Journal of Chromatography A, 656 (1993) 549–576
Elsevier Science Publishers B.V., Amsterdam

CHROM. 25 326

Review

Electrical double-layer models of ion-modified (ion-pair) reversed-phase liquid chromatography

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ABSTRACT

Stoichiometric models of ion-modified reversed-phase liquid chromatography are based on chemical equilibria between ionic modifiers and analyte. These are briefly discussed. Non-stoichiometric models portray the ionic solute as being under the summed influence of all of the ions in the system. Chromatographic theories have been developed that are based on the Poisson–Boltzmann equation, which quantitates the summed influence of the ions in the system on the solute. These ideas and quantitative predictions are described and are critically discussed.

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1. INTRODUCTION

In modern reversed-phase liquid chromatography (RPLC) the *non-polar stationary phase* is usually an alkyl bonded phase which is prepared by covalently attaching an alkyl group, via a siloxane linkage, to the surface silanol groups of silica gel [1,2]. This type of packing is a reversed-phase bonded phase (RPBP). A second type of modern stationary phase that is used for RPLC is a non-polar adsorbent, such as a macroporous styrene–divinylbenzene copolymer [3,4] or pyrolytic carbon [1]. The *mobile phase* in RPLC is typically an aqueous solution, which may or may not contain a miscible organic solvent (*i.e.* organic modifier). Under RPLC chromatographic conditions neutral, non-polar analyte compounds are well retained (sorbed) but ionic analytes are weakly retained.

In order to increase the retention and to improve the separation of ionic analyte species, *ion-modified reversed-phase liquid chromatography* (IM-RPLC) is employed. It is often called a ion-pair reversed-phase liquid chromatography (IP-RPLC) or ion interaction chromatography. In this mode of reversed-phase chromatography, a salt composed of a large hydrophobic ion and a small hydrophilic, oppositely-charged ion is added to the aqueous/organic mobile phase. The large hydrophobic ion has been referred to as the *pairing ion* and its salt is the *ion-pair reagent*. In this review they will be called the *modifier ion* ($M^{\pm}$) and the *modifier ion reagent* (MIR). An inert salt, such as sodium dihydrogen phosphate, and a buffer are usually also added to the mobile phase. In the presence of the MIR, analyte ions whose charge is opposite to that of the modifier ion experience a marked increase in retention.

Over the past twenty years, in the liquid chromatography literature, several different interpretations have been proposed to explain this enhanced retention, each of which has employed a different system of nomenclature. In addition, while some of the proposed interpretations have invoked concepts that are well established in the fields of surface and colloid chemistry, other interpretations have been formulated completely in terms of stoichiometric equilibrium expressions.

Therefore, in an attempt to put IM-RPLC in perspective, this review will start with brief discussions of the following topics: the origin of the name "ion-pair chromatography"; the classical surface-science view of ionic sorption; the thermodynamic expression for the capacity factor; the observed sorption behavior of electrolytes on RPBP- and non-polar adsorbent systems; and some questions of nomenclature. In these introductory sections, most of the literature cited as references will be review articles, which give informative overviews of the relevant background concepts.

1.1. *Ion-pair chromatography*

Originally, both normal-phase- and reversed-phase-liquid chromatography were performed in the liquid–liquid partition mode (LLC), in which the stationary phase is a liquid that is immiscible with the mobile phase and is coated as a thin layer on the surface of an inert solid support. This thin layer of liquid stationary phase is thick enough (as in gas–liquid chromatography) that the distribution of solute between the stationary and mobile phases can be treated as a partitioning between bulk liquid phases [5–8], just as in solvent extraction.

Ion-pair solvent extraction, as performed in a separatory funnel, is a well established technique which is understood to involve the presence of actual ion pairs, such as tetra-*n*-butyl-ammonium picrate, in the organic solvent-rich phase [9]. Therefore, when normal-phase- and reversed-phase-liquid–liquid chromatography are performed on ionic analytes in the presence of an ion pair reagent, it is quite appropriate to refer to this as "ion-pair chromatography" [10–14].

Chromatographic *bonded phases* were invented primarily to overcome the volatility of the stationary liquid phase in gas–liquid chromatography [15] and the partial miscibility of the stationary liquid phase with the mobile liquid phase in LLC [16]. At that time, bonded phases in liquid chromatography were popularly viewed as being equivalent to a "mechanically-held liquid phase" [17] having properties resembling, though not identical to, those of a bulk liquid [18–22]. Therefore, it is not surprising that early workers assumed that the enhanced retention of analyte ions which occurs on RPBPs in the presence of "ion-pair reagents" was due to the partitioning of ion pairs into an, essentially, bulk-liquid stationary phase [23–26] and, hence, transferred the name "ion-pair chromatography" from LLC systems, where it was demonstrably appropriate, to RPBP systems where its appropriateness had not yet been experimentally tested. It is worth noting here that, even if the bonded phase does have bulk-liquid solvent properties, the layer of bonded phase is so thin (*e.g.* ≤20 Å for a C_{18} bonded phase [27], that the surface area-to-bonded phase volume ratio is extremely high.

1.2. Surface-science view

The properties of electrically charged interfaces in contact with aqueous electrolyte solutions constitute one of the most important and extensively studied subjects in the field of surface and colloid science. For a sorbent which is neither a metal nor a semiconductor and which does not possess ionizable (*i.e.* ionogenic) surface groups, an electrical charge can be developed at its surface, which is in contact with the solution, as a result of differences in the affinity of the sorbent and the solution phases for ions of one charge or the other [28,29]. This is true whether the sorbent is a solid onto the surface of which selective adsorption of ions occurs from the electrolyte solution, or whether the sorbent is an immiscible liquid into which selective dissolution of ions occurs from the electrolyte solution.

Such systems are treated in terms of electrical double-layer (DL) theory [28–37], according to which the sorbed ion, which will here be called the *potential-producing ion*, PPI, is often considered to be present in a layer at or very near the sorbent-solution interface. (The term potential-producing ion has been coined for this review as a generic and non-specific descriptor of a sorbed ion which contributes to the potential difference between the phases, whether sorbed by adsorption on or dissolution in the reversed phase.) In this introductory discussion of the surface-science view, the case in which the PPI is adsorbed will be the focus of interest. The case in which the PPI is dissolved in a liquid phase rather than begin adsorbed at the interface will be considered later. In the context of IM-RPLC, both the modifier ion $M^{\pm}$ and the sample ion $S^{\pm}$ are PPIs. The resulting *charge-surface* has an electrical potential, Ψ_0, which is different from that in the bulk solution. Nearly always, the potential of the bulk solution is defined as zero. In the simplest version of DL-theory, the Gouy–Chapman theory, there exists in the solution adjacent to this charge-surface an equivalent excess of opposite ionic charge consisting mostly of an excess of ions (*i.e. counterions*) having a sign of charge opposite to that of the PPI. Because of thermal motion, this opposite charge is present not in a thin layer, but rather in a *diffuse layer* which can be from several Ångstroms to several hundred Ångstroms thick, depending on the ionic strength of the solution [29,30,33,35–37].

DL-theory has been widely employed, for many years, to describe the sorption of ions onto minerals and polar adsorbents [28,38,39], onto non-polar adsorbents such as graphitized carbon [40–42], and onto the interface between immiscible liquids [28,33,34,43,44]. In the last of these categories may be included the phenomena giving rise to "liquid-membrane" ion-selective electrodes [34,45] as well as phenomena related to "ion transport between immiscible electrolyte solutions" (ITIES) [34,46,47] and to the development of charge on self-assembled films [48]. More-or-less sophisticated versions of DL-theory have been developed. The more classical ones are summarized in refs. 28–36.

1.3. Thermodynamics of sorption

The strength of sorption of a species i is expressed by its distribution coefficient, K_i. This equilibrium constant is the ratio of the concentration of i on the sorbent phase to its concentration in the solution phase. The units of K_i can be, as examples, $(\text{mol/cm}^2)(\text{mol/cm}^3)^{-1}$ or cm for interfacial adsorption of i; or $(\text{mol/cm}^3)(\text{mol/cm}^3)^{-1}$ or unitless for partitioning of i. K_i is related to the overall free energy of transfer of one mole of i from the bulk solution phase to the sorbent phase, by the expression

$$K_i = B \exp\left(-\frac{\Delta G_i^{\circ\prime}}{RT}\right) \tag{1}$$

where B is the thickness of the adsorbed layer (cm) in the case of adsorption, or it has the unitless value of 1 in the case of partitioning. The use of $\Delta G_i^{\circ\prime}$, rather than ΔG_i°, allows for transfer of i from infinite dilution in bulk solution phase to infinite dilution in the stationary phase without requiring all other conditions, such as ionic strength, in the phases to be standard state conditions. The overall free energy of transfer, $\Delta G_i^{\circ\prime}$, may be viewed as the sum of free energies of transfer arising from differences in several types of "interactions [1,31,32,49]. It incorporates differences in the *enthalpies* arising from ion–dipole interactions, dispersion interactions, coulombic interactions, etc.; as well as differences in *entropies* associated with such effects as translational motions of solute and solvent. Thus, for example, $\Delta G_i^{\circ\prime}$ includes the increase in entropy associated with a decrease in solvent structuring that occurs when solute i leaves the aqueous mobile phase (*i.e.* the so-called "solvophobic effect").

The quantity $\Delta G_i^{\circ\prime}$ pertains to an infinite dilution of solute i in each phase and therefore pertains to the case in which solute species i undergoes interactions with the components of the phases but not with itself or with other solutes. If solute–solute interactions occur in either or both phases, then it is customary to add activity coefficients $\gamma_{i,\mathrm{M}}$ and/or $\gamma_{i,\mathrm{S}}$ as a multiplier or divisor on the right-hand side of eqns. 4 and 5. Theoretical analysis reveals that there is also a solvent-based entropy change that occurs when a solute is transferred into or out of a solution [50]. It arises because the solute and solvent share an increased volume when they form a solution. Inclusion of this effect would result in the inclusion of an additional, molar-volume-based, multiplier term on the right-hand side of eqns. 4 and 5. The magnitude of this solvent-based entropy effect has not been tested in IM-RPLC.

It will be useful in some of the subsequent discussions to distinguish between "electrostatic" (el) and "chemical" (ch) types of interactions [32]:

$$\Delta G_i^{\circ\prime} = \Delta G_{i,\mathrm{ch}}^{\circ\prime} + \Delta G_{i,\mathrm{el}}^{\circ\prime} \tag{2}$$

In this review, only coulombic interactions are included in $\Delta G_{i,\mathrm{el}}^{\circ\prime}$. Other nominally electrostatic interactions (ion–dipole, dipole–dipole, etc.) are included in $\Delta G_{i,\mathrm{ch}}^{\circ\prime}$. Therefore $\Delta G_{i,\mathrm{el}}^{\circ\prime}$ may be expressed in terms of the electrical potential Ψ_x at the location, x, in the sorbent phase at which an ionic species $i^{\pm}$ is sorbed:

$$\Delta G_i^{\circ\prime} = \Delta G_{i,\mathrm{ch}}^{\circ\prime} + Z_i F \Psi_x \tag{3}$$

Here Z_i is the charge (with sign) of ion $i^{\pm}$ and F is the Faraday constant. If the ion $i^{\pm}$ is sorbed onto the charge-surface, then Ψ_x is identical to the surface potential Ψ_0 that was discussed above. Furthermore, these potentials may arise wholly or in part as a result of sorption of the ionic species $i^{\pm}$ itself. Eqn. 3 is often called the "electrochemical potential" of ionic species $i^{\pm}$. Naturally, if the sorbed species i is not an ion then $Z_i = 0$ and $\Delta G_{i,\mathrm{el}}^{\circ\prime} = 0$.

Chromatographically, k_i', the *capacity factor* (mass distribution coefficient) of $i^{\pm}$ is a more directly useful descriptor for the sorption of $i^{\pm}$. The capacity factor is the ratio of the moles of $i^{\pm}$ in the sorbent (stationary) phase to the moles of $i^{\pm}$ in the solution (mobile) phase in the chromatographic column and is related to K_i and to $\Delta G_i^{\circ\prime}$. If the stationary phase region is isoergonic at $\Delta G_{i,\mathrm{ch}}^{\circ\prime}$ and isopotential at Ψ_x, then the relationship is

$$k_i' \equiv \frac{n_{i,\mathrm{s}}}{n_{i,\mathrm{m}}} = \frac{V_\mathrm{s}}{V_\mathrm{m}} \cdot K_i = \frac{V_\mathrm{s}}{V_\mathrm{m}} \cdot B \exp\left(-\frac{\Delta G_i^{\circ\prime}}{RT}\right) \tag{4}$$

$$k_i' = \frac{V_\mathrm{s}}{V_\mathrm{m}} \cdot B \exp\left(-\frac{\Delta G_{i,\mathrm{ch}}^{\circ\prime} + Z_i F \cdot \Psi_x}{RT}\right) \tag{5}$$

(If the stationary phase is not isoergonic or is not isopotential, then $\Delta G^{\circ\prime}_{i,\mathrm{ch}}$ or Ψ_x, respectively, have values that are a function of distance r in the stationary phase and k'_S becomes a function of distance. In this case $\Delta G^{\circ\prime}_{i,\mathrm{ch}}(r)$, $\Psi_x(r)$ and $k'_S(r)$ would replace $\Delta G^{\circ\prime}_{i,\mathrm{ch}}$, Ψ_x and k'_S in eqn. 5 and the equation would have to be summed or integrated over the various sub-regions of the stationary phase.) In eqns. 4 and 5, V_s/V_m is the "phase ratio" of the amount of stationary phase to the amount of mobile phase in the chromatographic column. Note that the product V_sB/V_m must be unitless, so that the symbol V_s need not be volume but may also have other units, such as cm^2, as appropriate to the nature of the stationary phase. V_s may be more generally referred to as "space" in order to include either volume or area [51].

The far-right expression in eqn. 4 reveals that retention of a solute in chromatography can be formulated in terms of two factors. One factor is the free energy, $\Delta G^{\circ\prime}_i$, discussed above, which is an intensive property. The second factor is "space" (*i.e.* volume or surface area), which is an extensive property. In chromatography the space variables V_s and V_m have a statistical character, in the following sense. In either phase the number of locations (*e.g.* sites) onto or into which a solute i can be placed and still have the same free energy is limited both by the fact that i occupies space and by the fact that the free energy of i in a phase is likely to change as the crowding of i in that phase is made greater due, for example, to stronger interactions between i's and to changes in entropy of both solute and solvent. The change in free energy for such reasons is accommodated by including activity coefficients, as discussed above. However, if one ignores this change in free energy with packing density of i, then the total number of isoergonic locations in which i can be placed in a particular phase is equal to the total space available in the initially unoccupied phase divided by the size of the solute i [50]. When some locations in the phase are already occupied by an i molecule (or by another type of solute molecule) then the number of remaining possible locations is reduced. As a result the *probability* of sorbing the next molecule of i is lower in proportion to the number of remaining unoccupied locations, even though $\Delta G^{\circ\prime}_i$ remains (hypothetically) unchanged. It is in this sense that the space-related factors V_s and V_m are statistical factors —their values decrease with loading.

A familiar example in which this statistical effect on k'_i is addressed in chromatography is the use of the Langmuir isotherm to describe what happens in an adsorbent stationary phase. In the simplest version of the Langmuir isotherm for sorption of i, the free-energy $\Delta G^{\circ\prime}_i$ in eqn. 4 is assumed to be independent of the amount of sample sorbed. A more realistic version of the Langmuir isotherm for cases where the adsorbed species is an ion $i^{\pm}$ is the "potential-modified Langmuir isotherm" in which the electrical potential produced by the already-sorbed $i^{\pm}$ ion is recognized as altering the value of $\Delta G^{\circ\prime}_{i,\mathrm{el}}$ and thereby causing $\Delta G^{\circ\prime}_i$ in eqns. 2–4 to become less negative and consequently less favorable for adsorption of additional $i^{\pm}$. (This effect is discussed in more detail below.) Although it is more realistic for the sorption of ions, by virtue of allowing for a change in $\Delta G^{\circ\prime}_{i,\mathrm{el}}$ with increasing sorption of $i^{\pm}$, the "potential-modified Langmuir isotherm" still employs the approximation that $\Delta G^{\circ\prime}_{i,\mathrm{ch}}$ is independent of the amount of sorbed $i^{\pm}$. In principle, inclusion of appropriate activity coefficients in eqns. 4 and 5 would eliminate this approximation, but the values of such activity coefficients are, in practice, not accurately predictable.

From the above discussion it is seen that attempts to include the space-related, statistically produced variation in V_s or V_m generally involve assumptions that are not completely realistic. If $i^{\pm}$ is present in both the sorbent phase and the solution phase at very low concentrations, so that it occupies only a small fraction of the total number of locations in each phase, then V_s, V_m and $\Delta G^{\circ\prime}_{i,\mathrm{ch}}$ will all be constants whose values are essentially independent of the (small) amount of $i^{\pm}$ that is sorbed. In analytical IM-RPLC this is often the situation when $i^{\pm}$ is the sample ion, $S^{\pm}$. However, when $i^{\pm}$ is the modifier ion, $M^{\pm}$, the stationary phase loading is higher and a decision must be made about which errors to incur —those associated with ignoring the statistical effect or those associated with employing something like a "potential-modified Langmuir isotherm" which assumes a particular, and sometimes quite erroneous, shape for the isotherm.

1.4. RPLC of ionic species

Chromatographic studies reveal that ionic species tend to be less strongly sorbed on RP-stationary phases than are non-ionic species with similar structures. This trend is most clearly observed when comparing the retention of an ionic weak acid or base with that of its non-ionic conjugate species [1,3,52]. An exception is zwitterionic species [52]. The important point here, however, is that all of these studies reveal that ionic species are, in fact, sorbed, even in the absence of a modifier ion reagent. Furthermore, a notable characteristic of the sorption of ions is the marked increase in their sorption which occurs when the ionic strength of the solution is increased. Any physico-chemical model that is proposed to explain the sorption of an ionic species on an RPLC sorbent must explain this experimental observation.

Early studies involving sorption of ionic species on modern RP sorbents seem to have ignored the electrical double layer models that were prevalent in the literature of surface science. Instead, they either invoked the formation of a neutral ion pair between the sorbed ion and small inorganic counterions from the mobile phase, such as Na^+ or $H_2PO_4^-$ [53,54]; or they employed a variation of "solvophobic theory" in which the influence of an increasing concentration of inert electrolyte on the retention of an ionic species was said to be due to a combination of a decreasing ionic activity for the ion and an increasing surface tension, in the solution phase [1,54]. The key difference between these models of ionic sorption and the DL models is that the former are not expressed in terms of an electrical potential, Ψ_x, that is created by, and influences further sorption of, the sample ion. In other words they consider only "chemical" contributions to free energy, *i.e.* $\Delta G^{\circ\prime}_{i,\mathrm{ch}}$ in eqns. 2–5.

It wasn't until about 1979 that DL models were proposed to explain the sorption of ions in RPLC-phases. Since then, DL models have been invoked on a regular basis [56–66]. According to this view, if the ion $i^{\pm}$ is sorbed, and if this sorbed ion is the only source of charge in or on the sorbent phase and, therefore, the only source of potential Ψ_x, then it follows that only the "chemical" contributions to the free energy, *i.e.* $\Delta G^{\circ\prime}_{i,\mathrm{ch}}$ in eqns. 2–5, favor the sorption of $i^{\pm}$. Before any i is present $\Delta G^{\circ\prime}_{i,\mathrm{el}} = 0$. As more $i^{\pm}$ is added to the solution, more $i^{\pm}$ is sorbed at equilibrium and consequently Ψ_x increases. However, since Ψ_x has the same sign as does Z_i, the sign of $\Delta G^{\circ\prime}_{i,\mathrm{el}}$ is necessarily positive and therefore leads to a less negative value of the overall $\Delta G^{\circ\prime}_i$ and a smaller value of K_i.

1.5. Sorption of modifier ion

In the original model of IM-RPLC, which was based upon the sorption of ion pairs [14,23–26,55], there was no special role to be played by sorbed modifier ions, and so sorption of the modifier ion was not considered. However, in later non-DL models, including the "dynamic ion exchange" model [67], the "ion interaction" model [68] and later versions of the "ion-pairing" model, including the "dynamic complex exchange" version [1,69–71], sorption of the modifier reagent or of the modifier ion was included and is, of course, required by experimental observation. In DL models (electrostatic models) of IM-RPLC the sorption of the modifier ion is a fundamental requirement and is the principal source of surface charge, σ_0, and surface potential, Ψ_0 [56,60,72].

Essentially, sorption of the modifier ion is the same phenomenon as sorption of an ionic sample. The difference is that the reagent is present at significantly higher concentrations on the sorbent than is the sample ion. This same kind of distinction between reagent and sample, it may be noted, is made in other retention models of IM-RPLC, such as in the "dynamic ion exchange" models where the ion exchange capacity, which is due to the sorbed modifier reagent, is negligibly affected by the sorption of sample ion. In the DL model the modifier ion is the principal PPI, which establishes the value of Ψ_x or the values $\Psi_x(r)$. This value of Ψ_x or these values or $\Psi_x(r)$ influence(s) the sorption of both the modifier ion itself and of the oppositely charged sample ion via an equation of the form of eqn. 5. The sample ion has little effect on the value(s) of Ψ_x or $\Psi_x(r)$ because there is so little of it present.

The fundamental conceptual difference between DL models and non DL models of IM-RPLC is the fact that the electrical potential is included explicitly in the former, as in eqn. 5. Thus, for example, the "ion interaction" model [68] includes a sorbed primary layer of modifier ion and a dissociated secondary layer of oppositely charged inorganic counterion, but the influence of the coulombic attraction of the primary-ion layer for a sample ion is never treated quantitatively, as in the classical surface science approach, in terms of the electrical potential that the modifier ion creates.

1.6. *Terminology*

The word "model" is used in the sense of a physico-chemical description of the equilibrium distribution of the components and species, and of the thermodynamic energy-terms responsible for this distribution. The older word, "mechanism", which was often used in the past and is still sometimes used, is inappropriate to describe the equilibrium condition, as was pointed out several years ago [73]. The term "sorption" is used when it is desired to avoid the question of whether sorbed species are adsorbed onto or partitioned into a bonded phase [51]. As has been stated, DL theory is traditionally applied to both liquid–solid and liquid–liquid interfaces.

A useful distinction has been made between "stoichiometric" and non-stoichiometric" sorption models [69]. Models for which balanced chemical reactions (homogeneous and heterogeneous) can be written and in which the energy changes corresponding to the balanced reactions completely account for the driving force of the sorption in IM-RPLC, are stoichiometric models. Ion-pairing, dynamic ion exchange and ion interaction models are in this category. DL models are, at least in part, non-stoichiometric. The sorption of modifier ions creates the interfacial electrical potential which, in turn, influences the sorption of sample ion, but there is no fixed stoichiometric relationship between modifier ion sorption and sample ion sorption. It should be noted that under some conditions sorption models that are based on DL theory give rise to stoichiometric terms [72,74]. Throughout this review, $M^{\pm}$ is used to represent the modifier ion, $S^{\pm}$ is used for the sample ion and $i^{\pm}$ is used when it is desired to be non-specific.

1.7. *Organization of this review*

The remainder of this paper is organized as follows: First, non-double-layer models are discussed. Following that, double-layer models are considered. Their discussion starts with a qualitative introduction to electrical double layer theory and is followed by examinations of the major DL models that have been applied to IM-RPLC including a surface adsorption DL model, a liquid partition DL model, a surface adsorption, diffuse layer ion-exchange DL model, and a surface ion-exchange, diffuse layer ion-exchange DL model. The discussion concludes with a comparison of these DL models.

When addressing non-DL models there is no attempt made to present details. These have previously been summarized in a variety of excellent reviews which are cited herein. It is assumed that the interested reader will consult them. What is done here regarding non-DL models is simply to make some observations about the assumptions of the models that may not be clearly evident in what has already been written about them.

The purpose is discussing DL models is different. More details are given but, for the sake of brevity only those details are mentioned which are needed to grasp the basic concepts. First an attempt is made to introduce the uninitiated into the mysteries of electrical double-layer theory. Beyond that, the discussion is intended to serve as a "road map" through the major DL models that have been proposed to explain IM-RPLC. It is assumed that the interested reader will have the relevant papers immediately at hand.

Earlier reviews on various models of IM-RPLC may be found in references cited below.

2. NON-DOUBLE-LAYER MODELS OF IM-RPLC

Notable among these are the "ion pairing model", the "dynamic ion exchange model" and the "ion interaction model". The non-DL models are primarily stoichiometric models.

2.1. *Ion-pairing model [12,14,52,69]*

The idea was already discussed that ion pairs have been legitimately invoked in liquid–liquid chromatographic experiments. In bonded-phase chromatography, the surface area/volume ratio of the stationary phase is so high that the surface effects, which in liquid–liquid systems can easily be ignored, tend to dominate the sorptive behavior of solutes. This is not to suggest that ion pairs could not form, or that their formation necessarily does not matter. Rather, it is meant to suggest that bulk phase–bulk phase distribution phenomena may be poor models of bonded phase behavior.

It is intuitive that the attraction between oppositely charged ions will lead to an association between them. Any association between two solutes will lower the chemical potential of both of them. To understand the influence of ion pairing on solute distribution consider first the two phase system, consisting of phase A and phase B, at equilibrium with the two species in the absence of ionic association. The ionic modifier will be distributed between the phases, as will the sample ion. Now, if association occurs between the ionic modifier and the sample ion in phase A only, the chemical potential of both species is reduced in phase A. As a result, the tendency of the sample ion and the ionic modifier to dissolve in (adsorb to) phase A is increased, and some of each ion will move from phase B to phase A.

For the sake of clarity it was assumed that there is no association between sample ion and ionic modifier in phase B. If such association were to exist, then the chemical potential of the sample ion would decrease in each phase, and ionic distribution would occur to the phase in which the activity was lowered the most. Thus, the association of the sample ion with a counterion lowers its chemical potential, and shifts the distribution equilibrium towards the phase in which association predominates.

These phenomena have important practical consequences, namely indirect detection. The chromatographic ramifications of this are as follows. If ion-pair formation occurs in the mobile phase, but not the stationary phase, then the influence of the MIR will be to *decrease* sample ion retention. At the same time, the concentration of the MIR in the mobile phase will be higher in the presence of the sample ion than on either side of the band containing the sample ion. On the other hand if ion-pair formation occurs in the stationary phase, but not the mobile phase, then the influence of the presence of the MIR will be to *increase* sample ion retention. The concentration of the MIR in the sample ion band will be locally higher in the stationary phase.

What conditions favor the formation of ion pairs? Of course, charged species always attract each other, but the attraction is modulated by the solvent dielectric constant and the ionic strength. The dielectric constant is the measure of the ability of the fluid to respond to an electric field; the response is to lower the effective field. In fact, the electric field that exists in a dielectric is a fraction $1/D$ of the field that would have existed in a vacuum. Here D is the dielectric constant of the medium. Solvents of high dielectric constant stabilize charges. In a similar way, by responding to an ion's electric field, other ions which are present in solution also stabilize charges (at concentrations typical for chromatography). The influence of the dielectric constant is much larger. The model of Bjerrum for ion pairs, which simply accounts for the electrostatic attraction between ions, shows that the formation constant for ion pairs depends on the cube of the dielectric constant. Thus the coulombic association of ions because of electrostatic effects is greatly influenced by the solvent dielectric constant, and more weakly influenced by the presence of other ions (solution ionic strength).

The association of ions with each other may also be promoted by chemical forces, in addition to simple coulombic attraction. For example, hydrophobic association of ions may occur in water, while hydrogen bonding can direct ion pair formation in non-polar media. In these cases, the charges are a part of the overall free energy balance, but perhaps not the dominant factor. Obviously, the presence of opposite charges augments the tendency of ion-pair formation that may be primarily driven by other forces.

In a two-phase system, in which ions associate in both phases, it may be that the chemical forces responsible for the joining together of a pair of ions in one phase are not the same forces that cause the ion-pair formation in the other phase. As a result, the formation of ion pairs in the stationary phase of a chromatographic system does not *necessarily* mean that there will be ion pairs in the mobile phase or *vice versa*. As an analogy, it is well known that many liquid–liquid ion-pair extractions work very effectively even though ion pairs cannot be detected in the aqueous phase.

The role of ion pairs in reversed-phase chromatography is difficult to determine through the use of chromatography alone. The formation constant for ion pair formation in *both* phases must be known, as must the concentration of the ionic modifier, and its activity coefficient, in the stationary phase. The formation of ion pairs in the mobile phase alone decreases the retention of the sample ion [73], while the formation of ion pairs alone in the stationary phase will increase it [12]. In the presence of both influences, retention may increase, decrease or remain constant in the presence of an ionic modifier. Clearly, experiments other than chromatographic ones are needed to completely elucidate the ion pair picture.

2.2. Dynamic ion-exchange model [1,52,67,69]

What is apparently neglected in the ion-pair model is the continuous presence of the ionic modifier in the stationary phase. A model incorporating this, called the dynamic ion exchange model, has the reversed-phase surface covered with modifier ion reagent, so the surface becomes like that of an ion exchanger. However, as has been shown most clearly by Knox and Hartwick [73], the mathematical relationships governing the dynamic ion exchange model and the ion-pairing model are formally the same. The dependences of the retention times of ions on the concentration of the ionic modifier and on equilibrium constants is the same. Thus, either the ion-pair model or the dynamic ion-exchange model can be used to predict the same range of behavior of k'_S *vs.* the concentration of $M^{\pm}$. The major assumptions are that the space (volume or area) of the stationary phase is limited, so all sorbed species compete for it, and the solute is present in trace quantities.

In the formulation of the equations by Knox and Hartwick, the sorption of the ionic modifier is assumed to follow a Langmuir isotherm if the buffer concentration is high. If the concentration of buffer and ionic modifier are in the same range, then the assumed isotherm is more complex, because the sorption is pictured as an equilibrium distribution of the ionic modifier and the prevailing counterion.

For the case in which the modifier ion is an anion M^- and the sample ion is a cation S^+, an expression which is correctly charge balanced, and which uses the minimum number of equilibria to describe the distribution of solute is given as [73]

$$k'_S = \frac{V_s}{V_m}[L] \cdot \frac{K_1 C_Y + K_4 C_M}{(1 + K_2 C_M)(1 + K_3 C_M C_X)} \tag{6}$$

For this case, [L] is the concentration of unoccupied "ligand" sites in/on the RPBP; C_M is the concentration of modifier ion M^- in bulk solution; C_X is the concentration of electrolyte cation X^+ in bulk solution; and C_Y is the concentration of electrolyte anion Y^- in bulk solution. The equilibrium constants K_1–K_4 pertain to the following equilibria which are assumed to occur. The lower case subscripts m and s refer to bulk solution mobile phase and to RPBP stationary phase, respectively:

Adsorption of sample ion onto L:

$$S^+_m + Y^-_m + L_s \overset{1}{\rightleftharpoons} SYL_s$$

Ion-pair formation in mobile phase:

$$S_m^+ + M_m^- \overset{2}{\rightleftharpoons} SM_m$$

Adsorption of modifier ion into L:

$$X_m^+ + M_m^- + L_s \overset{3}{\rightleftharpoons} CML_s$$

Adsorption of sample ion and modifier ion giving ion pair in stationary phase

$$S_m^+ + M_m^- + L_s \overset{4}{\rightleftharpoons} SML_s$$

Eqn. 6 will be discussed below.

2.3. *Ion interaction model [68]*

Sensing the limitations of the dynamic ion-exchange/ion-pair model, Bidlingmeyer *et al.* [75] proposed a qualitative model which was capable of explaining ghost peaks seen when RI detectors are used. Stranahan and Deming [76] later put this model, called ion interaction, on a quantitative footing. In this model, retention of the sample ion is due to three free energy terms: (i) the activity coefficient of the sample in the mobile phase (from a pure solute reference state); (ii) the influence of the interfacial surface tension on the hydrophobic sorption of the sample as modulated by mobile phase additives; (iii) an activity coefficient in the stationary phase which is simplified to contain only the product of the energy of interaction between the sample and ionic modifier and the stationary phase concentration of ionic modifier. The model can be fit to data of k'_S *vs.* mobile phase concentration of ionic modifier. An interesting feature of such plots is that it can show a maximum.

Stranahan and Deming assumed a Langmuir isotherm for the adsorption of ionic modifier, to allow for saturation of the stationary phase. However, an ion pairing effect was not included. Conditions used in [76] were similar to conditions explored by Bidlingmeyer *et al.* [75] in which no evidence for ion pairing in the mobile phase was found. Thus the neglect of that process *in the mobile phase* was justified, and some new approach was also justified. Stranahan and Deming used a surface tension term, which is non-stoichiometric, to account for the influence of the ionic modifier on the hydrophobic adsorption of the sample. Through this process, they were able to account for the maximum. Increasing quantities of the surfactant (their ionic modifiers were all surfactants) diminished the hydrophobic interaction free energy between the sample and the reversed phase. This negative influence on k'_S was prevalent when the surface was nearly saturated.

Maxima in plots of k'_S *vs.* C_M have long held the attention of model-makers in IM-RPLC. Here it may be noted that maxima can also be rationalized in terms of the ion pair/dynamic ion exchange model, though such rationalization had not been carried out quantitatively at the time of Stranahan and Deming. Eqn. 6 [73] shows that k'_S can display a pronounced maximum as a function of ionic modifier concentration, even when ionic strength is held constant. Investigation of the expression in Knox and Hartwick has led to the observation that there are two key criteria that control the shape of the k'_S curve. The criteria will be expressed in terms of the concentration of ionic modifier in the mobile phase, C_M. The ideas are exemplified in Fig. 1. One important criterion is that the experimental range of C_M includes the value at which the surface coverage by $M^{\pm}$ is 0.50. The other important criterion is that the same range of C_M includes the value at which the fraction of sample ion $S^{\pm}$ in the mobile phase as ion pairs is 0.50. A conclusion that can be drawn from this is that if a pronounced maximum in k'_S *vs.* C_M is observed at constant ionic strength, and if no ion pairing can be measured in the mobile phase in

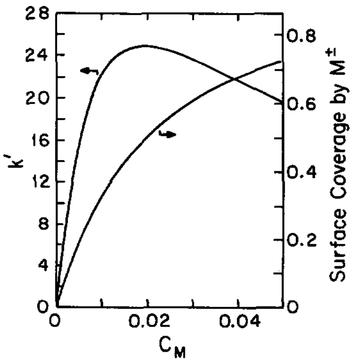

Fig. 1. Plot of k' *vs.* C_M and adsorption isotherm of modifier ion; $V_s/V_m = 1.0$, $[L] = 1.0$, $K_1 = 0.0$, $K_2 = 50$, $K_3 = 100$, $K_4 = 100$, $C_x = 0.5$ and $C_y = 0.5$.

independent experiments, then the experimental results are inconsistent with the ion-pair/dynamic ion-exchange model.

3. ELECTRICAL DOUBLE-LAYER (ELECTROSTATIC) MODELS OF IM-RPLC

There are several published reports that describe the retention of ionic species in IM-RPLC without reference to the formation of stoichiometric compounds. The essential feature of these is that the retention of the sample ion is, in a chemical sense, indirectly or remotely influenced by the ionic modifier. The ionic modifier is not viewed as forming a stable chemical complex with the sample ion. Rather, it establishes an electrical potential distribution in space, and the sample ion responds to that electrical potential. The influence of the ionic modifier is indirect. There is not an integral stoichiometry associated with this interaction, whereas there is with the simpler models of RPLC with ionic modifiers. In this section a more detailed description of this subject will be presented. However, first zeta potential measurements will be described. These provide a more direct experimental demonstration of the development of an electrical potential on the RPLC sorbent as a result of the sorption of electrolyte from solution.

3.1. *Zeta potential*

When an essentially neutral sorbent particle sorbs a PPI it acquires a surface potential Ψ_0. In the presence of an applied external electrical field, the particle will electromigrate (electrophorese) and its migration can be observed with a microscope. Adsorbed PPIs as well as a certain amount of water of hydration will move with the particle as the migrating unit. The boundary between this migrating unit and the surrounding solution is called the "plane of shear" and its location is approximately at the Outer Helmholtz Plane, which will be discussed below [28,29,32,35]. The electrical potential difference between the plane of shear and the bulk solution is the zeta potential (ζ). It is ζ which can be measured in the microscope electrophoresis (microelectrophoresis) experiment.

Microelectrophoresis measurements have been performed on macroporous styrene–divinylbenzene non-polar adsorbent particles with sorbed diphenylguanidinium ions [56] and on an ODS bonded phase with sorbed octylsulfate ions [73]. These experiments demonstrate, unambiguously, the development of an electrical potential on the particles as a result of the sorption of ions.

3.2. *Double-layer theory*

The characteristics of the electrical double layers which develop at charged interfaces have been reviewed in many places [28–37,77]. Here are highlighted only those features which are necessary to understand the DL models that have been advanced to explain RPLC with ionic modifiers. It should be recalled that, in a porous particle, most of the surface is lining the pores and the pores are filled with solution.

The charge in the sorbent phase can arise in either of three ways in the present context. First, a PPI may adsorb onto/into the interface between the reversed-phase stationary phase and the adjacent pore solution. This possibility exists for both non-polar adsorbent particles and for bonded phase particles. Second, the PPI, along with a less than equivalent amount of oppositely charged "counterion", can dissolve in the pseudo-liquid bonded phase. Third, there may be some charge arising from ionogenic groups (such as residual silanol groups) that are present as impurities on the surface of the non-polar adsorbent or on the silica support underlying the bonded phase. This third category of charge represents a complication, since it arises from ionic groups that have not been sorbed from solution. As a result of one or more of these three processes the reversed phase contains a "surface-excess" of either positive or negative charges, Γ (mol/cm^2). The ions responsible for the surface excess may be at the interface, within the "bulk" of the bonded phase and/or on the underlying silica surface.

The situation in which the surface charge is essentially at the interface will be considered first. In RPBP systems it is a result of adsorption of ions at the interface between the RPBP and the solution filling the pores. A surface-charge density σ_0 (coulomb/cm^2) develops at the charge-surface which is located at or very near the surface. This gives rise to a surface-potential Ψ_0 at the charge surface. The value of Ψ_0 depends on the concentration of the PPI in the bulk solution, on the ionic strength of the bulk solution, on the dielectric constant of the solution near the interface, and on temperature.

In most versions of DL theory the surface-charge is assumed to be uniformly "smeared-out" over the surface so that the surface is considered to have the same (averaged) charge density at all points. An alternative view in which the adsorbed ions are viewed as discrete charges [28,31,32,78] may be more realistic but leads to more complex calculations. Experimental measurements of the distribution of a PPI may be used to determine the surface charge. However, a subtle but important factor must be accounted for in order to derive the correct result. The PPI will have a positive surface excess, as it is certainly sorbed. However, this excess underestimates the amount sorbed at the interface. To see why, the distribution of charges in space, must be considered.

Electroneutrality requires that on the solution side of the interface there must be a sufficient charge of opposite sign to balance exactly that which is in the charge-surface. This counter-charge in the solution is made up of both a positive excess of counterions (*i.e.* ions with sign opposite to that of surface charge) and a negative excess, or depletion, of co-ions (*i.e.* ions with the same sign as the surface charge). One of the types of co-ions is, of course, the PPI. This is an important point because it means that in the solution part of the double layer there will be a decreased concentration of the PPI. By invoking some reasonable assumptions, it is possible to calculate the fraction of the surface excess in the solution part of the double layer that is due to a positive excess of counterions and that which is due to a negative excess of co-ions [35], and to calculate how much of the PPI has been expelled from the solution part of the double layer [56,65]. This amount may then be added to the experimentally measured amount of sorbed PPI in order to determine the amount adsorbed at the charge-surface.

If ions in solution are assumed to be point charges, then non-surface-sorbed ions in the solution can approach the charge-surface very closely. In that case, the entire solution part of the double layer is a *diffuse layer*. The original version of DL theory, called the Gouy–Chapman theory, employed this approximation and, as well, assumed that the charge-surface is flat and that the solution phase is very thick (semi-infinite). In the Gouy–Chapman theory, the electrical potential decreases (or increases) from the value of Ψ_0 at the charge-surface to a value of 0 in bulk solution, in accordance with an expression that is obtained by solving the Poisson–Boltzmann equation for planar, semi-infinite conditions. The solution to this equation takes on an approximately exponential form when Ψ_0 is below about 0.025 V and the so-called "Debye-Hückel" approximation can be made [28,29,35]. The *thickness of the diffuse layer* is taken as the distance at which the potential has decayed to (Ψ_0/e). Importantly, this thickness of the diffuse layer is inversely proportional to the square root of the ionic strength of the bulk solution.

In a later version of the theory, proposed by Stern, the fact that non-surface-sorbed ions have a finite size was taken into account. In the Stern–Gouy–Chapman (SGC) theory the assumption was made that non-sorbed ions in the solution could approach the charge-surface no closer than the hydrated radius of the counterion [28,29,35]. The essential features of the SGC model described here are shown in Fig. 2. In the SGC theory the solution part of the double layer is now composed of two parts. The *compact part* of the double layer extends from the charge-surface to the center-of-charge of the hydrated counterions in the plane-of-closest approach. In terms of the widely accepted concepts introduced by Grahame [35] this plane-of-closest approach of non-sorbed ions is called the Outer Helmholtz Plane (OHP). In the compact part of the DL the electrical potential decreases (or increases) linearly from Ψ_0 at the charge-surface to Ψ_{OHP} at the OHP. That is, the compact part of the DL is a capacitor with a relatively constant capacitance regardless of σ_0, Ψ_0 or ionic strength of the bulk solution.

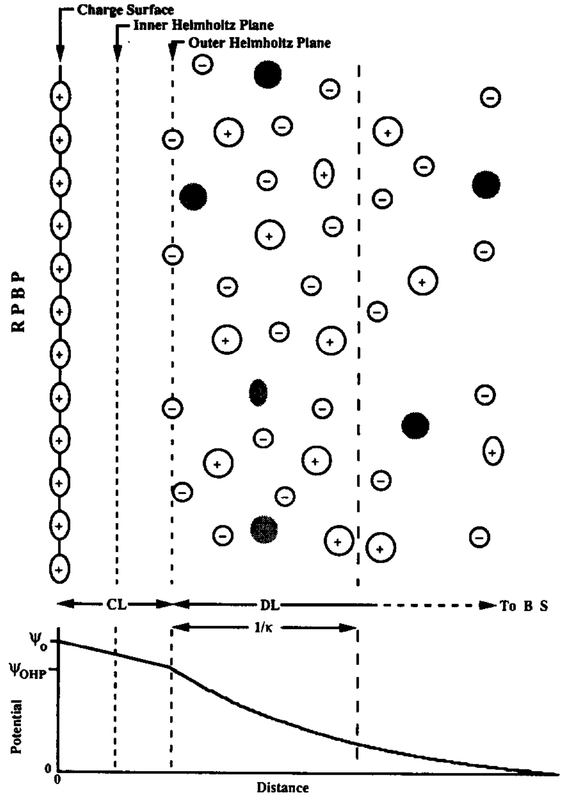

Fig. 2. Diagrammatic representation of the electrical double layer region for a RPBP with adsorption of a cationic PDI (oval shaped ions) at the interface to create the charge-surface, having potential Ψ_0. Circular cations and anions are from the inert (non-adsorbed) electrolyte. Potential decreases linearly over the compact layer (CL) to a value Ψ_{OHP} at the Outer Helmholtz Plane, which is the plane of closest approach of non-adsorbed negative counterions. The thickness of the diffuse part (DL) of the double layer is $1/\kappa$ and depends on ionic strength of the bulk solution (BS). The potential decays approximately exponentially across the DL toward a value of 0 V in the BS. The surface excess of interfacially adsorbed PDI's (Γ_i^{AD}) is counterbalanced by an equal surface excess of negative ions in the DL, which is due partly to the attraction of negative counterions into the DL in numbers exceeding their concentration in bulk solution, and partly to expulsion of cationic co-ions from the DL which causes the cation concentrations in the DL to be lower than in bulk solution giving a negative surface excess of co-ions. These absent cations are shown as stippled "ghosts". PDI co-ions are expelled along with inert co-ions, which creates a negative excess of PDI's in the DL (Γ_i^{DL}) and causes the total number of PDI's in the whole double layer region to be lower than the number that are interfacially adsorbed.

In the SGC theory the diffuse part of the double layer now extends outward from the OHP, rather than from the charge surface. The OHP and ions in it belong to the diffuse layer, not to the compact part of the DL. The properties of the diffuse part are given by the same equations, based on the Poisson–Boltzmann equation, as in the Gouy–Chapman theory except that Ψ_{OHP} replaces Ψ_0 in all of those equations and the thickness of the diffuse part is measured from the OHP, rather than from the charge-surface.

The SGC theory also can accommodate the presence of "specifically adsorbed" counterions or co-ions. These are partially dehydrated ions that are present in another charge-layer, the Inner Helmholtz Plane (IHP), located between the charge-surface and the OHP [28,29,35]. According to the SGC theory, there may or may not be ions in the IHP, depending on the nature of the ions and the nature of the reversed phase and of the solution phase. Furthermore, it should be noted that there are systems whose double layer behavior under some conditions seems to be adequately described by the simple Gouy–Chapman theory without the need to invoke even an OHP and compact layer. It may also be noted that although a planar charge-surface is easiest to model mathematically, the properties of the double layer at curved surfaces, such as the outer surfaces of a sphere and a cylinder, have been modeled [28].

Consider now the second possible way that a bonded phase can acquire a surface excess of sorbed PPIs; that is, where the RPBP behaves as a bulk liquid and the sorbed ions are dissolved in it rather than being totally at or very close to the interface. In this case a "double diffuse double layer" is created [28,33,34,43,44]. On both sides of the interface there is a diffuse layer which grades away into a bulk solution. In eqn. 5, for both sides of the interface, Ψ_x should be replaced with $\Psi_x(r)$. There are generally no compact parts of the double layers.

When salts are in a two-bulk-phase system, there will be a partitioning of ions between the phases. Each ion has its own free energy of transfer from a reference phase to a solvent, but it is not possible to measure it in a thermodynamically rigorous way because any experiment must necessarily employ a salt [79]. Even so, when a salt distributes between phases, there is a charge separation at the interface between the two phases. The charge separation results from the tendency of one of the ions to prefer one phase over the other to a degree that is different from that of its counterion. For example, tetrabutylammonium ion tends to prefer organic solvents over water, while chloride tends to prefer water over organic solvents [79]. When ions are extracted without an equivalent quantity of counterions, then there is a so-called space charge layer (diffuse layer) where there is excess charge of one sign. Experience indicates, however, that there is not bulk separation of one ion in one phase from its counterion in another. The very charge separation creates an electrical potential of the same sign as the charges that are in excess. This potential works against further charge separation. When there are two bulk phases at equilibrium, the potential difference between the two phases will be simply related to the single ion free energies of transfer ($\Delta G^{\circ\prime}_{i,\mathrm{ch}}$) in the following way

$$\Delta\Psi = \frac{\Delta G^{\circ\prime}_{+,\mathrm{ch}}}{-Z_{+}F} - \frac{\Delta G^{\circ\prime}_{-,\mathrm{ch}}}{-Z_{-}F} \qquad (7)$$

where Z is the sign and magnitude of ionic charge, F is Faraday's constant, and the subscripts refer to the sign of each ion's charge.

In a typical two-bulk-phase system with a salt, the potential changes in a roughly exponential manner from the interface into both phases, increasing in one phase and decreasing in the other as shown in Fig. 3. If the bulk solution of one phase is chosen as the reference, for example the less polar phase, as in Fig. 3, the potential can be set to zero far from the interface in that phase (*i.e.* in bulk solution). As the interface is approached closely the potential begins to rise or fall at an increasing rate. It will rise, becoming more positive, if the cation of the salt favors the other, more polar, phase. In the more polar phase the potential continues to rise but the rate of increase diminishes with distance away from the interface until the potential becomes a constant value far from the interface. The value of the potential difference is governed by the single-ion free energies of transfer as shown above in eqn. 7.

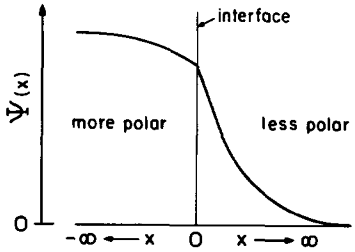

Fig. 3. Distribution of potential at a liquid–liquid interface.

Whether the PPI is adsorbed at the interface or dissolved in the RPBP, one may ask: "Where will a sample ion be found at equilibrium in such a system?". An ionic solute, like any solute, will distribute itself as shown in eqn. 5, according to a space (volume or area) term and a free energy term. The special feature of an ionic solute is that its free energy is a function of its charge and the local electric potential. In the situations just described, the potential is a function of the distance from the interface. Thus the free energy of a single ion is a continuous function of its position in space. The electrical potential is dependent on distance from the interface, which means that the influence of the potential determining ions reaches into the stagnant mobile phase. The stagnant mobile phase thus becomes a different energetic environment for sample ions than the flowing mobile phase.

Mathematical details have been omitted from the above qualitative descriptions of DL theories. The cited literature may be consulted for a quantitative treatment. It is clear, however, that regardless of whether PPIs are adsorbed at the interface or "dissolved" in a bonded phase, there are really three, rather than two, "phases" present which can contain modifier ions and sample ions. First, there is either the adsorbent interface or the solvent-like bonded-phase; second, there is the diffuse part of the double layer including the OHP, if one is present, and extending into the stagnant mobile phase solution in the pores; third, there is the *bulk* solution phase, which occupies virtually all of the interparticle space and some fraction of the intraparticle (pore) space. For typical, highly porous packing materials such a small fraction of the surface lies at the outside of the particle, in direct contact with the flowing mobile phase, that its double layer and its contribution to sample sorption can be neglected. Thus the bulk solution phase is constituted of all of the "flowing mobile phase" and part of the "stagnant mobile phase". The ionic strength of the bulk solution phase determines the fraction of the pore liquid which is in the diffuse layer. At lower ionic strengths the thickness of the diffuse layer is greater so that it occupies an increased fraction of the pore liquid. The IHP, if one exists, could conceivably be considered as a fourth "phase" but usually it is either omitted from the model or considered to be unoccupied. Chromatographically then, there is the peculiar situation in which the *stationary phase* is considered, as one possibility, to be composed of both the interface/bonded phase and the aqueous solution in the diffuse layer; while the *mobile phase* is all of the aqueous solution that is present in both the pores (including bulk solutions and diffuse layer) and the interparticle spaces. The question of what part of the chromatographic system should be considered the stationary phase and what part should be considered the mobile phase will be addressed in the discussions of the various DL models below.

In the following sections are considered the major DL models that have been proposed to explain IM-RPLC. The assumptions and other features that are special to each model are discussed and, at the end, the models are compared to one another.

3.3. Surface adsorption DL model

Ståhlberg and co-workers have developed a DL model in which the modifier ion (called the "amphiphilic ion" by them) is assumed to adsorb at the interface (*i.e.* surface) between the bonded phase and the aqueous solution to create a charge-surface with a charge-density of σ_0 and a surface-potential of Ψ_0 [61,80–88]. In earlier versions of this model the relationship between σ_0 and Ψ_0 is calculated via the Gouy–Chapman theory which assumes a planar charge-surface. There is no compact layer. On the aqueous solution side of the DL there is, as usual, a diffuse layer which grades away into bulk solution. However, in the model the diffuse layer is not considered to be part of the stationary phase. The *stationary phase* is just the interfacial charge-surface. The *mobile phase* is, as usual, all of the interparticle solution and all of the pore solution.

Adsorption of both the modifier ion and the sample ion at the interface are, of course, influenced by Ψ_0 which alters the energy contribution to adsorption. In addition, the occupancy of the interface by some adsorbed ions decreases the magnitude of the statistical or "space" factor, V_s, for adsorption of additional ions.

For the modifier ion, both the energy and the statistical effects are taken into account by assuming that its adsorption can be described by a "surface-potential modified Langmuir isotherm" [61,80]. This approach is based on a DL model previously employed to describe the adsorption of surfactant ions at a liquid–liquid interface between, for example, *n*-heptane and water [89] and it comes originally from the ideas of Stern who assumed a "potential-modified Langmuir isotherm" to describe adsorption of ions in the IHP at a mercury electrode surface [28,29,35]. The surface concentration of adsorbed modifier ions $M^{\pm}$, n_{M} (*e.g.* mol/cm^2) is given by an equation of the form:

$$n_{\mathrm{M}} = \frac{n_{0,\mathrm{M}} K_{\mathrm{Lang,M}} C_{\mathrm{M}} \exp\left(-\frac{Z_{\mathrm{M}} F \Psi_0}{RT}\right)}{1 + K_{\mathrm{Lang,M}} C_{\mathrm{M}} \exp\left(-\frac{Z_{\mathrm{M}} F \Psi_0}{RT}\right)} \tag{8}$$

where C_{M} (*e.g.* mol/cm^3) is the modifier ion concentration in bulk aqueous solution, $n_{0,\mathrm{M}}$ (*e.g.* mol/cm^2) is the limiting monolayer surface concentration and $K_{\mathrm{Lang,M}}$ (*e.g.* cm^3/mol) is an equilibrium constant for adsorption of $M^{\pm}$ onto the interface at an infinitely dilute surface concentration of $M^{\pm}$. At infinitely dilute surface concentration, $\Psi_0 = 0$ V and the statistical "space" factor has its maximum value. It will be recognized by comparison with eqn. 5 that $K_{\mathrm{Lang,M}}$ is equal to $Bn_{0,\mathrm{M}}^{-1} \exp(-\Delta G^{\circ\prime}_{M,\mathrm{ch}}/RT)$ and that $(\Delta G^{\circ\prime}_{M,\mathrm{ch}} + Z_{\mathrm{M}} F \Psi_0)$ is the electrochemical potential for adsorption of $M^{\pm}$. Since σ_0 is equal to $Z_M F n_M$ and since Ψ_0 will have the same sign as the modifier ion and will increase in magnitude as σ_0 increases, in accordance with the Gouy–Chapman theory, then the contribution of $Z_M F \Psi_0$ in eqn. 5 to the electrochemical potential will increasingly disfavor the free energy of adsorption for $M^{\pm}$ as n_M increases. In a later paper [81] Ståhlberg calculated the relationship between σ_0 and Ψ_0 using a form of the Poisson–Boltzmann equation that applies to the inside surface of a cylinder [90], rather than using the Gouy–Chapman theory that applies to a planar surface. It was felt that a cylinder would more accurately represent the surface of a pore. However, the form of the cylindrical solution that was used is valid only at low values of Ψ_0, at which the Debye–Hückel approximation is valid.

Experimentally, the validity of eqn. 8 was tested on sorption isotherms for tetra-*n*-butylammonium ion ($TBA^+ \equiv M^+$) measured on an ODS bonded phase in the presence of three different inert salt counterions ($H_2PO_4^-$, Cl^-, Br^-) and at two different ionic strengths [80]. When isotherms were plotted as n_{TBA} *vs.* C_{TBA} they were all displaced from one another, but when they were plotted as n_{TBA} *vs.* $C_{TBA} \exp(-F\Psi_0/RT)$, as suggested by eqn. 8, the isotherms all fell on top of one another. In these calculations, values of Ψ_0 were obtained from chromatographic data via eqn. (10) (see below) and then corresponding values of n_{TBA} were obtained from Ψ_0 using the cylindrical solution of the Poisson–Boltzmann equation. The fact that all of the points fell on a single isotherm supports the validity of eqn. 8.

For the sample ion $S^{\pm}$ adsorption is assumed to take place at the same interfacial charge-surface as for $M^{\pm}$. Under conditions that are relevant to IM-RPLC, the $S^{\pm}$ concentration is much lower than the $M^{\pm}$ concentration so that, even though $S^{\pm}$ is adsorbed, its surface concentration n_S is so much lower than n_M that its contribution to Ψ_0 can be ignored. The capacity factor for the sample ion is given by eqn. 5 which can be written in the form:

$$k'_S = k'_{S,0} \exp\left(-\frac{Z_S F \Psi_0}{RT}\right) \tag{9}$$

Here $k'_{S,0}$ is the capacity factor that is obtained in the absence of $M^{\pm}$ [61]. Rearranging eqn. 9 to the form [80]

$$\Psi_0 = \frac{RT}{Z_S F} \ln\left(-\frac{k'_{S,0}}{k_S}\right) \tag{10}$$

suggests that the value of Ψ_0 in the presence of $M^{\pm}$ can be estimated from the ratio of the chromatographically measured values of the capacity factor for $S^{\pm}$ in the presence and absence of $M^{\pm}$.

Since the value of Ψ_0 is expected to be independent of the (small) amount and type of sample ion, eqn. 10 was used as the basis of an experimental test of Ståhlberg's model for IM-RPLC [81,82]. This was done by measuring both k'_S and $k'_{S,0}$ for various sample ions using mobile phases containing a variety of concentrations of $M^{\pm}$ but having the same ionic strength and organic modifier concentration. Under conditions where n_M is low enough to be in the *linear part* of the surface potential modified Langmuir isotherm of $M^{\pm}$ (*i.e.* where a plot of n_M *vs.* $C_M \exp(-Z_M F\Psi_0/RT)$ is linear), and where Ψ_0 is lower than about 0.03 V so that the Debye–Hückel approximation is valid and Ψ_0 is proportional to n_M, it can be shown that for a cylindrical charge-surface, plots of

$$-\frac{Z_M}{Z_S}\ln\left(\frac{k'_S}{k'_{S,0}}\right) + \ln\left[-\frac{RT}{Z_M Z_S F}\ln\left(\frac{k'_S}{k'_{S,0}}\right)\right] \quad vs.\ \ln C_M$$

should be linear with a slope of 1 and that all sample ions should fall on the same straight line for a given modifier ion and a constant ionic strength and organic modifier concentration [81]. Experiments were performed using a variety of univalent cation and univalent and divalent anion sample ion $S^{\pm}$ and using a variety of modifier ions $M^{\pm}$, such as tetra-*n*-butylammonium, tetra-*n*-pentylammonium and octyl sulfate. It was found that these plots were linear, although the slopes in general were somewhat lower than 1 (range 0.71 to 1.08 for 26 determinations [81]). The results were interpreted as supporting the surface adsorption-DL model of IM-RPLC. It may be noted that if the Gouy–Chapman theory is used rather than the cylindrical solution to the Poisson–Boltzmann equation, then plots of

$$-\frac{Z_M}{Z_S}\log\left(\frac{k'_S}{k'_{S,0}}\right) \; vs. \log C_M$$

are expected to have the same shape for all sample ions [82]. Experimentally, this prediction was also observed to be generally true. Thus, since models based on both the cylindrical and the planar treatment of the charge surface support the DL-interpretation of IM-RPLC, there does not seem to be much advantage to using the more complicated cylindrical treatment over the planar one. It was shown that for constant ionic strength and organic modifier concentration, if one considers only the *linear part* of the surface potential modified Langmuir isotherm and if Ψ_0 is between about 0.005 and 0.050 V where the planar Gouy–Chapman equation predicts Ψ_0 proportional to n_M, then [83,87]

$$\log k'_S \approx K_2 - \frac{1}{2}\cdot\frac{Z_S}{Z_M}\log C_M \tag{11}$$

where K_2 is a constant. Eqn. 11 is valid for any magnitude of charge on the sample ion and for a univalent charge on the pairing ion [87].

The surface adsorption DL model has been extended to high surface concentrations of modifier ion where the space-limited statistical effect might be significant and might be expected to include competition for space between modifier ion and sample ion [83,84]. Since both ions $S^{\pm}$ and $M^{\pm}$ are assumed to follow surface potential modified Langmuir isotherms, the combined effects of potential and competition for space are expressed in terms of a "surface potential modified *mixed* Langmuir isotherm". However, as an approximation at these high surface concentrations of $M^{\pm}$, the contribution of the sample ion to σ_0 and Ψ_0 is neglected. The surface charge density is calculated simply as:

$$\sigma_0 = FZ_M n_M \tag{12}$$

Thus, the only effect which the sorption of $S^{\pm}$ is assumed to have on the sorption of $M^{\pm}$ is that arising from the competition for space. The fact that the sorption of $S^{\pm}$ will produce a small change in Ψ_0, which will produce a small change in the amount of $M^{\pm}$ sorbed, is neglected.

The surface adsorption DL model has also been extended to include the role of the organic modifier solvent [85,86]. As the volume fraction of organic solvent in the mobile phase is increased both $\Delta G^{\circ\prime}_{S,ch}$ for the sample ion and $\Delta G^{\circ\prime}_{M,ch}$ for the modifier ion become less negative. The former change decreases $k'_{S,0}$ in eqn. 9 and the latter change decreases $K_{Lang,M}$ and, consequently, n_M in eqn. 8. The decrease of n_M decreases σ_0 which decreases the (absolute) value of Ψ_0. The effect of organic solvent composition on the Poisson–Boltzmann derived equations, via the change that it causes in solvent dielectric constant, is ignored in this treatment. If the sample ion $S^{\pm}$ has the opposite sign of charge from $M^{\pm}$, as is the case in IM-RPLC, then the decrease in absolute value of Ψ_0 produced by the organic solvent will lead to a further decrease in k'_S beyond that resulting from a decrease in $k'_{S,0}$, as can be seen in eqn. 9. On the other hand, if $S^{\pm}$ has the same sign of charge as $M^{\pm}$ then increasing organic modifier solvent concentration will cause the term $\exp(-Z_S F\Psi_0/RT)$ in eqn. 9 to increase, which is in opposition to the solvent effect on $k'_{S,0}$.

The effect of mobile phase pH on k'_S for samples having monofunctional acid/base properties was also treated in terms of the surface adsorption DL model of Ståhlberg [88]. If $M^{\pm}$ is essentially free of acid-base character then the pH effect on retention is associated with the change in fraction of the sample component ionized.

3.4. Liquid partition DL model

A second DL-derived model for IM-RPLC is based on the assumption that the RPBP is a liquid into which salts of the modifier ion and of the sample ion can partition. Under the chromatographically important conditions where the sample ion is a trace component, the creation of the electrical double layer is a consequence of the sorption, by the RPBP, of an excess of the modifier ion $M^{\pm}$ over its counterions. In this "double diffuse-double layer" model, proposed by Weber and Orr [60,64], the two parts of the *stationary phase* are the liquid-like RPBP and the diffuse-layer portion of the stagnant liquid in the pores. The *mobile phase* is composed of the flowing solution zone outside of the particle as well as all of the pore solution. That portion of the pore liquid which is in the diffuse layer is simultaneously part of the mobile and stationary phases. The way in which this dual role of the diffuse layer is handled mathematically will be discussed below.

The solvent characteristics of the phases are described as follows: The RPBP is treated as a liquid. When an organic modifier solvent such as acetonitrile is present in the aqueous mobile phase, then the RPBP is assumed to have some of the organic solvent dissolved in it. So, for example, if the aqueous mobile phase contains 50% (v/v) of acetonitrile, the RPBP might be represented as a 90% (v/v) acetonitrile solution [60]. The (solvent modified) RPBP is only about 20 Å thick. The stagnant liquid throughout the pore is assumed to have the same solvent composition as the bulk liquid solution (*e.g.* 50% acetonitrile).

Sorption of the modifier ion $M^{\pm}$, which establishes the electrical potential distribution in the system, results because, for chemical reasons, the affinity of the (organic solvent modified) RPBP is different for anions of the modifier ion reagent (MIR) salt than it is for cations of the MIR. It is possible that only anionic (or cationic) modifier ion $M^{\pm}$ from the MIR dissolves into the RPBP but it is also possible that some of the MIR salt dissolves into the RPBP along with the excess of the $M^{\pm}$ ion [64]. In the diffuse layer of the pore liquid there is an equivalent amount of charge of opposite sign to that in the RPBP.

Two different geometries were investigated in order to get away from the presumably unrealistic assumptions of either planarity of the pore wall or semi-infinite solution [64]. In one case the pore is treated as an infinitely long cylinder of diameter $2R$ whose wall is the silica surface. Lining the pore wall is layer of RPBP with thickness $(R-a)$ and filling the central cylindrical cavity of radius a is the stagnant liquid. In the other case the pore is considered to have a "sandwich" geometry with two planar parallel silica walls. Here $2R$ is the distance between the walls, $(R-a)$ is the thickness of each of the RPBP layers lining the walls and a is one-half the thickness of the central layer of stagnant solution.

Expressions relating the "surface excess" of $M^{\pm}$ dissolved in the RPBP to the electrical potential distributions within the RPBP and pore liquid are obtained by solving the Poisson–Boltzmann equation for the specified geometries [64]. An analytical solution has been provided for the cylindrical geometry when consideration is limited to low surface excesses of $M^{\pm}$ and low potentials, where the Debye–Hückel approximation is valid. For the "sandwich" geometry, only numerical solutions have been provided. In addition, for the latter geometry the statistical factor has been modified to account for the fact that space limitations in the RPBP will become evident at high excesses of $M^{\pm}$. This was done by employing a "potential modified Langmuir isotherm" for the distribution of $M^{\pm}$ between the RPBP and the bulk solution [64]. Because the solvent properties of the RPBP and the pore liquid differ from one another there are two forms of the differential equation which must be solved. For the *pore liquid, from* $0 \leqslant r \leqslant a$, where r is distance from the center axis of the cylindrical pore, the differential equation is

$$\nabla^2\Psi(r) = -\frac{4\pi}{\varepsilon_1}\sum_i Z_i \cdot FC_i \exp\left(-\frac{Z_iF\Psi(r)}{RT}\right) \quad (13)$$

Here $\Psi(r)$ is the electrical potential as a function of distance. This function is of course the solution of the equation. ε_1 is the permittivity of the pore liquid, which is related to its dielectric constant, and, C_i is the concentration (*e.g.* mol/l) of ion $i^{\pm}$ in the bulk solution. The sign Σ_i indicates that a summation is made over all ions. Usually only one type of ion, $M^{\pm}$, out of all the ions $i^{\pm}$ partitions into the RPBP in excess over its counterions. However, in compensation, the diffuse part of the pore liquid will contain a positive surface excess of all types of counterions and a negative surface excess of all types of coions, including $M^{\pm}$.

For the *(organic solvent modified) RPBP, from* $a \leqslant r \leqslant R$, the differential equation is:

$$\nabla^2\Psi(r) = \frac{4\pi}{\varepsilon_2}\left[\frac{\sum_i Z_iFC_i \exp\left(-\frac{\Delta G^{\circ\prime}_{i,\mathrm{ch}} + Z_iF\Psi(r)}{RT}\right)}{1 + \sum_i Z_iFC_i\alpha_i \exp\left(-\frac{\Delta G^{\circ\prime}_{i,\mathrm{ch}} + Z_iF\Psi(r)}{RT}\right)}\right] \tag{14}$$

In this equation ε_2 is the permittivity of the RPBP and α_i is the molar volume of ion $i^{\pm}$. If it happens that $M^{\pm}$ is the only in which partitions into the RPBP in excess over its counterions, this would be a consequence of the fact that $\Delta G^{\circ\prime}_{i,\mathrm{ch}}$ values for all ions except $M^{\pm}$ are equal to one another but $\Delta G^{\circ\prime}_{\mathrm{M,ch}}$ has a larger (negative) value than for the other ions. The large bracketed term on the right-hand side of eqn. 14 has the form of a potential-modified Langmuir equation and takes into account the limited volume in the RPBP for sorption of solute.

Solutions of eqns. 13 and 14, or of simplified forms of these equations, give the value of Ψ_x at various locations through the pore liquid and the RPBP [64]. Using either analytical or numerical solutions, such equations have been solved using various assumed values of ε_1, ε_2, C_i's, Z_i, and $\Delta G^{\circ\prime}_{i,\mathrm{ch}}$. As ionic strength is lowered the diffuse layer extends farther into the pore liquid, increasing the fraction of pore liquid from which at least some coion exclusion (negative surface excess of co-ions) occurs.

Weber has have also considered the situation in which charge develops as a result of ionogenic groups on the pore surface, whose ionization produces fixed charge sites. (Such sites were incorrectly identified as anion-exchange sites in ref. 64. They are cation-exchange sites.) These might be, for example, negatively charged ionized residual silanol groups. Solutions of simplified versions of eqns. 13 and 14 have been obtained for various values of $\Delta G^{\circ\prime}_{i,\mathrm{ch}}$ for the counterion of the fixed charge site and for various ionic strengths of the bulk solution. As noted previously, charges arising from fixed-charge sites present a complication in modeling IM-RPLC because they do not arise as a result of sorption of the modifier ion $M^{\pm}$.

The distance dependence of $\Psi_x[=\Psi_x(r)]$ complicates the calculations of k'_S for a sample ion which is sorbed from bulk solution into a large number of locations $X[=f(r)]$ within the diffuse layer and RPBP. In essence, what must be done is the calculation of a series of k'_S values, starting from the flowing mobile phase, which is taken to be homogeneous bulk solution, into small segments of the stagnant mobile phase (pore liquid) and the RPBP with volume dV_{SM} and dV_{RPBP}, respectively. For any particular small segment, for example in the RPBP, eqn. 5 takes a form in which the incremental k'_S value, $dk'_{S,X}$ is:

$$dk'_{S,X} = \left(\frac{dV_{\mathrm{RPBP}}(x)}{V_m}\right)\exp\left[-\left(\frac{\Delta G^{\circ\prime}_{S,\mathrm{ch}} + Z_SF\Psi_x}{RT}\right)\right] \tag{15}$$

An expression comparable to eqn. 15 can be written for sorption into the stagnant mobile phase, except that there $\Delta G^{\circ\prime}_{S,\mathrm{ch}} = 0$. To predict the overall, experimentally accessible value of k'_S it is necessary to integrate eq. 13 over the whole of the pore liquid (stagnant mobile phase, SM) and eqn. 14 over the whole RPBP. When this is done at low potentials, eqn. 5 becomes:

$$k'_S = \frac{\int_a^R dV_{\mathrm{RPBP}} \exp\left(-\frac{\Delta G^{\circ\prime}_{S,\mathrm{ch}} + Z_SF\Psi(x)}{RT}\right) + \int_0^a dV_{\mathrm{SM}} \exp\left(-\frac{Z_SF\Psi(x)}{RT}\right) - V_{\mathrm{SM}}}{V_M} \tag{16}$$

Here, V_{SM} is the stagnant mobile phase volume (*i.e.* total aqueous solution in pores) and V_m is, as usual in chromatography, the sum of V_{SM} plus the interparticle mobile phase volume. Eqn. 16 can be expressed as the sum of two capacity factors, one for sorption from bulk liquid into the RPBP and the other for sorption from bulk liquid into the diffuse layer:

$$k'_S = k'_{\mathrm{RPBP}} + k'_{\mathrm{SM}} \tag{17}$$

Included in k'_{RPBP} is the first integral in the numerator of eqn. 16, divided by V_{m}. Included in k'_{SM} is the second integral minus V_{SM}, divided by V_{m}. Subtraction of V_{SM} in the latter case is necessitated by the fact that experimental k'_{S} values are measured chromatographically by using as an "unretained component" a small, neutral molecule which does not enter the RPBP but enters all of the mobile phase, stagnant or flowing, uninfluenced by electrical potential and having $\Delta G^{\circ\prime}_{\mathrm{ch}} = 0$. Thus, the first term in eqn. 16 accounts for the distribution of $S^{\pm}$ from bulk mobile phase to the RPBP, the second term accounts for the distribution of $S^{\pm}$ from bulk mobile phase to the entire stagnant mobile phase, while the final term *corrects* the second term by subtracting the number of $S^{\pm}$ which would be in the pore volume in the absence of coulombic effects.

Even though the model predicts a distance dependent potential, experimentally one sees the average effect of the potential on k'_{S} as shown in eqn. 16. It is desirable to express the effect of the presence of a modifier ion as a single term, as Ståhlberg has done with Ψ_0 in eqn. 9. The parameter chosen by Weber is $\Delta\Psi$, the "volume-weighted average" potential difference between stationary phase and bulk solution. The validity of the liquid partition DL model was tested by Weber by comparing the model-predicted value of $\Delta\Psi$ with an experimentally measured value. *Experimental* measurement of $\Delta\Psi$ is, strictly speaking, impossible since it is essentially a potential at a single interface. However, it can be estimated from experimental measurements by making the extra-thermodynamic, "tetraphenylarsonium–tetraphenylborate reference electrolyte assumption" [60,64], which has previously been employed in studies of liquid–liquid systems. Here it is assumed that the ions $\phi_4\mathrm{As}^+$ and $\phi_4\mathrm{B}^-$ will interact *chemically* with a given solvent in an identical manner. Thus, for transfer of either of these ions as a sample between bulk solution and RPBP the values of $\Delta G^{\circ\prime}_{\phi_4\mathrm{A}}$ and $\Delta G^{\circ\prime}_{\phi_4\mathrm{B}}$ are identical. From eqn. 5 or eqn. 16 it is expected that the *ratio* of the values of $k'_{\phi_4\mathrm{B}}$ to that of $k'_{\phi_4\mathrm{A}}$ will be determined only by the effect of $\Delta\Psi$ on the opposite charges of these two sample ions. Using chromatographically measured values of $k'_{\phi_4\mathrm{B}}$ and $k'_{\phi_4\mathrm{A}}$, the experimental $\Delta\Psi$ may be calculated as follows [64]

$$\frac{F\,\Delta\Psi}{RT} = \frac{1}{2}\ln\frac{k'_{\phi_4\mathrm{B}}}{k'_{\phi_4\mathrm{A}}} \tag{18}$$

The *model-predicted* (theoretical) value of $\Delta\Psi$ is readily calculated from the assumed pore geometry once the differential equations (*e.g.* eqns. 13 and 14) have been solved for Ψ_x as a function of r in both pore liquid and RPBP. The averaging is done over both of these parts of the stationary phase taken together. Values are found by calculating the values for k'_{S} using eqn. 16, then using the calculated values of k'_{S} in eqn. 18 to arrive at $\Delta\Psi$. Comparison of the model-predicted values of $\Delta\Psi$ with the experimentally-estimated values for ODS systems revealed similar trends, but suggested a significant contribution to the potential from fixed-charge sites on the silica surface [60,64]. The quantity $\Delta\Psi$ has also been called the "effective potential difference".

3.5. Surface adsorption, diffuse layer ion-exchange DL model

A third DL-derived model which has been used to interpret IM-RPLC was proposed by Cantwell in 1984 [74], based on earlier studies of the sorption of ions by the non-polar styrene–divinylbenzene adsorbent Amberlite XAD-2 [56] and by low-capacity ion exchangers made from it [91–93]. The proposed model was recently tested on an ODS-bonded phase [65,72].

According to this model, adsorption of the modifier ion $M^{\pm}$ occurs onto/into the interface between the RPBP and the aqueous pore solution to create a charge-surface with a charge-density of σ_0 and a surface-potential Ψ_0, as in the model of Stahlberg. Also, the diffuse part of the double layer in the solution at and beyond the OHP is considered to be part of the stationary phase, as in the model of Weber. A compact part of the double layer is assumed to exist between the charge-surface and the OHP on the solution side of the interface. However the compact part is generally assumed to be empty (*i.e.* no IHP).

In this model an adsorbed PPI (*i.e.* $M^{\pm}$ or $S^{\pm}$)

is considered to be a *potential-determining ion* (PDI). In surface and colloid science this term has a restricted but, historically, somewhat ambiguous definition. In the most restricted sense, a PDI is an ion which is present in the crystal lattice of the solid phase, such as Ag^+ or Cl^- in AgCl(s), and whose bulk solution concentration (activity) is related to the surface potential by the Nernst equation [ref. 28, p. 19; ref. 31, p. 231]. Adsorbed foreign ions are said not to be PDIs but, rather, to be "specifically adsorbed". However, the term potential-determining ion is often used for H^+ and OH^- on an acid/base ionizable surface ~~(ref. 28, p. 20) and~~ it has also been used for Cl^- ion sorbed on elemental gold [94] and for ions such as Ag^+, Ca^{2+} and Al^{3+} sorbed on SnO_2(s) [95]. A key point is that the sorbed ion is desolvated and so closely sorbed to the surface that it can be considered to have left the solution phase completely and to contribute to the primary (*i.e.* surface) charge (ref. 31, p. 231), rather than to reside in a Stern plane or an Inner Helmholtz Plane which would be the situation of a "specifically adsorbed" ion.

In Cantwell's model, the adsorbed ions $S^\pm$ and $M^\pm$ create the primary surface-charge and the surface potential Ψ_0. The plane at which these adsorbed ions reside is, by definition, the "surface". The ions $M^\pm$ and $S^\pm$ are potential-determining ions in that Ψ_0 is assumed to be constant when the *activity* of these ions in solution is held constant (see below). It is *not necessary* to further assume that the Nernst equation applies, although it is interesting, incidentally, to note that Nernstian behavior has been observed for an organic cation adsorbed on a porous polymer [56].

In this model no assumptions are made about the shape of the $M^\pm$ sorption isotherm (*e.g.* it is not assumed to be a potential-modified Langmuir isotherm). The sorption isotherm, which is a plot of Γ_M *vs.* C_M, must be experimentally measured [65]. The value of σ_0 is calculated from the sorption isotherm of $M^\pm$ using the surface excess of $M^\pm$ adsorbed at the interface, Γ_M^{AD}, via the relationship

$$\sigma_0 = Z_M F \Gamma_M^{AD} \tag{19}$$

$$\Gamma_M = \Gamma_M^{AD} + \Gamma_M^{DL} \tag{20}$$

where the value of Γ_M^{AD} is obtained from the sorption isotherm by making a correction for the *negative* surface excess of $M^\pm$ in the diffuse layer, Γ_M^{DL}.

The relationship between σ_0 and Ψ_0 is calculated via the Stern–Gouy–Chapman theory in which Ψ_{OHP} is related, simultaneously, to the experimentally obtained value of σ_0 by the Gouy–Chapman theory and to the surface-potential Ψ_0 via both σ_0 and the capacitance of the compact part of the double layer, C_1 (farad/cm^2) [56,65]. The equation relating these parameters is

$$\frac{1}{\sigma_0} = \frac{1}{C_1\Psi_0} + \frac{1}{2.28\cdot 10^{-4}c^{1/2}\Psi_0\left[\left(\frac{Z_M F\Psi_{OHP}}{RT}\right)^{-1}\sinh\left(\frac{Z_M F\Psi_{OHP}}{RT}\right)\right]} \tag{21}$$

in which c is ionic strength of the bulk solution. The constant $2.28\cdot 10^{-4}$ includes parameters such as the Faraday and ideal gas constants, the temperature and the permittivity of the solution. Solving for the relationship between σ_0 and Ψ_{OHP} by a simple iterative computation (not shown) is the way in which the correction is made for the negative excess (exclusion) of $M^\pm$ in the diffuse layer Γ_M^{DL} [56,65,74]. The bracketed term on the right-hand side of eqn. 21 accounts for the non-linearity in the relationship between σ_0 and Ψ_{OHP}. When $\Psi_{OHP} \leq 0.025$ V, then the Debye–Hückel approximation is valid, the bracketed term assumes the value $(Z_M F\Psi_{OHP}/RT)$, and Ψ_{OHP} becomes linearly related to σ_0.

Eq. 21 can be used to measure Ψ_0 and C_1 at conditions for which Ψ_0 is constant. This is done as follows. A family of sorption isotherms is measured for $M^\pm$, each isotherm being measured at a constant ionic strength c. Since $M^\pm$ is a PDI, the value of Ψ_0 will be a constant, regardless of the solution ionic strength, provided that the *ionic activity*, a_M, of $M^\pm$ in the solution is constant. Thus, each isotherm is re-plotted as Γ_M *vs.* a_M, where a_M is the product of C_M and an ionic activity coefficient. Then, for each a_M chosen, a plot is made of σ_0^{-1} *vs.* $\{c^{1/2}[(Z_M F\Psi_{OHP}/RT)^{-1}$ sinh $(Z_M F\Psi_{OHP}/$

$RT)]\}^{-1}$. From the slopes and intercepts of the resulting straight lines the values of C_1 and Ψ_0 may be obtained, the latter corresponding to the particular a_M at which the plot was made. The linearity of such plots and the constancy of C_1 (*i.e.* independent of a_M and c), which are nearly always obtained, constitute an experimental test of the validity of eqn. 21 and indirectly justifies the use of the planar, semi-infinite solution of the Poisson–Boltzman equation as a viable approximation of the dependence of Ψ_{OHP} on σ_0, even in porous HPLC sorbents.

For the sample ion S^+ sorption is assumed to be due both to adsorption onto/into the same interfacial charge surface at which $M^{\pm}$ is adsorbed, and to sorption in the diffuse layer. Surface adsorption of $S^{\pm}$ at the interface between the RPBP and the pore liquid is similar to what is assumed in the Ståhlberg model but different from partitioning into a bulk-liquid-like RPBP that is assumed in the Weber model. Conversely, sorption of $S^{\pm}$ in the diffuse layer is similar to the assumption which is in the Weber model but which is absent from the Ståhlberg model. The overall k'_S is given by

$$k'_S = k'_{S,ADS} + k'_{S,DL} \qquad (22)$$

For surface adsorption of the sample ion eqn. 5 takes the form [56,72]

$$k'_{S,ADS} = E\frac{\gamma_S}{\gamma_{S,ADS}}\exp\left(-\frac{Z_S F\Psi_0 + \Delta G^{\circ}_{S,ch,ADS}}{RT}\right) \qquad (23)$$

where E is a constant, γ_S is the ionic activity coefficient of $S^{\pm}$ in bulk solution and $\Delta G^{\circ}_{S,ch,ADS}$ (without a prime) is the chemical potential for transfer to the uncharged thermodynamic reference state surface which is taken to be the surface having an infinitely low value of Γ_M^{AD}. The *non-ionic* surface activity coefficient for adsorbed $S^{\pm}$, $\gamma_{S,ADS}$, accounts for two effects that could possibly arise as a result of having an appreciable amount of $M^{\pm}$ adsorbed on the surface. It provides for a possible space-related statistical effect in the form of a competition for space between $S^{\pm}$ and $M^{\pm}$. It also provides for a possible change in the "chemical" character of the adsorbent interface at higher surface concentrations of $M^{\pm}$, as was discussed in connection with eqns. 4 and 5, above [74]. In practice it has been found that $\gamma_{S,ADS} \approx 1$, or is at least constant, as the concentrations of $M^{\pm}$ and $S^{\pm}$ employed in linear chromatography [72]. This observation, according to Cantwell, justifies having made the simplifying approximation of neglecting both any space-related, statistical effects and any changes in chemical character of the adsorbent surface.

The sorption process that is responsible for $k'_{S,DL}$ is assumed to take place throughout the diffuse layer which, as has been discussed, extends into the pore liquid for various distances depending on the ionic strength of the bulk solution. It has previously been shown that since an equation of the form of eqn. 5 pertains to each ionic species at every point throughout the diffuse layer, and since the value of Ψ_x is unique at any point x in the diffuse layer, it is possible to combine equations of the form of eqn. 5 (or eqn. 15) for the sample ion $S^{\pm}$ and for the principal counterion $X^{\pm}$ of the swamping electrolyte in order to eliminate Ψ_x from the equation [93]. What is left is an equation for the *ion exchange* of $S^{\pm}$ for $X^{\pm}$ between the diffuse layer and the bulk solution. Thus, treatment of the diffuse part of the double layer at a charged interface as an ion exchanger is in keeping with the classical principles of surface science [35]. For a uni-univalent swamping electrolyte the bulk solution ionic strength is essentially equal to the concentration of $X^{\pm}$ and may be substituted for it in the ion exchange equation. The resulting expression for $k'_{S,DL}$ $(=k'_{S,IEX})$ is [72,74,91]

$$k'_{S,DL} = k'_{S,IEX} = \frac{K_{S,IEX}A}{V_m}\cdot\frac{\Gamma_M}{c} \qquad (24)$$

where A is the total area of interface in the column and V_m is the column void volume as measured with a small, unretained, non-ionic molecule. The surface excess of $M^{\pm}$ is the value Γ_M as in eqn. 20, not Γ_M^{AD}. The *ion-exchange capacity* of the column is given by

$$Q_{wt} = A_{sp}\cdot\Gamma_M\ (\text{equiv./g}) \qquad (25)$$

where A_{sp} is the specific surface area (cm^2/g). It is evident that the ion exchanger that is described here is in fact a "dynamic ion exchanger", since Γ_M varies with C_M and c.

An experimental test of eqns. 22–24, which describe sample sorption, was made by Liu and Cantwell [72] for the system in which tetra-*n*-butylammonium ion is $M^{\pm}$, *p*-nitrobenzenesulfonate is $S^{\pm}$ and the chromatographic sorbent is an ODS bonded phase. Examination of eqns. 23 and 24 reveals two things: first, that each equation contains only one unknown constant, *i.e.* $K_{S,IEX}$ in eqn. 23 and $\Delta G^{\circ}_{S,ch,ADS}$ in eqn. 24 (if $\gamma_{S,ADS} \approx 1$); second, the ionic strength dependences of the two equations are different from one another. Thus the validity of eqns. 22–24 was tested by making plots of the distribution coefficient of $S^{\pm}$ *vs.* c at several activities of $M^{\pm}$. Non-linear least-squares fits were performed on each curve to see how well eqns. 22–24 fit the data. In general, the fits were very good and supported this surface adsorption, diffuse layer ion-exchange DL model.

3.6. *Surface ion-exchange, diffuse layer ion-exchange DL model*

In 1981 Deelder and Van den Berg published a paper which revealed a great deal of insight about the application of DL theory to IM RPLC [57]. Experimentally they used an alkanesulfonate as modifier ion M^- and an organic ammonium ion as sample S^+, on an ODS sorbent. Adsorbent of M^- at the interface between the RPBP and pore liquid was assumed to give rise to a surface potential Ψ_0 and to follow a surface-potential modified Langmuir adsorption isotherm. No compact layer was invoked and the value of Ψ_0 was calculated using the Gouy–Chapman theory for a planar surface. The surface excess of sorbed M^- was measured experimentally using chromatographic breakthrough curves for M^-. Although it was recognized that the surface excess, Γ_M, measured in this way was different from the adsorbed surface excess Γ_M^{AD}, due to expulsion of M^+ from the diffuse layer, this distinction was ignored because it was estimated that the difference between Γ_M^{AD} and Γ_M was small under the conditions employed. Experimental results for sorption of the modifier ion octane sulfonate agreed well with the predictions of this theory.

Sorption of sample counterions S^+, according to Deelder and Van den Berg, could occur in a spatially continuous manner at all locations in the double layer, starting at the interfacial charge-surface created by the ionic head groups of adsorbed M^- and extending throughout the diffuse layer. In fact, since the charge-surface could lie slightly on the solution side of the RPBP-solution phase boundary, it was considered that S^+ could even penetrate into the zone between the charge-surface and phase boundary. Ions of S^+ sorbed at or very close to the charge-surface were said to occupy a Stern plane which, as noted, is virtually identical to the charge-surface. The free energy of adsorption of S^+ ions in the Stern plane, in terms of eqn. 5, have contribution from finite values of both Ψ_0 and $\Delta G^{\circ\prime}_{S,ch}$. Furthermore, S^+ ions sorbed in this Stern plane were assumed to follow their own surface potential modified Langmuir isotherm. In contrast, the free energy of sorption of S^+ ions that are present as a surface excess in the *diffuse part* of the double layer has only an electrical contribution due to the local values of $\Psi_x(r)$. For them, $\Delta G^{\circ\prime}_{S,ch} = 0$, as in Weber's model.

Deelder and Van den Berg were attempting to explain, in DL-terms, the "dynamic ion exchange" sorption of S^+, for which the ion-exchange equilibrium constant is

$$K_{S,IEX} = \frac{\Gamma_S C_X}{\Gamma_X C_S} \tag{26}$$

where X^+ is the principal counterion from the electrolyte. For this reason they developed an expression for $K_{S,IEX}$ which would explain the existence of selectivity in the ion-exchange process:

$$K_{S,IEX} = \frac{1 - \alpha_{S,Stern}}{1 - \alpha_{X,Stern}} \tag{27}$$

Here $\alpha_{i,Stern}$ is the fraction of the total amount of sorbed counterion i^+ (either S^+ or X^+) that is in the Stern plane and $(1 - \alpha_{i,Stern})$ is the fraction in the diffuse layer. It is the values of $\alpha_{i,\mathrm{Stern}}$ that derive from DL theory

$$\alpha_{i,\mathrm{Stern}}=\frac{\Gamma_{\mathrm{S}}^{\mathrm{AD}}}{\Gamma_{\mathrm{S}}^{\mathrm{AD}}+\Gamma_{\mathrm{S}}^{\mathrm{DL}}} \tag{28}$$

3.7. Comparison of DL models of IM-RPLC

Comparisons are made here among the four major DL models; those of Ståhlberg, Weber, Cantwell and Deelder. Each of the groups that has published on this topic has used, directly or indirectly, the Poisson–Boltzmann equation and concept. The concept is that ions are distributed in solution in such a way that they satisfy Poisson's equation and Boltzmann's equation. To satisfy Poisson's equation, the second spatial derivative of the potential (the first derivative of the electric field) is proportional to the local charge density and inversely proportional to the local dielectric constant. To satisfy Boltzmann's equation, ions are concentrated or depleted in regions of space according to the sign and magnitude of the local potential.

Ståhlberg has focused on the interface between the RPBP and the pore solution. Both the modifier ion $M^{\pm}$ and the sample ion $S^{\pm}$ are adsorbed exclusively at this location. Statistical space limitations of the surface for the adsorption of $M^{\pm}$ are allowed for by using the "surface potential-modified Langmuir isotherm" which was originally formulated by Stern who assumed a Langmuir isotherm but recognized that the free energy of adsorption in the Langmuir equation must depend on the surface potential Ψ_0. In a very nice development, Ståhlberg determined what the adsorption isotherm of several alkylsulfonates would have been had they not been charged. This was possible because the electrical part of the electrochemical free energy was calculable from values of measured Ψ_0 and the charge on the ionic modifier.

Cantwell also includes interfacial adsorption of both $M^{\pm}$ and $S^{\pm}$ as one of the two processes responsible for sorption of these ions. In contrast to Ståhlberg's approach, the adsorbed ions are approximated as true potential-determining ions and no particular theoretical (and perhaps unrealistic) isotherm shape is imposed on the surface adsorption. This could be an advantage; but it also could be a disadvantage because the statistical effect of space limitations of the surface are, therefore, not implicit in the Cantwell formulation. However, the observation of linearity in experimental plots of σ_0^{-1} *vs.* $[c^{1/2}\,\mathrm{f}(\Psi_{\mathrm{OHP}})]$, according to eqn. 21, provides a criterion for identifying when the statistical effect on the surface can justifiably be neglected. The observed linearity of these plots also supports the approximation that the PPI is a PDI, since it supports the view that Ψ_0 is constant when the activity of the PDI is constant in solution.

In theoretical calculations of Ψ_0, Ståhlberg included the cylindrical solution to the Poisson–Boltzmann equation. This, in principle, is better than using the planar solution. The ions sorbed to the inside of a porous particle are certainly influenced by the presence of ions sorbed to a wall only 100 Å away if the ionic strength is low enough, so the planar model is unrealistic for many circumstances. In order to be appropriate, the double layer thickness must be much smaller than the radius of a pore. For a 1:1 electrolyte, the double layer thickness is about 3 $c^{-1/2}$ Å, where c is in *M*. Thus, for 100 Å pore diameter, the double layer thickness should be no more than 10 Å or so for the planar theory to apply. This corresponds to about 100 m*M* electrolyte. At lower ionic strengths the planar model is questionable. On the other hand, the planar solution can be performed readily for the high potential case, at which the cylindrical and "sandwich" solutions are difficult. High potentials are often involved under IM-RPLC conditions.

The major simplifying assumption of Ståhlberg's approach is the neglect of surface excess contributions of both $M^{\pm}$ and $S^{\pm}$ from the diffuse part of the double layer. The adsorbed surface-concentrations n_{M} and n_{S} differ from the true *adsorbed* surface excesses $\Gamma_{\mathrm{M}}^{\mathrm{AD}}$ and $\Gamma_{\mathrm{S}}^{\mathrm{AD}}$. Adsorbed surface charge density σ_0 should, in fact, be calculated from $\Gamma_{\mathrm{M}}^{\mathrm{AD}}$ rather than from n_{M} (or Γ_{M}). In addition the experimentally measured k'_{S} actually reflects the sum of the surface excess contributions of $S^{\pm}$ from both the charge-surface ($\Gamma_{\mathrm{S}}^{\mathrm{AD}}$) and the diffuse layer ($\Gamma_{\mathrm{S}}^{\mathrm{DL}}$). However, under some experimental conditions, the neglect of diffuse-layer surface excesses becomes a reasonable approximation. This is true for conditions which produce a relatively low value of Ψ_0 [72] because, when Ψ_0 is low $\Gamma_S^{AD} \gg \Gamma_S^{DL}$.

Both Ståhlberg and Cantwell have developed experimental methods to measure the surface potential (with the aid of extra-thermodynamic assumptions). With both methods, the presence of fixed ionic sites, such as ionized residual silanol groups, leads to errors in the measured values.

Weber's work has not been as comprehensively applied as that of Cantwell or Ståhlberg. It has been more of an analytical approach to the problem of understanding and measuring interfacial potential differences even in the absence of a dominant PPI. The approach to the determination of the effective potential difference between two phases is similar in principal to Ståhlberg's. Because only poorly hydrophobic ions were used to establish the potentials, the fixed anionic sites from silica played a large role in the establishment of the conditions.

Weber has tried to compare experiment and theory when the spatial extent of the diffuse layer(s) is(are) taken into account. One difficulty of this is that the lack of accurate knowledge of the actual situation at the interface leads to calculations requiring a large number of estimated parameters (free energies of transfer and molar volumes of all ions, stationary phase thickness, pore diameter, dielectric constant of each phase). Weber's approach is less solidly grounded in experimental observation, especially of the quantity of sorbed charge, than the others. On the other hand, it has been shown that the more exact theory converges to the theory used by Cantwell under certain conditions.

In comparison, the second sorption process invoked by Cantwell is essentially the same as the sorption of $S^{\pm}$ and the exclusion of $M^{\pm}$ that occurs in the pore liquid diffuse-layer in Weber's model. As discussed above, the formulation of $S^{\pm}$ sorption in the diffuse layer as an ion exchange process derives directly from electrical double layer theory and is consistent with the fundamental eqn. 5. However, compared to Weber's approach there is one difference. If the Weber formulation of $S^{\pm}$-sorption in the diffuse layer were re-cast as an ion-exchange process, which can be done without doing violence to Weber's model, the ion-exchange equilibrium constant $K_{S,IEX}$, as in eqn. 24, would have the value of unity. This is because the value of $\Delta G^{\circ\prime}_{i,ch}$ in eqn. 5, as applied to the transfer of any ion from bulk liquid to any location x in the diffuse layer, is assumed to be zero. (Recall the second numerator term in eqn. 16.) The argument for this is that solution in the diffuse layer is, chemically, essentially identical to bulk solution. In the Cantwell model $K_{S,IEX}$ need not be unity. The argument in this case is that the "chemical" properties of the solution in the diffuse layer in a pore, where it comes under the influence of the hydrophobic RPBP surface, need not be identical to the properties of the same solution in the bulk liquid. In support of this view, it has been reported that the alkali metal cations Na^+ and K^+ elute at different times from an IM-RPLC system in which octanesulfonate is the modifier ion [96]. Alkali metal ions are highly hydrated and are therefore likely to be retained by ion exchange in the diffuse layer but not by interfacial adsorption. In any event, the values of $K_{S,IEX}$ experimentally obtained by Cantwell from non-linear least squares plots of eqn. 24 were quite different from unity.

Technically, the planar interface model, which was used by Cantwell, does not give accurate predictions for the highly convoluted interface of the dimensions used. Of course, it is also true that the cylinder is only an approximate model of a pore, so there is no guarantee that the extra effort required to use the cylindrical geometry is worth it.

Comparison between the Deelder and the Cantwell models reveals a lot of similarity. Like Cantwell, Deelder employs the planar solution of the Poisson–Boltzmann equation but, unlike Cantwell, he uses the Gouy–Chapman solution without a compact layer. The Stern plane of Deelder is roughly the same as the adsorptive charge-surface of Cantwell and Stahlberg. It the term $\alpha_{X,\mathrm{Stern}}$ for sorption of a principal counterion such as Na^+ in the Stern plane is very small, then the sorption of S^+ in the Stern plane, where

$\Delta G^{\circ\prime}_{S,\mathrm{ch}}$ is not zero, becomes essentially the same as the surface adsorption invoked by Cantwell. In addition, Deelder invokes ion exchange in the diffuse layer, as does Cantwell, but Deelder assumes no selectivity here, in a manner that is more consistent with Weber's approach to diffuse-layer sorption of S^+.

The existence of selectivity in the ion exchange of a sample in the diffuse-layer would imply that the sample ion is not behaving as a completely "indifferent electrolyte" in the manner assumed in most double layer calculations [36]. This point will require examination in the future.

Finally, an observation can be made about "indirect UV detection" HPLC, in terms of DL-models. The "probe" species is often the modifier ion $M^{\pm}$ in these systems. It is reasonable to expect that a proposed IM-RPLC retention model should be able to explain the indirect detection of sample ions which is observed chromatographically. The observations generally are that when the "probe" species is the modifier ion, sample ions $S^{\pm}$ which have a sign of charge *opposite* to that of the probe increase the sorption of the probe, while $S^{\pm}$ with the same sign of charge as the probe decrease the sorption of the probe. The two phenomena that might be involved in decreasing probe sorption are competition for space in the stationary phase and increased electrostatic contribution to free energy of sorption of the probe ion due to a change in Ψ_x as a result of sorption of the sample ion [84,97]. *Increased* sorption of probe is likely to be caused by change in Ψ_x alone.

In formulating DL-retention models to explain the sorption of a small amount of sample ion $S^{\pm}$ in the presence of a much larger amount of modifier (probe) ion $M^{\pm}$, it is convenient and sufficiently accurate to neglect the contribution of $S^{\pm}$ to Ψ_x. However, this does not mean that small amounts of $S^{\pm}$ do not alter Ψ_x values. They do alter them, but only slightly. Therefore sorption of a small amount of $S^{\pm}$ will increase or decrease the sorption of $M^{\pm}$ by a small amount and cause a small change in absorbance of the mobile phase. The point is that in indirect UV detection the change in absorbance is, in fact, typically only a small fraction of the absolute value of the absorbance. Thus, in terms of the electrical potential effect, any of the double layer models correctly accounts for the observed signs and relative magnitudes of indirect detection of sample and system peaks.

4. ACKNOWLEDGEMENTS

This work was supported by the National Institutes of Health, grant GM 44842 (S.G.W.), and by the Natural Sciences and Engineering Research Council of Canada (F.F.C.).

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