The expression *chromatographic* bed or sorbent may be used as a general term to denote any of the different forms in which the stationary phase is used.

Note: Particularly in gas chromatography where the stationary phase is most often a liquid, the term *liquid phase* is used for it as compared to the *gas phase*, i.e., the mobile phase. However, particularly in the early development of liquid chromatography, the term 'liquid phase' had also been used to characterize the mobile phase as compared to the 'solid phase', i.e. the stationary phase. Due to this ambiguity the use of the term 'liquid phase' is discouraged. If the physical state of the stationary phase is to be expressed the use of the adjective forms, such as *liquid stationary phase* and *solid stationary phase*, *bonded phase* or *immobilized phase*, are recommended.

1.1.05.1. Bonded phase

A stationary phase which is covalently bonded to the support particles or to the inside wall of the column tubing.

1.1.05.2. Immobilized phase

A stationary phase which immobilized on the support particles, or on the inner wall of the column tubing, e.g. by *in situ* polymerization (cross-linking) after coating.

3.1.07. Packing

The active solid, stationary phase plus solid support or swollen gel contained in a tube.

6B. Characterization of Ion Exchange Chromatographic Stationary Phases

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Abstract

In order to characterize ion exchange chromatographic stationary phases the thermodynamic exchange constant and the free energy interaction parameters are recommended. These parameters are calculated from the experimentally available corrected selectivity coefficient *vs*. exchanger phase composition functions. The equations used for the calculations have been obtained by introducing the Friedman equation (developed for the calculation of the excess free energy change) into the thermodynamic derivation. The suggested parameters also make possible the estimation of the value of the selectivity coefficient at an arbitrary exchanger phase composition. The characteristic parameters of the ion exchange resins and the equations in a directly suitable form for the estimation of the selectivity coefficient are calculated and presented for several systems.

Introduction

Parameters for the physical and chemical characterization of chromatographic stationary phases including ion exchangers have already been defined [1]. The purpose of this paper is to introduce sensitive numerical parameters for the comparison of operation ion exchange chromatographic stationary phases based on their selectivity coefficient exhibited in a particular ion exchange equilibria. For two competing counter ions (*e.g.* A^{+} and B^{z+}) the problem arises not only because various selectivity coefficients may be assigned to the various commercially available products, but also because the exact value of the selectivity coefficient

may vary considerably with the degree of conversion of the exchanger phase as the ion exchange reaction (1) proceeds.

$$z \cdot \mathrm{RA} + \mathrm{B}^{z+} \leftrightarrow \mathrm{R_zB} + z \cdot \mathrm{A}^{+} \tag{1}$$

Here R represents the (usually monovalent) functional group covalently bond to a solid phase. The so-called corrected selectivity coefficient (K') is an experimentally available parameter defined for the above equilibria as:

$$K' = \frac{\bar{x}_\mathrm{B} \cdot a_\mathrm{A}^z}{\bar{x}_\mathrm{A}^z \cdot a_\mathrm{B}} \tag{2}$$

Throughout this article, symbols with overbars refer to the resin phase where the standard and reference states of RA and $\mathrm{R_zB}$ are taken to the respective mono-ionic forms of the exchanger in equilibrium with water. Symbols without a bar refer to the solution phase where the Henryan standard and reference states are accepted in accordance with conventional practice [2]. $\bar{x}$ denotes mole or, if $z > 1$, equivalent fraction (in general $\bar{x}_i = z_i \cdot \bar{m}_i / \sum z_i \cdot \bar{m}_i$ and the summation is carried out over all counterion molalities $\bar{m}_i$), a and the parameter $\bar{a}$ (see below) are the activities in the solution and resin phases respectively. For the ultimate characterization and comparison of the selectivity of the exchange reactions the more exactly defined thermodynamic exchange constant, K^T is recommended [2,3]:

$$K^\mathrm{T} = \frac{\bar{a}_\mathrm{B} \cdot a_\mathrm{A}^z}{\bar{a}_\mathrm{A}^z \cdot a_\mathrm{B}} \tag{3}$$

An extensive compilation of the K^T data for the various ion exchange equilibria has been made in an earlier report of the IUPAC [4]. Since the ion exchange equilibrium constant is directly related to the distribution coefficient of the ion studied its knowledge in the calculation of the retention volume, or generally in the design of ion exchange separations, is indispensable. Considering however, that in the majority of analytical ion exchange separations practically either one or the other end to the mole fraction scale is utilized ($\bar{x}_\mathrm{A} \approx 1$ or $\bar{x}_\mathrm{B} \approx 1$), the thermodynamic constant could be quite far from the actual (operational) value of the selectivity coefficient. The suggested characterization method is meant to provide a solution for these seemingly conflicting aspects.

Using the concentrated electrolyte solution model of the ion exchange resins, equations were derived for the composition dependence of the selectivity coefficient (see equations on pages 104 and 105 of reference [5]). From the experimentally available functions $\ln K'$ *vs.* $\bar{x}_\mathrm{B}$ the derived relationships make possible both the calculation of the thermodynamic exchange constant and the so-called free energy interaction parameters which, in turn, could be used to calculate the selectivity coefficient at any value of $\bar{x}_\mathrm{B}$. It was proved that the free energy interaction parameters are related to the selectivity controlling properties of the ion exchanger phase, such as the crosslinking of the polymer matrix, the type of the functional group and the size of the exchanging counter ions [5]. The purpose of the suggested method is to characterize the ion exchangers with these parameters in connection with their actual ion exchange reaction. It may also be considered as an operational characterization which uses both the thermodynamic constant and the above mentioned free energy interaction parameters to estimate the value of the corrected selectivity coefficient at an arbitrary exchanger phase composition.

Theoretical Background

When reaction (1) takes place a mixture of the concentrated electrolytes is always formed. The composition of this mixture ($\bar{x}_\mathrm{B}$) varies as the resin is converted from A^+ and B^{z+} form. According to H.L. Friedman [6] the excess free energy change (ΔG^E) accompanying the formation of a two component electrolyte solution mixture at constant ionic strength I (containing a common cation or anion) can be approximated by the equation:

$$\Delta G^\mathrm{E} = R \cdot T \cdot I^2 \cdot x_\mathrm{A} \cdot x_\mathrm{B} \cdot [g_0 + g_1 \cdot (x_\mathrm{A} - x_\mathrm{B})] \tag{4}$$

Here x_A and x_B are the mole fractions of the components (e.g. RA and $\mathrm{R_zB}$) and g_0 and g_1 are the so called free energy interaction parameters independent of the composition. These terms have been introduced by

Table 1 Summary of the equations used for the calculations

	$\ln K' = a_0 + a_1 \cdot \bar{x}_B + a_2 \cdot \bar{x}_B^2$	(5)	
$a_2 < 0$		$a_2 > 0$	
	$\bar{g}_0 = \dfrac{a_1 + a_2}{2 \cdot z}$	(6)	$\bar{g}_0 = \dfrac{a_1 + a_2}{2 \cdot z}$ (9)
	$\bar{g}_1 = \dfrac{-a_2}{6 \cdot z}$	(7)	$\bar{g}_1 = \dfrac{a_2}{6 \cdot z}$ (10)
	$\ln K^T = a_0 + z \cdot \bar{g}_0 + z \cdot \bar{g}_1$	(8)	$\ln K^T = a_0 + z \cdot \bar{g}_0 - z \cdot \bar{g}_1$ (11)

Friedman to account for the strength of pair and triplet interactions respectively in a concentrated two component electrolyte solution mixture. The existence of a similar mixture of concentrated electrolyte solutions is supposed to be present in the exchanger phase too. It has been pointed out [5] that by introducing eqn. (4) into the thermodynamic derivation the composition dependence of the selectivity coefficient can be expressed conveniently by these free energy interaction parameters. Equations suggested for the calculation of the characteristic ion exchange parameters ($\bar{g}_0$, $\bar{g}_1$ and $\ln K^T$) were taken from reference [5] and are summarized for our purpose in **Table 1**.

Although a direct, *a priori*, calculation of the free energy interaction parameters for the concentrated electrolyte solution of the exchanger phase is still not feasible a detailed analysis of several literature data proved that their value is dramatically influenced by the crosslinking of the inert (polymer) matrix, by the type and density of the active group of the resin and by the type of the counter ion [5]. Consequently, these parameters by themselves are characteristic for the ion exchange chromatographic stationary phase *i.e.* a difference in their values for the two compared stationary phases indicate differences in relevant structural parameters governing ion exchange selectivity.

Source of Experimental Data and Examples for the Suggested Ion Exchange Stationary Phase Characterization

An important criteria for the application of the equations shown in **Table 1** is that the exchange reaction should be completely reversible, where the exchange capacity is freely accessible to the competing counter ions. The exchange equilibrium should be studied at a constant temperature and ionic strength in the full range of mole fraction scale and the corrected selectivity coefficient, K' defined by eqn. (2) should be calculated at each exchanger phase composition. As an application of the above equations, we can consider the following experimental data obtained by Bonner [7] for the Na^+/H^+ exchange reaction on a strongly acidic Dowex 50×8 resin:

$\bar{x}_{Na}$:	0.12	0.22	0.32	0.42	0.58	0.70	0.75	0.86
$\ln K'$:	0.470	0.438	0.438	0.439	0.451	0.405	0.343	0.270

When eqn. (5) of Table 1 is fitted to the above $\ln K'$ *vs.* $\bar{x}_{Na}$ data pairs then the following coefficients are obtained: $a_0 = 0.400$, $a_1 = 0.398$, $a_2 = -0.624$ (the curve fitting program used for the calculation is given in reference [8]). Since $a_2 < 0$ eqns. (6, 7 and 8) of Table 1 can be used for the calculation of the characteristic parameters of the studied exchange equilibria. The obtained values are: $\bar{g}_0 = -0.113$, $\bar{g}_1 = 0.104$, $\ln K^T = 0.39$.

The function describing the dependence of $\ln K'$ on the exchanger phase composition can therefore be given by the so-called selectivity polynomial:

$$\ln K' = 0.400 + 0.398 \cdot \bar{x}_{Na} - 0.624 \cdot \bar{x}_{Na}^2 \tag{12}$$

If in the actual exchange process the estimated value of the stationary phase loading is e.g. 0.1 (or at the other extreme end of the mole fraction scale is e.g. 0.9) then the calculated $\ln K'$ value is 0.433 (or 0.253)

which are certainly more realistic values for the design of an ion exchange separation process than the value of $\ln K^{T}$ (0.39).

If the experimentally obtained ($\ln K'$ *vs.* $\bar{x}_B$) function is concave i.e. $a_2 > 0$ then eqns. (9, 10 and 11) of Table 1 should be used for the calculation of the above parameters. It may also happen that the experimental data fits well with a straight line. In this case the above equations are also valid but, of course, now $a_2 = 0$. The choice between the linear or the quadratic fitting procedures can be made by the comparison of the goodness of fit parameters. It is, in fact, automatically calculated by the referred curve fitting program and the improvement in the goodness of fit can be seen immediately when the degree of the polynomial is changed (e.g. from one to two).

In order to illustrate the wide scope of applicability of the suggested characterization method **Tables 2** and **3** show the calculated values of the above discussed equilibrium parameters for a set of systems. The equilibria

Table 2 Free energy interaction parameters ($\bar{g}_0$ and $\bar{g}_1$) and the selectivity polynomial for some ion exchnage equilibria

B^+	DVB%	$\bar{g}_0$	$\bar{g}_1$	$\ln K^T$	$\ln K'$	Ref.
			$RH + B^+ \leftrightarrow RB + H^+$			
Li^+	4	0.020	0.061	0.263	$0.304 - 0.327\,\bar{x}_B + 0.368\bar{x}_B^2$	9
	8	− 0.030	0.101	0.222	$0.353 - 0.669\,\bar{x}_B + 0.608\bar{x}_B^2$	9
	16	− 0.242	0.142	0.353	$0.737 - 1.338\,\bar{x}_B + 0.854\bar{x}_B^2$	9
Na^+	4	0.01	0.088	0.139	$0.041 + 0.548\,\bar{x}_B - 0.528\bar{x}_B^2$	9
	8	− 0.113	0.104	0.390	$0.400 + 0.398\,\bar{x}_B - 0.624\bar{x}_B^2$	9
	16	− 0.423	0.215	0.445	$0.653 + 0.444\,\bar{x}_B - 1.290\bar{x}_B^2$	9
K^+	4	− 0.612	0.102	0.474	$0.534 + 0.289\,\bar{x}_B - 0.613\bar{x}_B^2$	9
	8	− 0.314	0.144	0.729	$0.899 + 0.235\,\bar{x}_B - 0.863\bar{x}_B^2$	9
	16	− 1.039	0.106	1.019	$1.952 - 1.439\,\bar{x}_B - 0.640\bar{x}_B^2$	9
Rb^+	4	0.354	0.073	0.494	$0.775 - 0.270\,\bar{x}_B - 0.439\bar{x}_B^2$	10
	8	− 0.607	0.035	0.856	$1.458 - 1.423\,\bar{x}_B + 0.209\bar{x}_B^2$	10
	16	− 1.196	0.241	1.059	$2.014 - 0.946\,\bar{x}_B - 1.446\bar{x}_B^2$	10
Cs^+	4	− 0.398	0.083	0.587	$0.893 - 0.282\,\bar{x}_B - 0.496\bar{x}_B^2$	10
	8	− 0.891	0.006	0.832	$1.717 - 1.746\,\bar{x}_B - 0.035\bar{x}_B^2$	10
	16	− 1.487	0.093	1.082	$2.476 - 2.417\,\bar{x}_B - 0.557\bar{x}_B^2$	10
NH_4^+	4	− 0.156	—	0.303	$0.460 - 0.313\,\bar{x}_B$	9
	8	− 0.333	—	0.576	$0.909 - 0.667\,\bar{x}_B$	9
	16	− 0.647	—	− 0.763	$1.411 - 1.295\,\bar{x}_B$	9
$N(Me)_4^+$	7	− 0.649	—	0.081	$0.730 - 1.298\,\bar{x}_B$	11
$N(Et)_4^+$	7	− 4.245	—	− 0.489	$3.756 - 8.491\,\bar{x}_B$	11
$N(Pr)_4^+$	7	− 5.565	—	− 0.870	$4.695 - 11.130\,\bar{x}_B$	11
$N(Bu)_4^+$	7	− 9.371	—	− 0.785	$8.586 - 18.742\,\bar{x}_B$	11
			$RNa + B^- \leftrightarrow RB + Na^+$			
Cs^+	8	− 0.094	0.003	0.813	$0.445 - 0.173\,\bar{x}_B - 0.016\bar{x}_B^2$	12
Ag^+	8	− 0.184	0.033	1.308	$0.720 - 0.173\,\bar{x}_B - 0.196\bar{x}_B^2$	12
Tl^+	8	− 0.154	0.045	1.660	$0.810 - 0.081\,\bar{x}_B - 0.389\bar{x}_B^2$	12
			$RCl + B^- \leftrightarrow RB + Cl^-$			
Br^-	2	− 0.048	—	0.896	$0.945 - 0.097\,\bar{x}_B$	13
	4	− 0.085	—	1.028	$1.114 - 0.171\,\bar{x}_B$	13
	8	− 0.123	—	1.118	$1.311 - 0.245\,\bar{x}_B$	13
	10	− 0.214	—	1.411	$1.625 - 0.427\,\bar{x}_B$	13
I^-	2	− 0.087	—	1.219	$1.327 - 0.278\,\bar{x}_B + 0.213\bar{x}_B^2$	14
	4	− 0.121	—	1.487	$1.567 - 0.004\,\bar{x}_B - 0.246\bar{x}_B^2$	14
	8	− 0.197	—	2.297	$2.549 - 0.724\,\bar{x}_B + 0.329\bar{x}_B^2$	14
	10	− 0.287	—	2.946	$3.143 - 0.029\,\bar{x}_B - 0.546\bar{x}_B^2$	14
NO_3^-	2	− 0.084	0	0.643	$0.727 - 0.168\,\bar{x}_B$	14
	4	− 0.061	0	0.841	$0.903 - 0.123\,\bar{x}_B$	14
	8	− 0.149	0	1.171	$1.321 - 0.299\,\bar{x}_B$	14
	10	− 0.169	0	1.456	$1.653 - 0.393\,\bar{x}_B$	14
ClO_4^-	8	0.698	0.409	3.924	$5.033 - 3.855\,\bar{x}_B + 2.458\bar{x}_B^2$	15
ClO_3^-	8	0.195	0	0.891	$0.694 + 0.393\,\bar{x}_B$	15
BrO_3^-	8	− 0.077	0	0.354	$0.431 + 0.154\,\bar{x}_B$	15
IO_3^-	8	− 0.093	0.054	− 1.272	$-1.233 + 0.136\,\bar{x}_B - 0.323\bar{x}_B^2$	15
HCO_3^-	8	− 0.073	0.100	− 1.010	$-0.840 - 0.751\,\bar{x}_B + 0.605\bar{x}_B^2$	15
OH^-	8	− 0.315	0.118	− 2.371	$-2.174 + 0.077\,\bar{x}_B - 0.708\bar{x}_B^2$	15
SCN^-	8	− 0.481	0.142	3.29	$3.91 - 1.816\,\bar{x}_B + 0.854\bar{x}_B^2$	15

Table 3 Free energy interaction parameters ($\bar{g}_0$ and $\bar{g}_1$) and the selectivity polynomial for some anion exchange equilibria

B^{2-}	F.G.	$\bar{g}_0$	$\bar{g}_1$	$\ln K^T$	$\ln K'$	Ref.
			$2RCl + B^{2-} \leftrightarrow R_2B + 2Cl^-$			
Ox^{2-}	TMA^+	0.187	1.012	− 2.290	$-0.644 - 11.4\,\bar{x}_B + 12.15\bar{x}_B^2$	16
Ma^{2-}		0.460	0.565	− 3.048	$-2.838 - 4.942\,\bar{x}_B + 6.782\bar{x}_B^2$	16
Su^{2-}		0.288	0.017	− 3.760	$-4.303 + 0.945\,\bar{x}_B + 0.207\bar{x}_B^2$	16
Gl^{2-}		0.07	0.44	− 4.050	$5.07 + 5.00\,\bar{x}_B - 5.28\bar{x}_B^2$	16
Ad^{2-}		− 0.562	0.956	− 4.975	$-5.763 + 9.233\,\bar{x}_B - 11.47\bar{x}_B^2$	16
Pi^{2-}		− 0.922	0.102	− 5.384	$-5.58 + 8.590\,\bar{x}_B - 12.28\bar{x}_B^2$	16
Ox^{2-}		− 2.09	1.52	− 7.10	$-5.96 + 9.90\,\bar{x}_B - 18.29\bar{x}_B^2$	16
Ma^{2-}		− 0.845	0.81	− 5.46	$5.39 + 6.30\,\bar{x}_B - 9.68\bar{x}_B^2$	16
Su^{2-}		+ 0.097	0.17	− 4.05	$-4.59 + 2.44\,\bar{x}_B - 2.05\bar{x}_B^2$	16
Gl^{2-}	TEA^+	+ 0.387	0.32	− 3.29	$-3.43 - 2.29\,\bar{x}_B + 3.89\bar{x}_B^2$	16
Ad^{2-}		+ 0.006	0.07	− 4.25	$-4.42 - 0.95\,\bar{x}_B - 0.926\bar{x}_B^2$	16
Pi^{2-}		− 0.515	0.438	− 4.96	$-4.81 + 3.20\,\bar{x}_B - 5.26\bar{x}_B^2$	16

B^{2-}:Ox^{2-} = Oxalic, Ma^2 = Malonic, Su^2 = Succinic, Gl^{2-} = Glutaric, Ad^{2-} = Adipic, Pi^{2-} = Heptanedioic (Pimelic) acid anion F.G.: functionalities of the Amberlite resin, tetramethyl and tetraethylammonium groups (TMA^+, TEA^+).

selected, mostly from the 'classics' of the ion exchange literature are meant to represent both inorganic and organic cation and anion exchange reactions, where the crosslinking of the polymer matrix, the size of the active group and the size of the counter ion varies considerably.

Conclusion

The nonideal behaviour of the exchanger phase is recognized to be highly characteristic for the ion exchanger as a chromatographic stationary phase. As a quantitative measure of this nonideality the free energy interaction parameters are calculated from the data of equilibrium measurements. These data are then applied to construct the so-called selectivity polynomial which, in turn, can be used to estimate the selectivity coefficient at any required composition of the exchanger phase. Beyond the highly specific, numerically sensitive feature of these parameters their recommendation for the characterization of ion exchange chromatographic stationary phases is further supported by their connection with thermodynamic equilibrium constant of the exchange reaction.

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