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THE DETERMINANTS OF DIVALENT / MONOVALENT SELECTIVITY IN ANION EXCHANGERS

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This research demonstrates that it is the distance of fixed-charge separation in the resin which is the primary determinant of divalent / monovalent selectivity. Anion resins, particularly acrylics and epoxies, with closely spaced N-containing (amine) functional groups are inherently divalent-ion selective. This is because the uptake of a divalent anion, e.g. sulfate, requires the presence of two closely-spaced positive charges.

Results from this study of 30 commercially-available, strong- and weak-base, anion resins indicate that in order to bring positive charges into close proximity within a resin one can: (1) incorporate the amine functional groups into the polymer chains as opposed to having them pendant on the chains; (2) minimize the size and number of organic ("R") groups attached to the N atom, i.e., minimize the size of the amine; and (3) maximize the resin flexibility, i.e., its ability to reorient to satisfy divalent counterions, by minimizing the degree of crosslinking.

The distance-of-charge-separation theory is not restricted to divalent anion exchangers but also applies to cation exchangers and to polyvalent ions in general.

INTRODUCTION

Sulfate/nitrate selectivity may be an important factor in the design of an ion-exchange process for nitrate removal from potable water. That is because potable waters are quite dilute ($I = 0.010\ M$) and invariably contain sulfate, a divalent ion generally preferred by all exchangers in dilute solution. The expected dilute-solution selectivity sequence for the common ions is [1,2]:

sulfate > nitrate > chloride > bicarbonate.

When operating a strong-base chloride

ion-exchange process for nitrate removal from a typical groundwater containing sulfate, chloride and bicarbonate, the sensitivity of the process to the sulfate/nitrate separation factor is shown in Fig. 1. For a resin which is nitrate-selective with respect to sulfate ($\alpha_{S/N} < 1.0$), the BVs (bed volumes) to nitrate breakthrough calculated using equilibrium multicomponent chromatography theory [3,4] increase sharply as the resin becomes less sulfate-selective. For the more common case of a sulfate-selective resin ($\alpha_{S/N} > 1.0$), the run length is improved slightly as $\alpha_{S/N}$ increases. In this region it is the monovalent/monovalent, nitrate/chloride selectivity which is the primary determinant of run length.

Sulfate/chloride selectivity is a significant factor in the ion-exchange desulfation of seawater [5]. In studying possible seawater desulfation resins, Boari et al. [6] found that at a typical ionic strength of 0.6 *M*, the expected divalent/monovalent selectivity reversal had taken place for many resins, and that chloride was preferred to sulfate. Nevertheless, they found some resins, notably weak-base resins, whose divalent preferences remained high even at ionic strengths above 0.6 *M*. Their work clearly demonstrated that functionality is an important determinant of divalent/monovalent selectivity. Their data showed that resins with amine functional groups prefer sulfate in the following order:

primary > secondary > tertiary > quaternary.

This sequence was explained theoretically in terms of basicity. However, this is not the basicity sequence of monomeric amines in water, as can be seen in Table 1. The basicity of a series of amines is determined by the electron releasing character of the alkyl groups attached to the N atom. Thus, secondary amines are more basic than primary amines. Tertiary amines, however, are less basic than secondary ones because of lower water solubility and sterically hindered protonation [8]. Boari et al. [6] also noted that resin matrix seemed to have an influence on sulfate selectivity but did not elaborate.

In addition to the above examples of the commercial importance of $\alpha_{S/N}$ and $\alpha_{N/Cl}$, there are analytical examples. In ion chromatography, it is possible to improve resolution or analysis time by manipulating the resin's preference for sulfate, nitrate, or chloride.

Our research was aimed at determining the causes of sulfate and nitrate selectivity in anion resins. We found resin matrix and func-

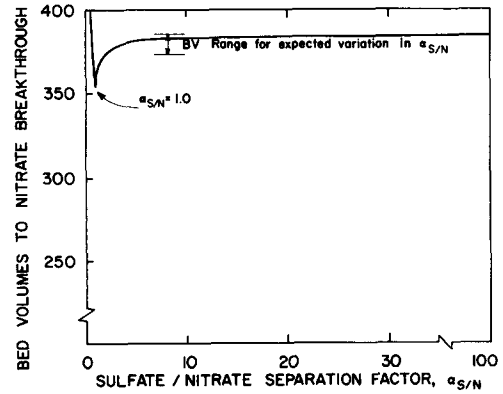

Fig. 1. Nitrate breakthrough point as influenced by the resin's preference for sulfate over nitrate, $\alpha_{S/N}$, during single-bed, chloride-form anion exchange with typical groundwater (0.0078 *N*).

TABLE 1

pK_b values for alkylamines in water at 25°C [7]

Amine functionality	Amine	pK_b
	Methylamines	
Primary	$(CH_3)NH_3^+OH^-$	3.38
Secondary	$(CH_3)_2NH_2^+OH^-$	3.23
Tertiary	$(CH_3)_3NH^+OH^-$	4.20
Quaternary	$(CH_3)_4N^+OH^-$	< 1.0
	Ethylamines	
Primary	$(C_2H_5)NH_3^+OH^-$	3.37
Secondary	$(C_2H_5)_2NH_2^+OH^-$	3.07
Tertiary	$(C_2H_5)_3NH^+OH^-$	3.28
Quaternary	$(C_2H_5)_4N^+OH^-$	< 1.0

tionality to be the most important factors as will now be shown.

The basic experimental approach was to determine the sulfate/nitrate and nitrate/chloride separation factors of 30 commercially-available anion exchangers. Then the magnitudes of the separation factors (dependent variables) were visually and statistically related to the controllable resin properties, viz., matrix, functionality, porosity, capacity, type, and pK_a (the independent variables).

EXPERIMENTAL DETAILS

Resin conditioning

Thirty anion resin samples, including Amberlite, Dowex, Duolite, and Ionac resins, were obtained and conditioned before being tested. The manufacturers' descriptions of their important characteristics (matrix, functionality, and porosity) are given in Table 2. The conditioning procedure involved extensive backwashing followed by two acid/base cycles using 2.0 N HCl and 1.5 N NaOH with intermediate and final distilled water rinses.

Conditioned base-form resins were converted in columnar fashion to the nitrate form prior to being used in the 0.00500 N batch equilibrium tests. To eliminate errors from imbibed and adhering electrolytes, the resins were treated with a 400% stoichiometric excess of 2.0 N HNO_3 followed by a 12-hour slow rinse in 0.00500 N HNO_3. Prior to air drying, the resins were transferred to a filter funnel attached to a vacuum flask and the interstitial 0.00500 N HNO_3 solution was removed by two quick (5 s) rinses using 0.001 N HNO_3. Similar procedures were used to prepare chloride- and sulfate-form resins.

Equilibrium isotherms

Equilibrium isotherm data points were developed by placing β g resin per litre solution in 100 ml of 0.00500 N H_2SO_4 or HCl, where β was estimated from eqn. (1):

$$\beta = \frac{(1-\alpha)x_N^2 + (\alpha - 2)x_N + 1}{Q/C_T}, \tag{1}$$

where x_N = equivalent fraction of nitrate in solution at equilibrium; α = the estimated separation factor, $\alpha_{S/N}$; Q = resin capacity, meq/g; and C_T = total solution concentration, 5.00 meq/l.

In the very sulfate-selective resins the original estimate ($\alpha_{S/N} = 2.5$) was far from the true value and trial and error had to be used to obtain five well-spaced equilibrium points. The resin/water mixtures were placed in 125 ml French square bottles tumbled at 13 rpm for 16 hours at an ambient temperature of approximately 25°C. After equilibration the liquid phase was analyzed for sulfate (x_S) and nitrate (x_N) and the resin phase equivalent fractions (y_S, y_N) were calculated from the previously measured values of x_N, x_S, Q and C_T. The separation factor, $\alpha_{S/N}$, rather than the mass action selectivity coefficient, $K_{S/N}$, was chosen as the measure of selectivity because the magnitude of α is independent of the concentration units used and it is the most straightforward measure of relative affinity available.

$$\alpha_{S/N} = \frac{\text{distribution of } SO_4^{2-} \text{ between phases}}{\text{distribution of } NO_3^- \text{ between phases}} = \frac{y_S/x_S}{y_N/x_N}. \tag{2}$$

Values of $\alpha_{S/N}$ greater than 1.0 indicate a preference for sulfate and the magnitude of $\alpha_{S/N}$ indicates the magnitude of the preference.

Average separation factors were used to summarize the isotherm data because neither the individual separation factors ($\alpha_{S/N}$) nor the selectivity coefficients ($K_{S/N}$) were constant over an entire isotherm. This was espe-

TABLE 2

Anion resin characteristics

No.	Mfg. designation	Matrix	Functionality	Porosity	HCl Cap. (meq/ml)	pK_a	Avg. $\alpha_{S/N}$	Avg. $\alpha_{N/Cl}$
15	Amberlite IRA-400	STY–DVB	Q-I	Micro	1.53	SBA	1.89	
17	Amberlite IRA-900	STY–DVB	Q-I	Macro	1.10	SBA	1.71	3.41
21	Dowex SBR	STY–DVB	Q-I	Micro	1.66	SBA	1.89	2.90
27	Ionac ASB-1	STY–DVB	Q-I	Micro	1.39	SBA	1.87	
32	Ionac AFP-100	STY–DVB	Q-I	Macro	1.07	SBA	1.76	2.97
16	Amberlite IRA-402	Polystyrene	Q-I	Iso	1.16	SBA	3.09	3.11
19	Dowex SBR-P	Polystyrene	Q-I	Iso	1.02	SBA	2.96	
22	Dowex 11	Polystyrene	Q-I	Iso	1.17	SBA	3.37	
24	Duolite A-101-D	Polystyrene	Q-I	Iso	1.32	SBA	2.59	
28	Ionac A-641	Polystyrene	Q-I	Fm	1.21	SBA	3.30	3.30
30	Ionac ASB-1P	Polystyrene	Q-I	Iso	1.13	SBA	2.59	
14	Amberlite IRA-910	STY–DVB	Q-II	Macro	1.31	SBA	3.26	2.85
18	Amberlite IRA-410	STY–DVB	Q-II	Micro	1.40	SBA	2.40	
20	Dowex SAR	STY–DVB	Q-II	Micro	1.50	SBA	3.04	
23	Duolite A-102-D	STY–DVB	Q-II	Micro	1.48	SBA	3.26	
29	Ionac ASB-2	STY–DVB	Q-II	Micro	1.33	SBA	3.04	3.64
33	Amberlite IRA-458	Acrylic-amine	Quaternary	Micro	1.20	SBA	8.20	
1	Amberlite IRA-93	STY–DVB	Tertiary	Macro	0.98	7.7	3.75	4.86
5	Dowex MWA-1	STY–DVB	Tertiary	Macro	1.15	7.6	2.67	4.43
8	Duolite ES-368	STY–DVB	Tertiary	Macro	1.43	7.8	2.83	3.87
12	Ionac AFP-329	STY–DVB	Tertiary	Macro	1.26	8.5	3.07	4.14
3	Amberlite IRA-45	STY–DVB	Poly	Micro	1.76	7.9	12.7	3.89
2	Amberlite IRA-68	Acrylic-amine	Tertiary	Micro	1.42	11.1	23.4	1.89
10	Duolite ES-374	Acrylic-amine	Poly *	Macro	2.59	9.9	94.0	3.85
6	Duolite A-7	Phenol–HCHO–PA	Poly **	Macro	1.67	7.7	108	3.35
9	Duolite ES-561	Phenol–HCHO–PA	Poly	Macro	1.22	6.8	109	2.65
11	Ionac A-260	Aliphatic-amine	Poly	Micro	1.81	10.6	54.0	2.25
4	Dowex WGR	Epoxy-amine	Poly	Micro	1.53	7.9	137	1.99
7	Duolite A-340	Epoxy-amine	Poly	Micro	2.54	8.7	82.9	1.70
13	Ionac A-305	Epoxy-amine	Poly $^+$	Micro	1.51		108	

Q-I = Quaternary amine—type I ($-N(CH_3)_3^+$).
Q-II = Quaternary amine—type II ($-N(CH_3)_2C_2H_4OH^+$).
Iso = Isoporosity or "improved porosity".
Fm = Fixed macropore (manufacturer's terminology).
Poly = Polyamine not including quaternary amine.
Poly * = Advertised as tertiary amine but titrates as polyamine.
Poly ** = Advertised as secondary amine but titrates as polyamine.
Poly $^+$ = Polyamine including quaternary amine.
SBA = Strong base anion resin, pK_a not determined.

cially true for polystyrene resins which all had inflection points in their isotherms. The average separation factor (ref. [9], p. 261) utilizes the entire isotherm and was calculated by trial and error from eqn. (3):

$$R_a = \frac{\text{area below isotherm}}{\text{area above isotherm}} = \frac{(\alpha^2 - \alpha - \alpha \ln \alpha)/(\alpha - 1)^2}{1 - (\alpha^2 - \alpha - \alpha \ln \alpha)/(\alpha - 1)^2}. \qquad (3)$$

Capacities

Exchange capacities for resins converted to the nitrate form at 0.00500 N were determined by columnar elution with 2.0 N HCl followed by analysis of the regenerant solution for nitrate. Chloride capacities were determined using 2.0 N HNO_3 as the eluent.

Basicities

Basicities, as indicated by relative pK_a ($pK_b = 14.0 - pK_a$; 25°C) values of the weak-base resins were calculated from resin titration curves performed in deionized water without added salt. Fourteen-point titration curves were developed for each of the resins using HCl, HNO_3, and H_2SO_4. This was done by tumbling the free-base form resin/acid mixtures for 16 hours, then measuring the final pH. The relative pK_a values were calculated from eqn. (4) based on reference [1], p. 84:

$$pK_a = pH + pCl + \log(Q/2) \qquad (4)$$

where the capacity Q is given in meq/ml and pH = pCl without added salt. Further details are in reference [9], pp. 63, 218–229, 247–248.

Analysis methods

Sulfate was determined by nephelometry following $BaCl_2$ addition. Nitrate was determined using UV absorbance (220 nm) after minor corrections for absorbance due to organics leached from some of the resins. Chloride was determined by potentiometric titration using $AgNO_3$ and an Ag-sensing electrode. Complete experimental details are given in reference [9], Appendix D.

RESULTS AND DISCUSSION

Trends from the isotherms

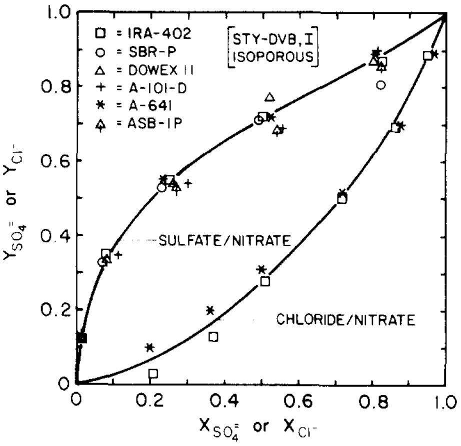

Fig. 2. Composite isotherms for STY–DVB, type I quaternary amine "improved porosity" gel resins. All isotherms (Figs. 2–11) at 25°C and 0.00500 N.

Individual sulfate/nitrate and nitrate/chloride isotherms were plotted for the resins tested. These plots suggested that resins with identical matrices and functional groups had very similar isotherms, regardless of manufacturer or capacity. Thus, composite isotherms (Figs. 2–6) were drawn combining the data from similar resins. It is evident when comparing Figs. 2–4 to Figs. 5 and 6 that the polystyrene resins have (a) lower sulfate/nitrate selectivities; (b) sulfate/nitrate isotherms with inflection points; and (c) higher nitrate/chloride selectivities. Not quite so evident in Figs. 2–6 and Table 2, but neverthe-

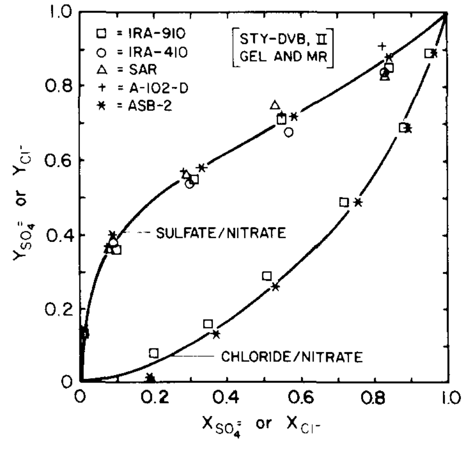

Fig. 3. Composite isotherms for STY–DVB, type II quaternary amine, gel and macroporous resins.

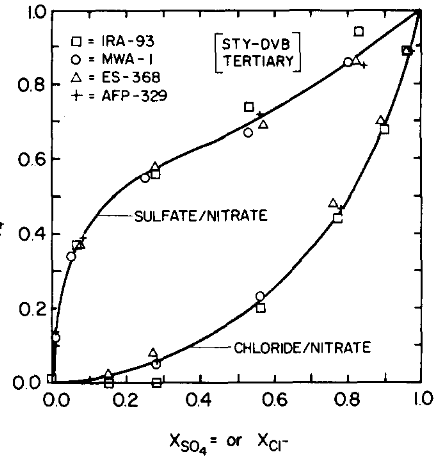

Fig. 4. Composite isotherms for STY–DVB, tertiary amine, macroporous resins.

less apparent was the importance of functionality as a determinant of $\alpha_{S/N}$. Figures 7–11 were plotted to illustrate the dependence of $\alpha_{S/N}$ on both matrix and functionality. The first three figures (7–9) of the set illustrate the effect of matrix on $\alpha_{S/N}$ for polyamine, tertiary amine, and quaternary amine resins respectively. In each figure, with amine functionality remaining constant, $\alpha_{S/N}$ is significantly greater for non-polystyrene resins (acrylics, epoxies, phenolics) compared to polystyrene resins.

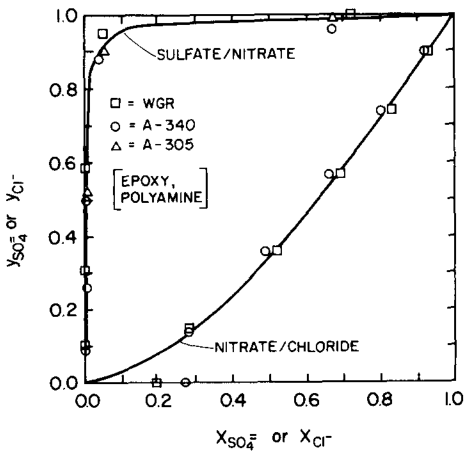

Fig. 5. Composite isotherms for epoxy-amine, gel resins with polyamine functionality.

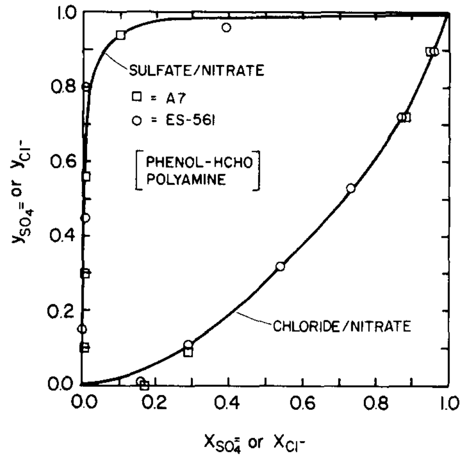

Fig. 6. Composite isotherms for phenol–HCHO, granular macroporous resins with polyamine functionality.

The very important influence of amine functionality on $\alpha_{S/N}$ is shown in Figs. 10 and 11 for polystyrene and non-polystyrene (acrylic) resins, respectively. For both kinds of matrices, the value of $\alpha_{S/N}$ increases in the order

polyamine > tertiary > quaternary.

This is the same influence as that reported on the divalent/monovalent ($\alpha_{S/Cl}$) selectivity by Boari et al. [6].

Because we used commercially-available re-

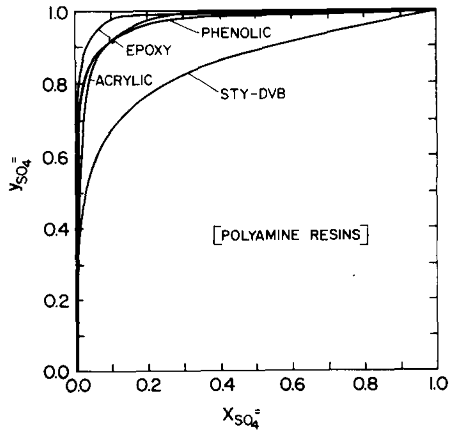

Fig. 7. The effect of resin matrix on the divalent/monovalent (SO_4^{2-}/NO_3^-) selectivity of polyamine resins.

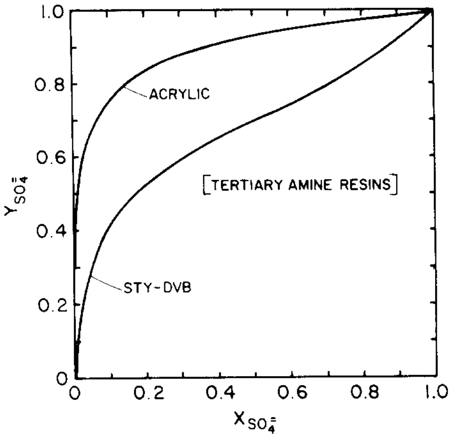

Fig. 8. The effect of resin matrix on the divalent/monovalent (SO_4^{2-}/NO_3^-) selectivity of tertiary amine resins.

sins in this research, we had no resins with just primary or secondary amine functionality. Thus the term "polyamine" was used to characterize the functionality of resins with mixed functional groups comprising mainly primary, secondary, and tertiary amines. Experimentally, the polyamine resins were characterized by inflectionless monovalent acid (HCl and HNO_3) titration curves and a marked preference for H_2SO_4.

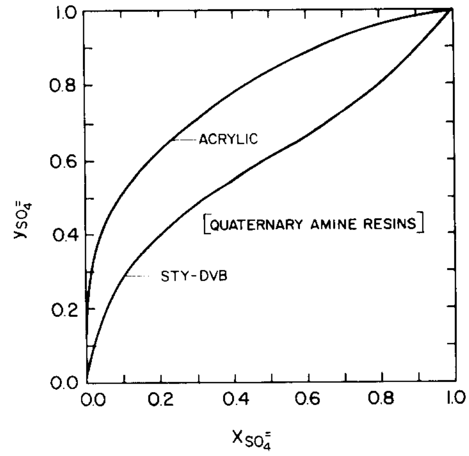

Fig. 9. The effect of resin matrix on the divalent/monovalent (SO_4^{2-}/NO_3^-) selectivity of quaternary amine resins.

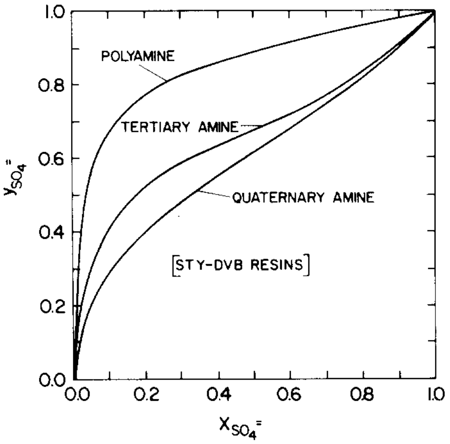

Fig. 10. The effect of amine functionality on the divalent/monovalent (SO_4^{2-}/NO_3^-) selectivity of STY-DVB resins.

Trends from the titration curves

Two typical sets of resin titration curves are shown in Figs. 12 and 13 for non-polystyrene and polystyrene resins, respectively. The behavior of the epoxy-amine polyamine resin (Fig. 12) was typical of non-polystyrene polyamine resins in general: (1) they markedly prefer divalent H_2SO_4 over HCl and HNO_3, as indicated by much greater H_2SO_4 capacity at any pH; (2) they exhibit little if any preference for HCl over HNO_3; and (3) they have

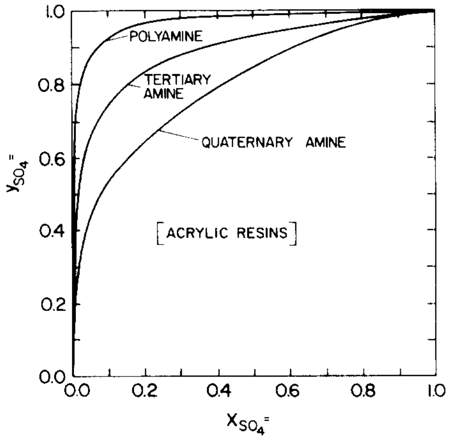

Fig. 11. The effect of amine functionality of the divalent/monovalent (SO_4^{2-}/NO_3^-) selectivity of acrylic resins.

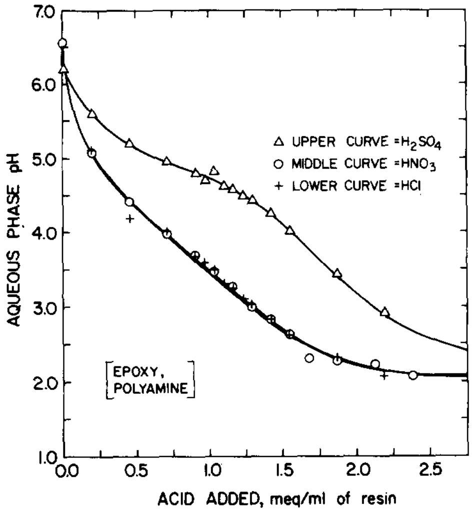

Fig. 12. Titration curves for epoxy-amine, gel resin with polyamine functionality (WGR).

discernible inflection points for H_2SO_4 but not for HCl or HNO_3. This latter observation indicates a preponderance of similar amine groups, properly spaced to satisfy divalent SO_4^{2-} ions in preference to two monovalent ions like Cl^- or NO_3^-.

Figure 13 demonstrates the behavior typical of polystyrene tertiary amine resins in general; they exhibit (a) inflection points for both monovalent and divalent acids, and (b) a clear and somewhat uniform selectivity sequence of

$H_2SO_4 > HNO_3 > HCl$.

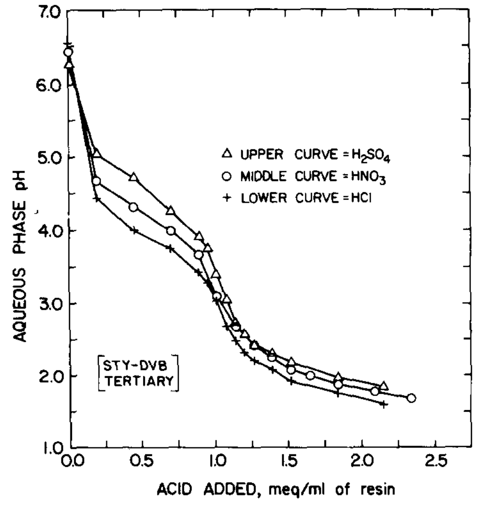

Fig. 13. Titration curves for STY–DVB macroporous resin with tertiary amine functionality (MWA-1).

It is recognized that the basic trend exhibited by the experimental titration curves is predictable from Donnan equilibrium theory. With the usual assumptions of (a) no specific resin preference for one ion over another, and (b) equal solvent uptake for all ions at equal fraction neutralization, a higher pH is predicted for a divalent acid at the same degree of neutralization. The differences, however, observed between the various titration curves (HCl, HNO_3, H_2SO_4) were greater than expected and highly variable from resin to resin. One of the assumptions was definitely violated; the resins clearly exhibited preferences for one ion over another. Thus, our variable pH titration curve data appear to support the constant pH isotherm evidence indicating the importance of both matrix and functionality as determinants of divalent/monovalent selectivity.

Statistical data analysis

The primary data analysis techniques used were analysis of variance (ANOVA) for the categorical variables: matrix, functionality, porosity, and type; and linear regression for the interval scale variables: relative distance of charge separation, relative size of amine group, exchange capacity, and pK_a. Computations were done using the Michigan Interactive Data Analysis System, MIDAS [10].

The natural log of the selectivity measure, $\ln \alpha_{S/N}$, rather than $\alpha_{S/N}$ was used as the dependent variable because preliminary data analyses showed $\ln \alpha_{S/N}$ to be better correlated with the independent variables.

Analysis of variance (ANOVA) of $\ln \alpha_{S/N}$

The variance represented by the mean sum of squared deviations within each category was compared to the variance between categories by taking the ratio:

$$F = \frac{\text{mean sum of squares between categories}}{\text{mean sum of squares within categories}}.$$

The higher the F ratio, the more significant is the effect of the categorization on selectivity as compared to that expected from random statistical variation. The null hypothesis (H_0) is that the mean ln $\alpha_{S/N}$ is the same for all categories. For $F \gg 1.0$, the null hypothesis is rejected. The corresponding level of significance (SIGNIF) indicated is a function of the number of cases and the number of categories; it is the probability of being wrong when rejecting the hypothesis.

The summary ANOVA data in Table 3 confirm the observations made from the isotherms—essentially all of the variation in sulfate/nitrate selectivity is explained by matrix and functionality. Sorting the resins into polystyrene (N-out-of-the-continuous-structure) and non-polystyrene (N-in-the-continuous-structure) categories was a much more effective stratification ($F = 304$) than just using the five different matrix categories ($F = 86.2$). A simple knowledge of whether N is in or out of the continuous structure tells more about the divalent/monovalent selectivity of a resin than any other description. Adding the functionality nearly completes the determination of divalent/monovalent selectivity for these resins.

Minor effects of type and porosity

After further analysis of the selectivity data, subsets of resins were identified whose sulfate/nitrate selectivities were clearly influenced by factors less important than matrix and functionality. The effects of secondary factors like porosity and quaternary type could not be clearly "seen" in the $\alpha_{S/N}$ data or the isotherms but did emerge in the ANOVA results. Categorizing all resins according to porosity and comparing mean ln $\alpha_{S/N}$ values indicated no real differences due to porosity—Table 3, entry D, $F = 1.24$. However, from insight gained during visual inspection of the isotherms, the sulfate/nitrate selectivity of type I, strong-base anion (SBA) resins appeared to be a function of whether a given resin was isoporous or not-isoporous. ANOVA E (Table 3) confirmed this apparent relationship with an F statistic of 76.5. Type I, isoporous SBA resins have measurably higher sulfate selectivity (average $\alpha_{S/N} = 2.97$) than do type I gel and macroporous resins (average $\alpha_{S/N} = 1.82$). Isoporous resins are not cross-linked with divinylbenzene and have a lower

TABLE 3

Analysis of variance—variables explaining sulfate/nitrate selectivity

ANOVA designation	Cases considered	Stratification (categories examined)	F statistic	Level of significance
A	All resins	Matrix (STY-DVB), (acrylic), (phenolic) (epoxy), (aliphatic)	86.2	0.0000
B	All resins	Matrix (nitrogen in), (nitrogen out)	304	0.0000
C	All resins	Functionality (poly), (tertiary), (Quaternary)	95.2	0.0000
D	All resins	Porosity (micro), (macro), (iso)	1.24	0.3036
E	Type I SBA resins	Porosity (gel or MR), (iso)	76.5	0.0000
F	Gel and MR SBA resins	Type (I, gel or MR), (II, gel or MR)	67.0	0.0000

relative degree of crosslinking than do gel or macroporous resins. The fact that relative degree of crosslinking has a minor effect on divalent/monovalent selectivity is understandable in physical terms. Lightly crosslinked resins are more flexible and thus better able to reorient to satisfy divalency, especially if the amine groups are pendant on their polymer chains as is the case with polystyrene resins.

Excluding isoporous resins, quaternary type II resins are more sulfate selective than type I resins. The idea to exclude isoporous resins from the comparison came from the results of ANOVA F (Table 3). In this stratification of the data, only the gel and macroporous resins have been considered so as to eliminate the nearly equal effect of porosity (flexibility) on $\alpha_{S/N}$. The fact that type II resins are more sulfate-selective and less basic than type I resins is in agreement with the inverse correlation between divalent selectivity ($\alpha_{S/Cl}$) and basicity suggested by Boari et al. [6]. In our sulfate/nitrate experiments, however, another factor, the hydrophobic/hydrophilic nature of the resin, was found to be important. Type II ($-N(CH_3)_2C_2H_4OH^+$) resins are less basic than type I ($-N(CH_3)_3^+$) because of the presence of the electron-withdrawing, hydrophilic $-C_2H_4OH$ group attached to the amine N. It is likely that this hydrophilic substitution significantly reduces the resin's preference for nitrate—an ion with an unusually high preference for hydrophobic phases [9,12]. Thus, the higher $\alpha_{S/N}$ values we observed for type II resins may have been largely due to a reduction in the resin's affinity for nitrate. Table 4 summarizes the effects of both porosity (flexibility) and type on $\alpha_{S/N}$.

TABLE 4

Effects of porosity and type on sulfate/nitrate selectivity

Resin	Average $\alpha_{S/N}$
Type I, SBA, gel and MR	1.82
Type II, SBA, gel and MR	2.98
Type I, SBA, isoporous	2.97

CONCLUSIONS

Matrix is the most important factor in the determination of the divalent/monovalent selectivity ($\alpha_{S/N}$). If the electrostatically-active nitrogen atoms are in the continuous polymer structure, the resin is highly sulfate selective. It is hypothesized that this extreme divalent ion preference is due to the guaranteed proximity (4.48 Å apart) of two active nitrogen atoms in the polymer backbone. This distance, 4.48 Å, is the nitrogen separation distance due to one ethylene group in the amine monomers diethylenetriamine (DETA) and triethylenetetraamine (TETA), commonly used to provide functionality and crosslinking in anion exchange resins:

$$\begin{array}{l} |\longleftarrow 4.48\ \text{Å} \longrightarrow| \longleftarrow 4.48\ \text{Å} \longrightarrow| \\ NH_2\text{-}CH_2\text{-}CH_2\text{-}NH\ \text{-}CH_2\text{-}CH_2\text{-}NH_2 \end{array}$$

Fixed pairs of properly-spaced, charged amines will tend to prefer single, divalent anions to pairs of monovalent ions for both entropic and electrostatic reasons. Such is not the case with tertiary and quaternary amines pendant on a polystyrene matrix. The natural electroselectivity of multiply-charged ions in dilute solution is reduced by the steric hindrance of the large functional groups and the lesser probability of their being properly spaced to interact with a "hard" divalent ion like sulfate. Summarily, the sulfate/nitrate selectivities ($\alpha_{S/N}$) can be ordered as

nonpolystyrene resins > polystyrene resins

Functionality (poly-, tertiary, or quaternary amine) is nearly as important as matrix (nitrogen proximity) in determining sulfate selectivity. Although the functionality effect on sulfate selectivity has previously been attributed to functional group basicity, no consistent correlation between proton basicity (pK_a) and $\alpha_{S/N}$ was obtained here. Additionally, there was no ($r^2 = 0.01$) correlation between pK_a and functionality for weak base resins. Rather, the size and steric hindrance produced by the functional groups seem to be the determining factors; large functional groups tend to prevent the required proximity of a pair of nitrogen atoms in addition to hindering the approach of the mobile counterions to the positively charged nitrogen centers.

Porosity is a major determinant of sulfate selectivity among type I strong-base anion resins where isoporous resins with a relatively low degree of crosslinking are considerably more sulfate selective ($\alpha_{S/N} = 2.98$) than are the more crosslinked gel and macroporous resins ($\alpha_{S/N} = 1.82$). Since hydration of the sulfate ion is not very significant, the screening by size due to higher degrees of crosslinking is not expected to be significant. Greater flexibility of the polymer matrix permitting freer movement of the quaternary groups to pair-up with the divalent ion is offered as a possible explanation. With this single exception of porosity being related to $\alpha_{S/N}$ for type I SBA resins, there are no significant effects of porosity on sulfate selectivity.

Type II, strong-base anion resins have higher sulfate selectivity ($\alpha_{S/N} = 2.99$) than do the type I resins ($\alpha_{S/N} = 1.82$). The major difference is basicity. Therefore, in this particular classification, i.e., gel and macroporous SBA resins, it appears that reducing the proton affinity increases the sulfate selectivity. However, for SBA resins as a group, porosity is as important as type in determining selectivity.

Capacity is not a significant variable for predicting $\alpha_{S/N}$ even though high capacity (equated with high internal molality) should theoretically produce high sulfate selectivity. Capacity was mildly correlated with $\alpha_{S/N}$ for weak-base resins ($r^2 = 0.32$) but not for strong-base resins ($r^2 = 0.00$).

TABLE 5

Variables influencing sulfate/nitrate selectivity, $\alpha_{S/N}$

	Anion resins in general	Strong-base resins	Weak-base resins	Polystyrene resins	Non-polystyrene weak-base resins	Type I strong-base resins
Nitrogen in continuous structure	+ +	+ +	+ +	NA	NA	NA
Increasing "R" group size	− −	(− −)	− −	− −	− −	NA
Increasing degree of crosslinking	0	−	0	0	0	−
Macroporous as opposed to microporous	0	0	0	0	0	0
Isoporous as opposed to gel or MR	NA	+	NA	NA	NA	+ +
Increasing capacity	+	0	+	NA	NA	NA
Type I as opposed to type II	NA	−	NA	NA	NA	NA
Increasing pK_a (increasing basicity)	−	0	0	0	−	NA
Increasing hydrophilic character	+	NA	+	(+)	NA	NA

+ + = Greatly increases $\alpha_{S/N}$.
+ = Increases $\alpha_{S/N}$.
0 = No significant effect on $\alpha_{S/N}$.
− = Decreases $\alpha_{S/N}$.
− − = Greatly decreases $\alpha_{S/N}$.
NA = Not applicable or not determined.
Values in parentheses are based on experiments by Guter [11].

Table 5 summarizes the effects of all the independent variables studied on the sulfate/nitrate selectivity of the resins studied.

VERIFICATION OF CHARGE SEPARATION THEORY

Polystyrene strong-base anion resins with deliberately separated N atoms have recently been made and shown to actually prefer nitrate over sulfate in dilute solution [11]. With $\alpha_{S/N} < 1.0$, they yield a significant increase in BV to nitrate breakthrough in typical nitrate removal applications as shown in Fig. 1. One such resin, a quaternary triethylamine, has such a reduced divalent selectivity that it is being used in ion chromatography for rapid elution of sulfate ahead of nitrate. This speeds up the analyses of common anions without loss of resolution between sulfate and nitrate. The structure of the triethyl resin is given in Fig. 14; its selectivity sequence is as follows:

nitrate > sulfate > chloride > bicarbonate.

Its exchange capacity and nitrate/chloride selectivity are not changed significantly compared to standard type I (trimethylamine) resins. Tripropyl- and higher alkanes and mixed alkanes are being considered for future research. Other, more polar, thus less nitrate selective functional groups, have also been studied by Guter [11]. (In some related research using nitrate/chloride exchange we also found that the more non-polar and hydrophobic a resin is, the better nitrate likes it (ref. [9], p. 117).)

We have also interpreted the chromatographic patterns of Igawa et al. [13] to be supportive of the theory that deliberate N atom separation reduces sulfate selectivity. Using water elution of mixed salts injected into a silica-coated polyamide crown ether resin column, they reported the following affinity sequence:

$$I^- > NO_3^- > Br^- > Cl^- > F^- > SO_4^{2-}.$$

No explanation was given for sulfate being less preferred than even fluoride. We are suggesting that it is due to the long distance (5 carbons) between N atoms in the continuous polymer structure shown in Fig. 15. We have some reservation, however, in making this conclusion because of the complex cation–anion exchange properties of the resin, the "silica coating" and lack of detail in the article. Yet the evidence appears strong for sulfate rejection being due to large N-atom separation.

Cation exchangers with guaranteed close spacing of the negative co-ions are extremely divalent ion selective and fit nicely into the charge separation distance theory. The structures of three commercially-available cation exchangers used to remove Ca^{2+} and Mg^{2+} from brines are given in Fig. 16. All may be considered chelating resins, especially the aminodiacetate [14] and aminophosphonic [15] resins whose selectivities for divalent ions are so great that they may be used to soften saturated NaCl solutions.

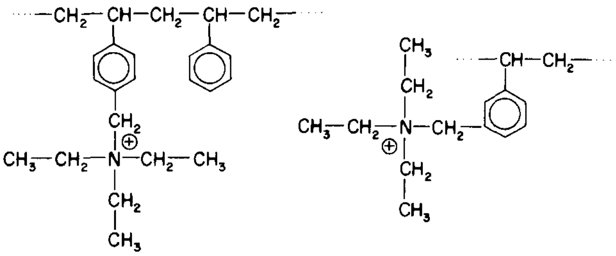

Fig. 14. Structure of a quaternary triethyl resin.

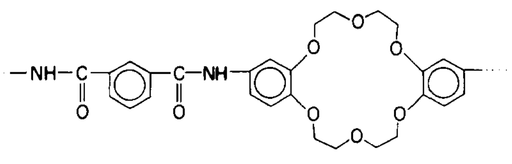

Fig. 15. Structure of a polyamide crown ether resin.

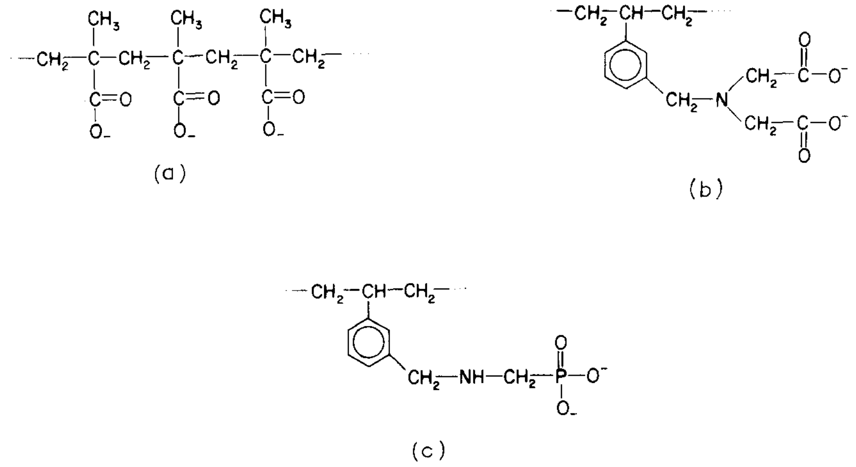

Fig. 16. Structures of three commercially available cation exchangers; (a): polyacrylate; (b): aminodiacetate; (c): aminophosphonic.

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