bar{V}/V is large, while it will be important for small values of the solid to liquid ratio. As can be seen in Fig. 4 the values of $(t_{1/2})_{fd}$ will become strongly dependent on D for values of \bar{V}/V less than about 3%. From the point of view of use of the axial filter for measuring D this is unfortunate because the amount of solution and thus the

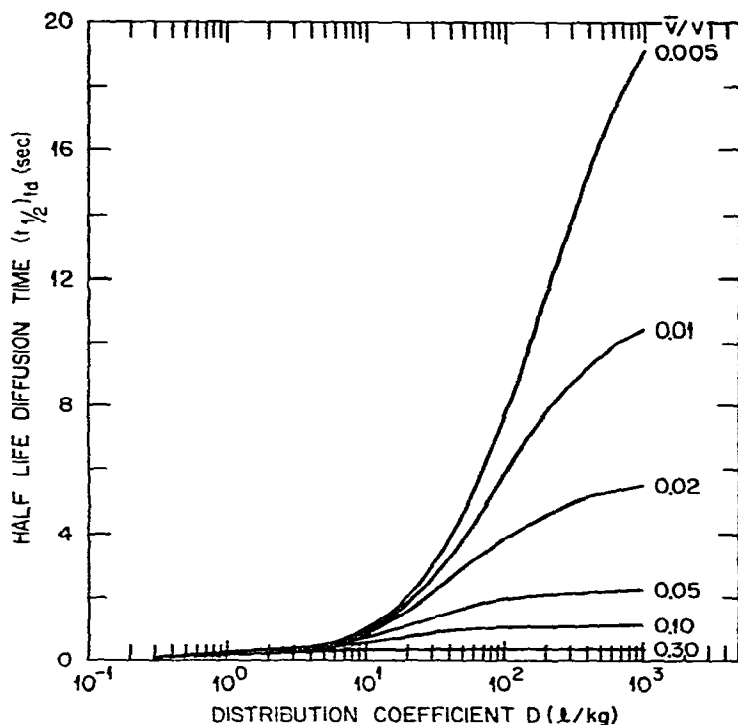


Fig. 4. Effect of volume ratio and distribution coefficient on film diffusion (particle radius 0.005 cm; mass transfer coefficient 0.01 cm/sec).

time required increases with V_E (see eqn. 6) which includes D , and care is required to avoid difficulties from slow film diffusion while minimizing the time required for the experiment.

EXPERIMENTAL

To check the validity of the assumption made to derive eqn. 6b and the method we have studied Zn^{2+}/Na^+ and Cd^{2+}/Na^+ exchange on the sodium form of the synthetic ion exchanger Dowex 50W (Bio-Rad Labs., Richmond, Calif., U.S.A.), using the 100–200 mesh fraction (for which the average bead radius is $r \approx 0.005$ cm) and Sr^{2+}/Na^+ exchange with the sodium form of montmorillonite ($r \ll 10^{-3}$ cm).

All the solutions of supporting electrolyte were made with reagent grade NaCl, and were buffered at pH 5 with sodium acetate–acetic acid buffer. The total sodium concentration was calculated from the composition of the solution. Stock solutions (ca. $1 \cdot 10^{-3}$ M) of Zn^{2+} , Cd^{2+} , and Sr^{2+} were prepared from reagent grade $ZnCl_2$, $CdCl_2$, and $SrCl_2$, respectively. Different aliquots of the same solution were used for batch equilibration and axial filtration experiments.

The resin was washed with methanol and then converted to the sodium form with concentrated NaCl solution. Montmorillonite was purified according to the Jackson procedure⁶ to remove soluble salts, carbonates, “soluble” iron and organic matter. Montmorillonite was then freeze-dried and analyzed for sand, humidity, water content, and NaCl (introduced during the purification), in order to be able to correct the experimental distribution coefficients.

The axial filter was the one designed and used by F. Nelson for most of his work reviewed in ref. 2. All the parts of the axial filter were made of stainless-steel except the external cylindrical sleeve which was made of lucite. The rotor was machined from a rod of stainless-steel and contained a number of 0.2-cm diameter radial holes. The diameter and the length of the rotor were 3.3 cm and 14.0 cm, respectively. The surface of the rotor was first covered with three layers of stainless-steel screen of different mesh sizes and then with a 0.5- μm Acropor AN filter (Gelman, Ann Arbor, Mich., U.S.A.) which was held in place with water repellent tape.

The amount of solution passing through the filter was measured with a digital balance (Digimetric Mod. 30 DTI). Weights were converted to volumes by measuring, with a 25-ml pycnometer, the density of the solution. The weights were corrected for the amount of solution withdrawn for analysis. For the measurements reported in this paper, two different sleeves were used. The corresponding values of the cell volume V_c were determined by performing several "loading" and "eluting" experiments without adsorbent. In a typical experiment the cell was filled with distilled water and a "loading" curve was obtained by pumping into the cell an aqueous solution of $\text{Cu}(\text{NO}_3)_2$ of *ca.* $1 \cdot 10^{-4}$ M. After loading the cell, Cu^{2+} ions were removed with distilled water. Both "loading" and "elution" curves gave the same values of V_c . The values were, for the two cells, 0.192 ± 0.003 l and 0.115 ± 0.002 l, respectively.

Concentrations of Cu^{2+} as well as those of all the other ions studied have been obtained by atomic absorption analysis using a Varian Techtron Model 1000 Instrument.

RESULTS

The main purpose of this paper is to show that the axial filter can be used to measure low distribution coefficients. We will therefore compare the results obtained with the axial filter with those obtained with a traditional method (batch equilibration). Our first goal is then to select the experimental conditions in such a way that the speed of film and particle diffusion is adequate. In the following sections we will then assess the effect of the flow-rate of the solution and of the rotational speed of the rotor on the axial filter results.

Effect of the flow-rate

$\text{Zn}^{2+}/\text{Na}^+$ exchange has been studied in 0.5 M total Na^+ at 2000 rpm. The flow-rate was varied from 0.05 cell volume/min to 0.5 cell volume/min (residence times of 20 min to about 2 min). The expected values of $(t_{1/2})_{pd}$ and $(t_{1/2})_{rd}$ on the basis of eqn. 11 and eqn. 13, respectively, assuming $\bar{V}/V = V_d/V_c$, are about 1 sec. The results of such a study are shown in Fig. 5 and in Table I. The method, a weighted linear least squares, used to calculate values of D_{obs} and the corresponding uncertainties is described in the appendix to this paper. As can be noted there is no significant variation of the distribution coefficient with flow-rate in this region; in addition, there is good agreement between loading ("loading 1, 2") and eluting ("eluting 1, 2") curves, and no systematic deviation from linear behavior described by eqn. 6b has been obtained.

Effect of the rotational speed of the filter

$\text{Zn}^{2+}/\text{Na}^+$ exchange on Dowex 50W at 0.7 M Na^+ was studied as a function of

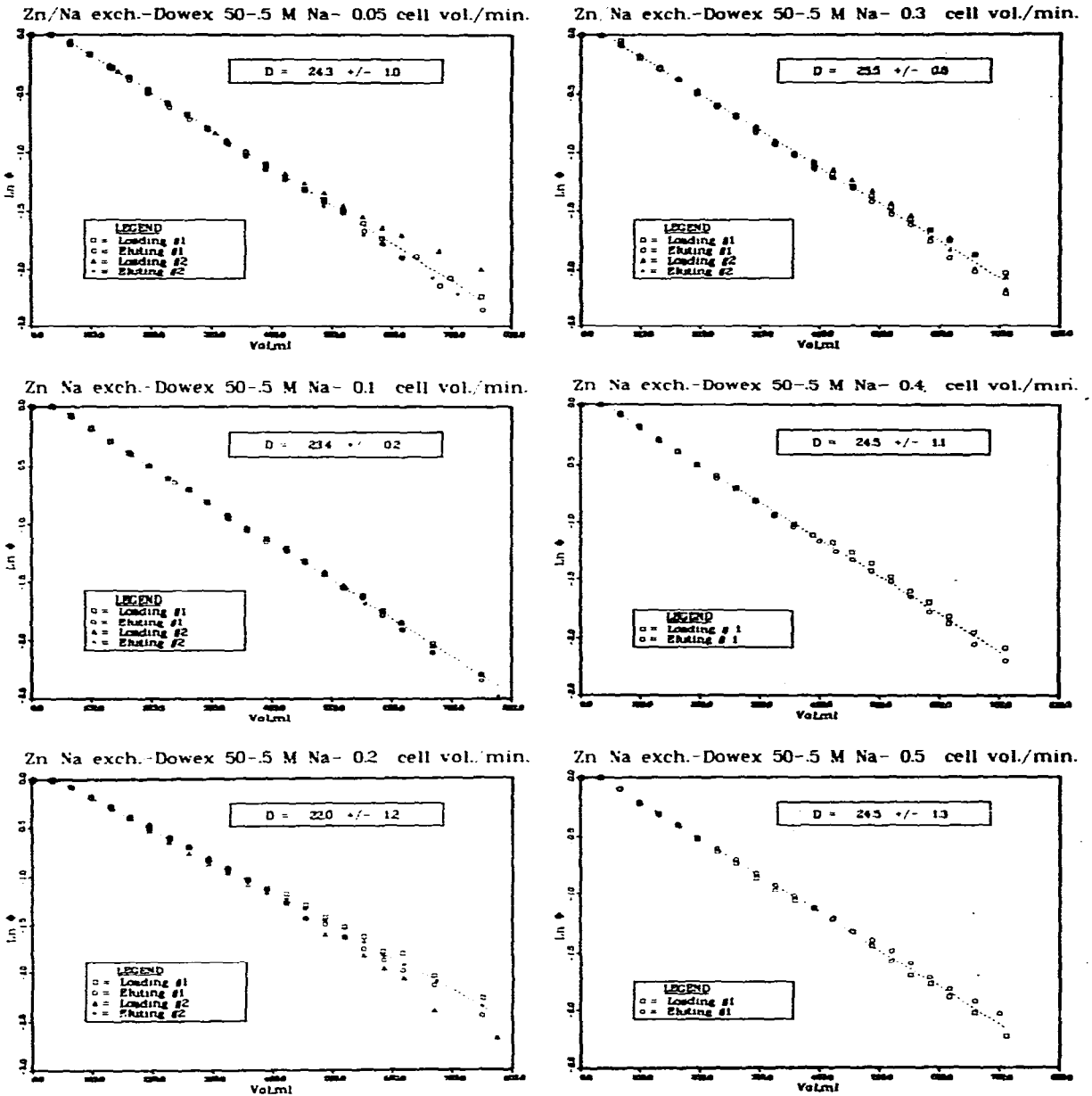


Fig. 5. Effect of residence time on axial filtration transients.

the rotational speed of the filter for 1000 to 3000 rpm at constant flow-rate of about 0.13 cell volume/min. Correspondingly, the residence time was about 8 min while the expected values of $(t_{1/2})_{pd}$ and $(t_{1/2})_{fd}$ are less than *ca.* 1 sec. Results are shown in Table II and Fig. 6. Within experimental error, all the points fall on the same line, and a distribution coefficient of 8.2 ± 0.2 l/kg was obtained.

Less systematic checks on the effect of rotational speeds (between 1500 and

TABLE I

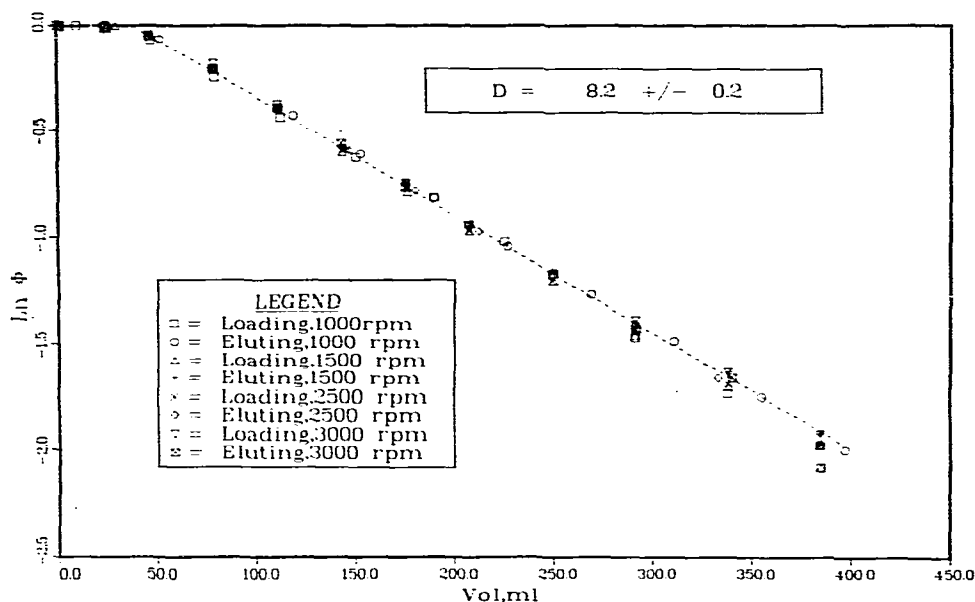
EFFECT OF FLOW-RATE ON DISTRIBUTION COEFFICIENTS (l/kg OF WET RESIN) FOR Zn^{2+}/Na^{+} EXCHANGE ON DOWEX 50WSupporting electrolyte: 0.45 M NaCl + 0.05 M acetate buffer (at pH 5); stirring at 2000 rpm; $V_d/V_c = ca. 0.04$

Flow-rate (cell vol/min)	D_{obs}				
	Loading 1	Eluting 1	Loading 2	Eluting 2	Weighted average
0.05	24.2 ± 0.2	23.4 ± 0.2	26.0 ± 0.4	22.4 ± 0.2	24.0 ± 1.0
0.1	23.4 ± 0.3	23.2 ± 0.3	23.8 ± 0.3	23.0 ± 0.3	23.4 ± 0.2
0.2	23.7 ± 0.4	21.3 ± 0.4	19.0 ± 0.4	24.0 ± 0.4	22.0 ± 1.2
0.3	25.0 ± 0.6	24.4 ± 0.4	27.2 ± 0.4	25.4 ± 0.4	25.5 ± 0.6
0.4	25.5 ± 0.5	23.5 ± 0.5			24.5 ± 1.0
0.5	23.2 ± 0.4	25.8 ± 0.4			24.5 ± 1.3

TABLE II

EFFECT OF STIRRING ON DISTRIBUTION COEFFICIENTS (l/kg OF WET RESIN) FOR Zn^{2+}/Na^{+} EXCHANGE ON DOWEX 50WSupporting electrolyte: 0.65 M NaCl + 0.05 M acetate buffer (at pH 5). Constant flow-rate of 0.13 cell vol/min; $V_d/V_c = ca. 0.04$.

Stirring (rpm)	D_{obs}		
	Loading	Eluting	Weighted average
1000	9.0 ± 1.0	8.3 ± 0.2	8.2 ± 0.2
1500	7.5 ± 0.4	8.4 ± 0.3	
2500	7.5 ± 0.4	8.2 ± 0.4	
3000	8.0 ± 0.4	8.2 ± 0.4	

Fig. 6. Effect of rotational velocity on axial filtration transients. Zn^{2+}/Na^{+} exchange on Dowex 50W

3000 rpm) on apparent distribution coefficients were carried out for Zn^{2+}/Na^+ exchange at 0.2 and 1 M Na^+ and for Cd^{2+}/Na^+ exchange at 0.2, 0.5 and 0.7 M Na^+ . For these, distribution coefficients varied between 1 and 100 l/kg. Estimated $(t_{1/2})_{pd}$ and $(t_{1/2})_{fd}$ were of the order of 1 sec or less. No effect of rotational speed on results was observed.

Study of Zn^{2+}/Na^+ and Cd^{2+}/Na^+ exchange on Dowex 50W at different Na^+ concentrations

Zn^{2+}/Na^+ and Cd^{2+}/Na^+ exchange on Dowex 50W was studied as a function of Na^+ concentration with the axial filter and batch equilibration methods. The results are shown on Table III and in Fig. 7.

TABLE III

EFFECT OF TOTAL Na^+ CONCENTRATION ON DISTRIBUTION COEFFICIENTS (l/kg OF WET RESIN) FOR Zn^{2+}/Na^+ AND Cd^{2+}/Na^+ EXCHANGE ON DOWEX 50W

Supporting electrolyte: $NaCl + 0.05 M$ acetate buffer (at pH 5); stirring at 2500 rpm; residence time 7 min for all Na^+ concentrations but 0.1, for which residence time was 12 min. (All the results reported in this table are self-consistent, in that they have been obtained with the same resin. However, in order to compare the data at 0.5 M Na^+ with data of Table I, correction for the different amount of moisture in the two samples of resin should be made.)

Total Na^+ (M)	D_{obs}						D_{obs} (Batch)			
		V_d/V_c	Loading 1	Elution 1	Loading 2	Elution 2	Weighted average			
	D_{zn}									
0.1	0.0004	609	± 5	473	± 9		535	± 66	751	± 24
0.2	0.03	122	± 5	130	± 5		126	± 4	132	± 1
0.5	0.04	19.2	± 0.2	16.4	± 0.2	17.8 \pm 0.5	17.7	± 0.6	17.8	± 0.5
0.7	0.26			See data in Table II			8.2	± 0.3	8.4	± 0.2
1.0	0.28	4.5	± 0.1			3.7 \pm 0.1	3.8	± 0.1	4.0	± 0.3
	D_{cd}									
0.2	0.03	31.9	± 0.3	33.8	± 0.2		33	± 1	32.0	± 0.5
0.5	0.04	2.4	± 0.4	1.4	± 0.3		2.0	± 0.6	2.3	± 0.1
0.7	0.26	0.92	± 0.05	1.03	± 0.05		1.0	± 0.1	0.91	± 0.05

All batch results are the averages of at least five independent determinations, while the axial filter results are the averages of at least one set of loading and eluting measurements. In all but one case the expected half life time for film and particle diffusion processes was less than about 1 sec and small compared with the residence time of the solution inside the cell. In agreement with eqn. 6b, straight lines of $\ln \Phi$ vs. V were obtained; moreover, agreement between loading and eluting curves was obtained in all the cases except for Zn^{2+}/Na^+ exchange in 0.1 M Na^+ . For this case, although straight lines of $\ln \Phi$ vs. V were obtained for the loading and the eluting curves, the agreement between the two curves was poor. This is not totally unexpected since here the film diffusion process is probably rate determining: in this case, in fact, the calculated value for $(t_{1/2})_{fd}$ was about 50 sec which in this system is too high for adequate measurements of D . On the other hand, excellent agreement between the two methods was found for both Zn^{2+}/Na^+ and Cd^{2+}/Na^+ exchange whenever D was about 100 l/kg or smaller.

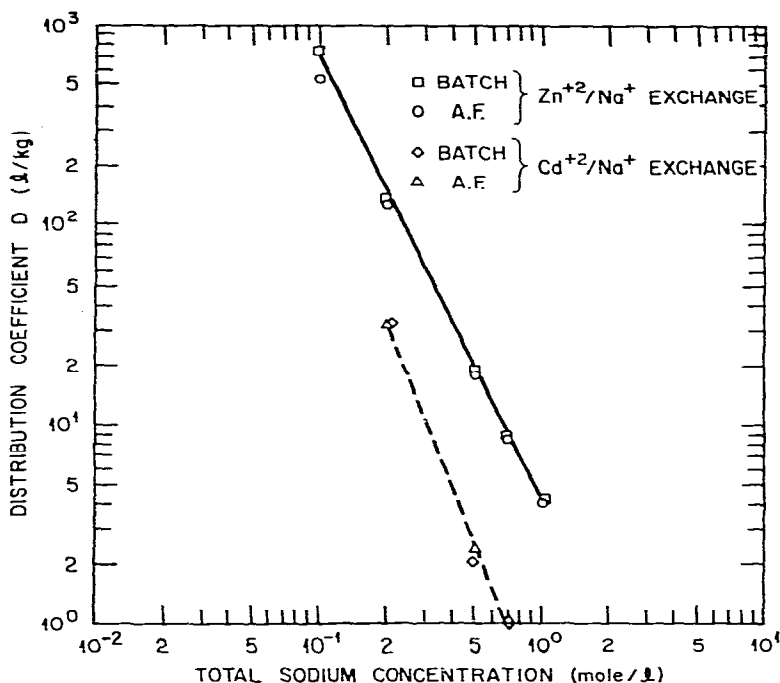


Fig. 7. Distribution coefficient measurements by axial filtration (A.F.) and batch equilibrations.

Measurements with a highly dispersed system

As mentioned earlier we think that the axial filter method is particularly suited for measurements in highly dispersed systems. To demonstrate applicability of the technique we performed a series of experiments with montmorillonite, a clay common in natural geological formations and known to be highly dispersible (especially in media of low ionic strength). We selected adsorption of Sr^{2+} on the sodium form of montmorillonite for investigation, using as supporting electrolyte aqueous NaCl solutions buffered at pH 4.7 with acetate buffer. For this system the speed of film and particle diffusion was expected to be adequate mainly because of the small size of the particles. Typical values of $(t_{1/2})_{pd}$ and $(t_{1/2})_{fd}$ calculated from eqns. 11 and 13, respectively, are of the order of a few milliseconds. The results are shown in Table IV. In two cases we started with the clay already loaded with Sr^{2+} ("loading 1" is therefore missing) while in two other cases, after loading the clay twice we did not elute Sr^{2+} ("elution 2" is therefore missing).

For two solutions, containing Na^+ at 3.6 and 5.0 mole/l, negative values of D_{obs} were obtained. This presumably means (see eqn. 7) that the specific exclusion volume V_{ex}/w is greater than D . Assuming that in the most concentrated solution (5.0 M), the distribution coefficient is negligible ($D = 0$) we estimate for V_{ex}/w a minimum value of about 0.5 l/kg, a surprisingly large value considering the high concentration of the supporting electrolyte. We shall not attempt to derive values of D from D_{obs} , because the specific exclusion volumes V_{ex}/w are expected to be different for the various solutions and because we are only interested here in comparing axial filter and shaking experiments. We think that the exclusion volume correction (eqns. 7 and 10) for both experiments should be practically the same. Fig. 8 shows a comparison of

TABLE IV

Sr²⁺/Na⁺ EXCHANGE ON MONTMORILLONITE

Supporting electrolyte: NaCl with or without acetate buffer; maximum concentration of Sr²⁺ ≈ 1 · 10⁻⁴ M. residence time ca. 12 min.

NaCl (M)	NaAc (M)	pH	V _d /V _c	D _{obs}				
				Loading 1	Elution 1	Loading 2	Elution 2	Weight average
0.30	0.00	6.8	0.04	14.5 ± 0.4	11.7 ± 0.2	13.8 ± 0.3	12.1 ± 0.5	13.1 ± 0.7
0.29	0.01	4.7	0.04	10.3 ± 0.1	9.1 ± 0.2	9.3 ± 0.2	9.2 ± 0.3	9.5 ± 0.3
0.20	0.10	4.7	0.04	11.3 ± 0.3	12.1 ± 0.2			11.7 ± 0.4
0.50	0.00	6.8	0.04		4.4 ± 0.4	6.3 ± 0.4	4.7 ± 0.3	5.2 ± 0.7
0.49	0.01	4.7	0.04	3.9 ± 0.4	4.2 ± 0.3	4.1 ± 0.5		4.1 ± 0.2
0.40	0.10	4.7	0.03	6.7 ± 0.9	4.8 ± 0.9			5.8 ± 1.0
1.00	0.00	6.8	0.05	2.2 ± 0.2	1.2 ± 0.3	1.6 ± 0.2	1.3 ± 0.2	1.5 ± 0.2
0.99	0.01	4.7	0.05	1.7 ± 0.2	1.5 ± 0.1	1.6 ± 0.1		1.6 ± 0.1
1.90	0.10	4.7	0.11	0.2 ± 0.2	0.5 ± 0.1	0.5 ± 0.2		0.4 ± 0.1
3.50	0.10	4.7	0.05		-0.1 ± 0.1	-0.7 ± 0.2	-0.6 ± 0.2	-0.4 ± 0.2
4.90	0.10	4.7	0.05	-0.9 ± 0.2	-0.6 ± 0.3	-0.5 ± 0.2	-0.2 ± 0.1	-0.6 ± 0.2

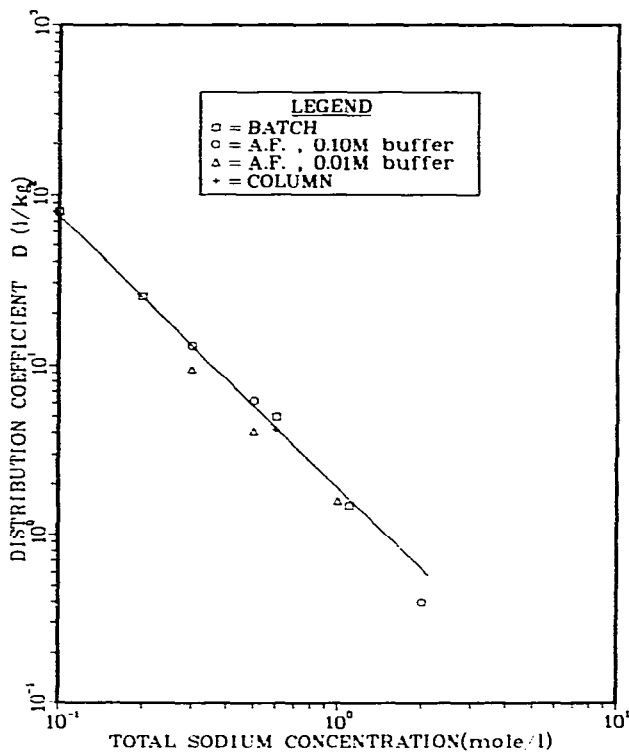


Fig. 8. Adsorption of Sr²⁺ on the Na⁺ form of montmorillonite. Comparison of axial filtration results with other methods.

present data on adsorption of Sr^{2+} on montmorillonite with those obtained in this laboratory by other techniques^{7,8}; as can be noted, the axial filter measurements are in good agreement with both column and batch equilibration measurements. Agreement was also found for an independent set of $\text{Sr}^{2+}/\text{Na}^+$ exchange measurements with the axial filter⁴.

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APPENDIX

Treatment of data

Eqn. 6b of this paper can be written as

$$y = I - k^{-1}x$$

where $y = \ln\Phi$, $I = \text{intercept}$, $k^{-1} = V_E$, and x is the volume of solution past the filter. Value of V_E can be easily obtained by means of a linear least square program provided the points are properly weighted. Assuming that p independent determinations of V_E are available, and indicating with y_{ij} , x_{ij} , and ω_{ij} the values of $\ln\Phi$, V , and of the weight of the j th point of the i th run containing n_i points, we get, for k_i^{-1} and the corresponding standard error,

$$k_i^{-1} = [(\sum_j \omega_{ij} x_{ij})(\sum_j \omega_{ij} y_{ij}) - (\sum_j \omega_{ij})(\sum_j \omega_{ij} x_{ij} y_{ij})]/D_i$$

$$\sigma(k_i^{-1}) = \{E_i \sum_j \omega_{ij} / [D_i(n_i - 2)]\}^{1/2}$$

where

$$D_i = \sum_j \omega_{ij} \sum_j \omega_{ij} x_{ij}^2 - (\sum_j \omega_{ij} x_{ij})^2$$

and

$$E_i = \sum_j \omega_{ij} \delta_{ij}^2$$

with $\delta_{ij} = y_{ij} - (I_i - k_i^{-1} x_{ij})$. To properly choose the weights ω_{ij} it is useful to introduce the dimensionless parameter a_{ij}

$$a_{ij} = \text{MOD} \left[\frac{c_{ij} - c_{\infty i}}{c_{\infty i} - c_{si}} \right]$$

where $c_{\infty i}$ and $c_{s i}$ are the value of concentration of adsorbate in solution at complete loading (or eluting) and at beginning, respectively. For purely random errors, ω_{ij} will be given by⁹

$$\omega_{ij}^{-1} = \left(\frac{\partial y_{ij}}{\partial \alpha_{ij}} d(\alpha_{ij}) \right)^2$$

in our case

$$\omega_{ij} = \alpha_{ij}^2 / [1 + (1 - \alpha_{ij})^2]$$

The weighted average of the p values at k_i^{-1} will be

$$\langle k^{-1} \rangle = \frac{\sum_i \omega_i k_i^{-1}}{\sum_i \omega_i}$$

where $\omega_i = D_i / \sum_j \omega_{ij}$ while its standard error will be

$$\sigma_1 = \left(\frac{\sum_i E_i}{\sum_i \omega_i \sum_i (n_i - 2)} \right)^{1/2}$$

or

$$\sigma_2 = \left[\frac{\sum_i \omega_i (k_i^{-1} - \langle k^{-1} \rangle)^2}{(p - 1) \sum_i \omega_{ij}} \right]^{1/2}$$

whichever is bigger. Evidently the ratio between σ_1^2 and σ_2^2 will give the F test value. From this value the level of confidence can be estimated.

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