

ADVANCES IN PAIRED ION CHROMATOGRAPHY

I. ION-INTERACTION MODEL

There continues to be a "substantial amount of activity" (1) in the application of paired ion chromatography to the separation of ionic species by reversed-phase HPLC. Recent reviews give numerous practical examples (2,3). Despite all the interest and activity, there is still a debate concerning the actual mechanism by which Waters' PIC® reagents and similar mobile phase modifiers actually accomplish the separation of ionic samples. Waters made a significant contribution toward the resolution of this controversy through the introduction of the ion-interaction model in 1979 (4).

Before describing the ion-interaction model, it is important to review the two models which existed before 1979, since both of these are still supported by some chemists:

1.) The Paired Ion Model

This simple model states that ion pairs form in the reversed-phase eluent, and that these ion pairs travel through the column as neutral species. This view is contradicted by experimental evidence from conductance titrations, which are the classical means for demonstrating the existence of ion pairs in a solvent. No evidence for the formation of ion pairs was seen at any combination of methanol and water (4) in one study.

2.) The Dynamic Ion-Exchange Model

This simple model states that paired ion reagents operate by first adsorbing onto the bonded alkyl stationary phase and then acting as adsorbed ion-exchange sites. This model is closer to agreement with experimental evidence but does not adequately explain the retention behavior of charged solutes. For example, in some cases a solute with a (2-) charge will be retained less than solutes with a (1-) charge in the presence of an oppositely charged paired ion reagent (4).

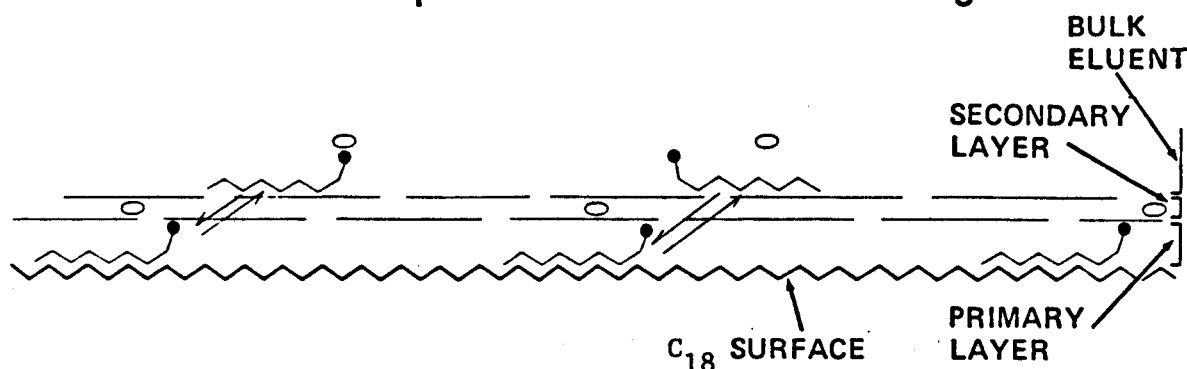
3.) The Ion-Interaction Model

Only the ion-interaction model acknowledges the dual forces which cooperate to bring about retention in paired ion systems: 1) An electrostatic force, and 2) A lipophilic force. Figure 1 depicts the double-layer system which exists in paired ion chromatography, according to the ion-interaction model. A primary layer of PIC® B-8 is shown, adsorbed onto a μ BONDAPAK™ C₁₈ stationary phase. This layer has the negative charge characteristic of the octanesulfonate anions. Nearby is a positively charged secondary layer of inorganic ions (e.g. Na⁺ or K⁺). Beyond this is the bulk eluent, containing an even mix of positive and negative ions. In Figure 1, open circles denote positive charge and filled circles denote negative charge, while zig-zag lines are used to represent an aliphatic carbon chain.

See reverse side for Figures 1 and 2.

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FIGURE 1 Distribution Equilibrium of Ion-Interaction Reagent

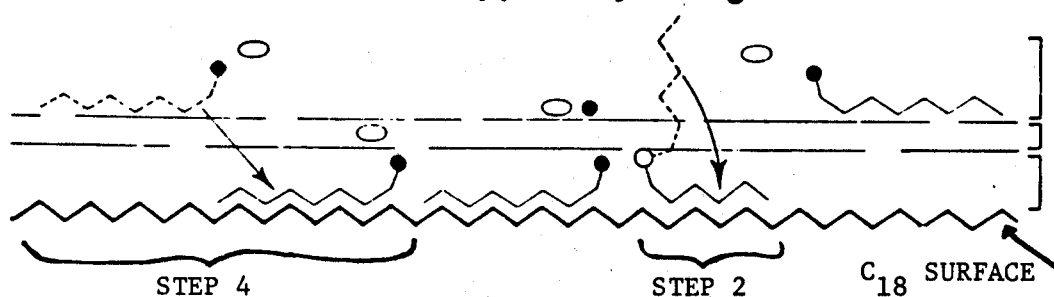


Retention of an oppositely charged sample is indicated in Figure 2. Here the open circles with tails represent a hypothetical positively-charged solute. This solute is retained by the following steps:

1. Solute competes for access to the secondary layer.
2. Solute is electrostatically attracted into the primary layer (see Step 2 below).
3. A lipophilic attraction between the carbon chain of the solute and the μ BONDAPAK™ C₁₈ surface also holds the solute in the primary layer.
4. Now an extra positive charge is present in the primary layer. To maintain electrical neutrality, an additional octanesulfonate ion enters the primary layer (see Step 4 below).
5. At this point, A PAIR OF IONS BUT NOT AN ION PAIR has entered the primary layer due to a combination of electrostatic and lipophilic forces.
6. This sequence is reversed to bring about desorption of a pair of ions (not necessarily the same pair, since a different reagent ion may be desorbed).

The ion-interaction model provides a useful basis for understanding the retention of hydrophilic ions by reversed-phase HPLC. The implications of the model for the design of effective paired ion systems will be discussed in upcoming Lab Highlights of this series.

FIGURE 2 Retention of an Oppositely Charged Molecule



1. Majors, R. E.; Barth, H. G.; Lochmuller, C. H. *Anal. Chem.* (1982) **54**, 323R.
2. Bidlingmeyer, B. A. *J. Chromatogr. Sci.* (1980), **18**, 525.
3. Hearn, M. T. W. *Adv. Chromatogr.* (1980), **18**, 59.
4. Bidlingmeyer, B. A.; Deming, S. N.; Price, W. P.; Sachok, B.; Petrusek, M. *J. Chromatogr.* (1979), **186**, 419.