

Retrograde adsorption isotherms: An impossible fact?

Friedrich G. Helfferich *

Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802, USA

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Abstract

“Retrograde” adsorption isotherms have been reported, but seem to violate thermodynamics and would cause concentration steps to migrate against the direction of fluid-phase flow. In general, what appears to be retrograde behavior is caused by one or more additional, uncontrolled variables. This is illustrated with adsorption of sulfonate on a weak-acid ion exchanger, where adsorption is accompanied by partial conversion of the ion exchanger to the sodium form.

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1. The problem

Adsorption isotherms are a key factor in chromatography. The steepness of the isotherm is directly related to the velocity with which a concentration or concentration step travels through a chromatographic column (see Eq. (1) farther below), and the isotherm curvature determines whether a concentration variation travels as a shock or a spreading wave. A “retrograde” adsorption isotherm is one with a local maximum at an intermediate fluid-phase concentration (see Fig. 1). Such behavior, first observed in 1944 [1], caused a flurry of excitement in the 1950s [2–3] and has since been reported a number of times in various fields [4–7], mostly, however, in proprietary intra-company literature in petroleum reservoir engineering and geology. Mechanistic explanations that may or may not be correct have been advanced for special cases, but apparently not for the underlying general principle. [The term retrograde is also used for isobaric adsorption with opposite temperature dependences in different temperature regions (see, e.g., ref. [8]), but this will not be discussed here.]

That retrograde isotherms are real has been proved beyond doubt, though they are supposedly impossible. Taken at face value they seem to defy thermodynamics by allowing transfer

of solute from a more dilute to a more concentrated solution without expenditure of free energy. To achieve this, let the adsorbent take up an incremental loading Δq from a large amount of solution of concentration c' , then transfer it to a large amount of solution of higher concentration c'' , into which it will discharge that same incremental loading (see Fig. 1). This hypothetical cycle can be repeated any number of times.

Moreover, a concentration step Δc in a chromatographic column could be made to travel backwards, against the direction of fluid-phase flow [3]. This is best seen from the wave equation of chromatography [9]:

$$v_{\Delta c} = \frac{v^0}{1 + (\rho/\alpha)\Delta q/\Delta c} \quad (1)$$

where $v_{\Delta c}$ is the velocity of step, v^0 the velocity of fluid-phase flow, q the concentration on adsorbent, c the concentration in fluid phase, Δ the difference across step, ρ the weight of adsorbent per unit volume of bed, α the fractional void volume of bed). Since α and ρ are constant, the second denominator term is proportional to the isotherm slope $\Delta q/\Delta c$ averaged over the concentration interval, and the velocity of travel of the step becomes negative if the isotherm slope is negative and steep enough. Of course, reservoir engineers in enhanced oil recovery would love to coax an injected high surfactant concentration back to the injection well bore simple by continuing the injection with a lower concentration!

* Tel.: +1 863 4675; fax: +1 814 865 7846.

E-mail address: fxh1@psu.edu.

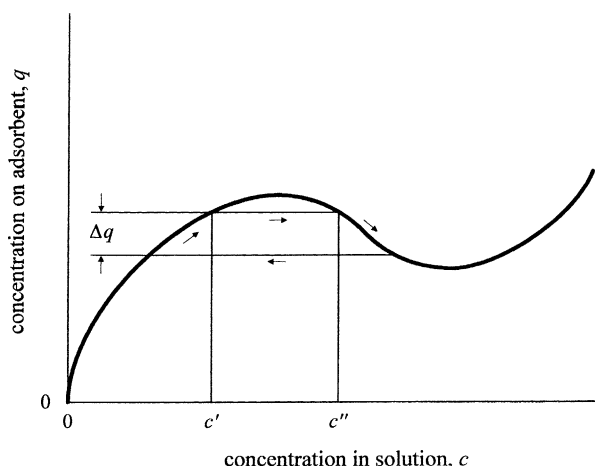


Fig. 1. Retrograde adsorption isotherm with cycle for no-cost transfer of solute from lower to higher concentration (schematic).

[For simplicity, Eq. (1) is written for a sharp concentration step. If the wave is diffuse, the retardation $\Delta q/\Delta c$ must be replaced by a partial derivative $(\partial q/\partial c)_z$, where z is the distance coordinate in the direction of flow [9]. The modified equation then applies at any point within the wave, granted local equilibrium and plug flow. The qualitative conclusions in the present context are not affected by such complications.]

2. The explanation

Needless to say, retrograde isotherms do not disprove thermodynamics. The underlying principle is simply that the solute concentration on the adsorbent depends not only on that in the fluid phase, but also on at least one additional, uncontrolled, “floating” variable. With one such floating variable, x , the real isotherm is not a curve in a two-dimensional plot of q versus c , but a surface $q(c, x)$ in the three-dimensional coordinate system $\{q, c, x\}$, and the points of isotherm measurement trace a path on that surface. This is shown in Fig. 2

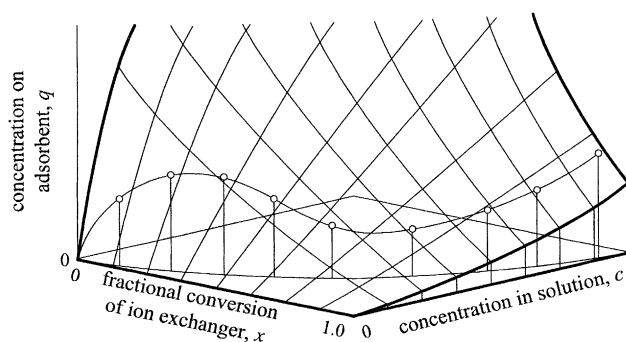
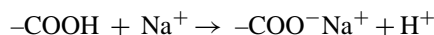


Fig. 2. Isotherm surface q as function of solution concentration c and additional variable x with trace described by standard isotherm measurements (o), as for adsorption of sulfonate anion on ion exchanger with carboxylic acid groups (schematic).

for a situation in which isotherms $q(c)$ at any constant value of x have monotonic positive slopes [and any $q(x)$ at constant c have monotonic negative slopes], yet the results of standard isotherm measurement at different fluid-phase concentrations c and correspondingly different values of x form a trace of retrograde shape on the $q(c, x)$ surface.

There are many different possibilities of what that floating variable x can be. Easiest to understand is a hypothetical case of adsorption of an organic sulfonate R^-Na^+ on an adsorbent with carboxylic acid groups, $-COOH$, that can exchange their hydrogen for sodium. Equilibrium of the adsorbent with solutions of the sodium sulfonate entails ion exchange that converts some acid groups to the sodium form:



In contrast to the almost completely undissociated free-acid form $-COOH$, the sodium form $-COO^-Na^+$ is ionized and the negative charge of the carboxyl groups repels the sulfonate anion and so reduces adsorption (so-called Donnan exclusion of electrolytes [10]). With x as the fraction of the groups converted to the sodium form, the sulfonate anion isotherms $q(c)$ at constant x are steep and Langmuir-shaped (Type I) at low x (undissociated free-acid form), and flat and with opposite curvature (Type III) at high x (dissociated sodium form) as is typical for Donnan exclusion if electrolytes [10]. The higher the solution concentration of the electrolyte, the greater is the extent of conversion of the adsorbent to the sodium form. Accordingly, the measurements of sulfonate adsorption q at different solution concentrations c automatically entail higher x at higher c , and their trace on the isotherm surface is as shown in Fig. 2.

It now becomes apparent that the conjectured no-cost transfer of solute from lower to higher concentration will not work. With repeated exposures to solutions of the sodium sulfonate, the adsorbent becomes largely converted to the sodium form; back and forth transfer then occurs along very flat isotherms near $x = 1.0$ (right-hand edge in Fig. 2). It can also be understood that what goes as retrograde isotherm behavior does not cause a concentration step to move against the direction of fluid-phase flow. In a chromatographic system with a variable x in addition to c and q , any concentration variation at the inlet is propagated not as a single concentration wave, but as two separate, “coherent” waves with different velocities [11]. In the example of sulfonate adsorption, coherence requires equality of $\Delta q_{R^-}/\Delta c_{R^-}$ and $\Delta q_{Na^+}/\Delta c_{Na^+}$ (granted complete dissociation of R^-Na^+ and $-COO^-Na^+$). A negative velocity of either wave would require its Δq_i and Δc_i to have opposite sign for both $i = R^-$ and $i = Na^+$. Instead, normally, Δq_i and Δc_i have the same sign for both $i = R^-$ and $i = Na^+$ in both waves.

This example, intended only to demonstrate the general principle, has been simplified. In a practical situation, micelle formation may occur, and ion exchange with micelles would then have to be accounted for. Moreover, in a surfactant flood in enhanced oil recovery, other cations such as Ca^{2+} are present and exchange with Na^+ and H^+ on the adsorbing

clay and the micelles. Chromatographic behavior with these complications has been elucidated, notably by Hirasaki [12]. Again, all waves advance in the direction of fluid-phase flow.

In general, the surface $q(c, x)$ – or hypersurface $q(c, x_1, x_2, \dots)$ if there is more than one floating variable – can have many different shapes, depending on the nature of x and the values of the respective coefficients. For each floating variable, say, the concentration of an additional sorbable solute, there will be an additional wave in the chromatographic pattern. A discussion of such rather complicated details goes beyond what is appropriate in a communication of only the principle of how retrograde adsorption isotherms can arise.

Can the existence of a floating variable be recognized? Yes, a chromatographic pattern will have more than one wave. Can it be recognized without a chromatographic experiment? Usually yes, in ways that depend on what that variable is. For instance, in our example of sulfonate adsorption, the shape of the observed retrograde isotherm will depend on the ratio of solution and ion exchanger.

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