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CLASSIFICATION AND CHARACTERIZATION OF STATIONARY PHASES FOR LIQUID CHROMATOGRAPHY

PART II. CHARACTERIZATION OF ION EXCHANGE CHROMATOGRAPHIC STATIONARY PHASES

(IUPAC Recommendations 1997)

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Classification and characterization of stationary phases for liquid chromatography

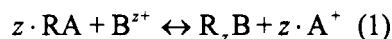
Part II. Characterization of ion exchange chromatographic stationary phases

(IUPAC Recommendations 1997)

Abstract: In order to characterise 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.

1. INTRODUCTION

Parameters for the physical and chemical characterisation 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.



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

$$K' = \frac{\bar{x}_B \cdot a_A^z}{\bar{x}_A^z \cdot a_B} \quad (2)$$

Throughout this article, symbols with overbars refer to the resin phase where the standard and reference states of RA and $R_z B$ are taken to be the respective mono-ionic forms of the exchanger in equilibrium with water. Symbols without a bar refer to the solution phase where the Henry 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 characterisation and comparison of the selectivity of the exchange reactions the more exactly defined thermodynamic exchange constant, K^T is recommended [2, 3]:

$$K^T = \frac{\bar{a}_B \cdot a_A^z}{\bar{a}_A^z \cdot a_B} \quad (3)$$

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 of the mole fraction scale is utilised ($\bar{x}_A \approx 1$ or $\bar{x}_B \approx 1$), the thermodynamic constant could be quite far from the actual (operational) value of the selectivity coefficient. The suggested characterisation 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}_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}_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 characterise the ion exchangers with these parameters in connection with their actual ion exchange reaction. It may also be considered as an operational characterisation 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.

2. THEORETICAL BACKGROUND

When reaction (1) takes place a mixture of the concentrated electrolytes is always formed. The composition of this mixture (\bar{x}_B) varies as the resin is converted from A^+ to 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

$$\Delta G^E = R \cdot T \cdot I^2 \cdot x_A \cdot x_B \cdot [g_0 + g_1 \cdot (x_A - x_B)] \quad (4)$$

Here x_A and x_B are the mole fractions of the components (*e.g.* RA and 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 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 (g_0 , g_1 and $\ln K^T$) were taken from reference [5] and are summarised for our purposes 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.

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)	
$a_2 < 0$	$a_2 > 0$
$\bar{g}_0 = \frac{a_1 + a_2}{2 \cdot z}$ (6)	$\bar{g}_0 = \frac{a_1 + a_2}{2 \cdot z}$ (9)
$\bar{g}_1 = \frac{-a_2}{6 \cdot z}$ (7)	$\bar{g}_1 = \frac{a_2}{6 \cdot z}$ (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)

3. SOURCE OF EXPERIMENTAL DATA AND EXAMPLES FOR THE SUGGESTED ION EXCHANGE STATIONARY PHASE CHARACTERISATION

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 X 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:

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

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. 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 characterisation method Tables 2. and 3. show the calculated values of the above discussed equilibrium parameters for a set of systems. The equilibria 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.

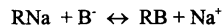
4. CONCLUSION

Table 2. Free energy interaction parameters (\bar{g}_0 and \bar{g}_1) and the selectivity polynomial for some ion exchange equilibria $RH + B^+ \leftrightarrow RB + H^+$

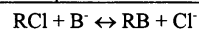
B ⁺	DVB %	\bar{g}_0	\bar{g}_1	$\ln K^T$	$\ln K'$	Ref.
Li ⁺	4	0.020	0.061	0.263	$0.304 - 0.327 \bar{x}_B + 0.368 \bar{x}_B^2$	9
	8	-0.030	0.101	0.222	$0.353 - 0.669 \bar{x}_B + 0.608 \bar{x}_B^2$	9
	16	-0.242	0.142	0.353	$0.737 - 1.338 \bar{x}_B + 0.854 \bar{x}_B^2$	9
Na ⁺	4	0.01	0.088	0.139	$0.041 + 0.548 \bar{x}_B - 0.528 \bar{x}_B^2$	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

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Table 2. continued



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



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

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Table 3. Free energy interaction parameters (\bar{g}_0 and \bar{g}_1) and the selectivity polynomial for some anion exchange equilibria
 $2RCl + B^{2-} \leftrightarrow R_2B + 2Cl^-$

B ²⁻	F.G.	\bar{g}_0	\bar{g}_1	$\ln K^\dagger$	$\ln K'$	Ref.
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⁻	TEA ⁺	-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⁻		+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

B²⁻ : Ox²⁻ = Oxalic, Ma²⁻ = Malonic, Su²⁻ = Succinic, Gl²⁻ = Glutaric, Ad²⁻ = Adipic, Pi²⁻ = Heptanedioic (Pimelic) acid anion
 F.G.: functionalities of the Amberlite resin, tetramethyl and tetraethyl ammonium groups (TMA⁺, TEA⁺)

The nonideal behaviour of the exchanger phase is recognised 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 characterisation of ion exchange chromatographic stationary phases is further supported by their connection with thermodynamic equilibrium constant of the exchange reaction.

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