Tech Fact

Ion Exchange Resins Selectivity

Introduction

Ion exchange resins, when placed in a solution, reach an equilibrium state between ions in the solution and ions on the resin. From this equilibrium state, selectivity coefficients (equilibrium constants) can be defined based on the ratios of ions in the solution vs. ions on the resin.

These selectivity coefficients are a measurement of a resins preference for an ion. The greater the selectivity coefficient, the greater the preference for the ion.

This document presents the relative affinity values of resins for different ions, the affinity of the cation resins for the H^+ ion and the affinity of the anion resins for the OH^- ion being defined arbitrarily as 1.0.

For example, a styrenic strong acid cation resin with 8% DVB cross–linking has a relative affinity for sodium vs. hydrogen of 1.56, while the selectivity for calcium vs. hydrogen is 4.06. As a result, calcium is selectively removed by the ion exchange resin over sodium.

In column operation, undesirable ions can be selectively removed by regenerating the resin with any ion of lower selectivity. For example, calcium can be removed from a solution by a strong acid cation resin when the resin is regenerated using salt (Na-cycle operation) or acid (H-cycle operation).

Selectivity coefficients can also be used to determine the order of elution in column operation. In a demineralizer (H-cycle operation), sodium with a relative affinity of 1.56 will elute before ammonium with an affinity of 2.01, which is followed by potassium, with an affinity of 2.28.

Ionic leakage from demineralizers can also be predicted by the use of selectivity coefficients. With a knowledge of the degree of regeneration, solution pH and the relative affinity value, an estimate of the ionic leakage can be calculated.

For a complete treatment of the subject, numerous textbooks can be consulted. One excellent reference is Ion Exchange, by Friedrich Helfferich, published by Dover Press under ISBN #61-15453.

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SAC resins selectivity coefficients

Relative affinities of various cations (compared with the hydrogen ion) on sulfonated polystyrene cation exchange resins with different degrees of cross-linking.

	Percentage of cross-linking of the copolymer			
Cation	4% DVB	8% DVB	10% DVB	16% DVB
Li^+	0.76	0.79	0.77	0.68
H^+	1.00	1.00	1.00	1.00
Na^+	1.20	1.56	1.61	1.62
NH_4^+	1.44	2.01	2.15	2.27
K^+	1.72	2.28	2.54	3.06
Rb^+	1.86	2.49	2.69	3.14
Cs^+	2.02	2.56	2.77	3.17
Ag^+	3.58	6.70	8.15	15.6
Tl^+	5.08	9.76	12.6	19.4
UO_2^{2+}	1.79	1.93	2.00	2.27
Mg^{2+}	2.23	2.59	2.62	2.39
Zn^{2+}	2.37	2.73	2.77	2.57
Co^{2+}	2.45	2.94	2.92	2.59
Cu^{2+}	2.49	3.03	3.15	3.03
Cd^{2+}	2.55	3.06	3.23	3.37
Ni^{2+}	2.61	3.09	3.08	2.76
Ca^{2+}	3.14	4.06	4.42	4.95
Sr^{2+}	3.56	5.13	5.85	6.87
Pb^{2+}	4.97	7.80	8.92	12.2
Ba^{2+}	5.66	9.06	9.42	14.2

SBA resins selectivity coefficients

Relative affinities of various anions (compared with the hydroxide ion) on polystyrenic strongly basic anion exchange resins, both Type 1 and Type 2.

Ion	Type 1	Type 2
OH^-	1.0	1.0
Benzene sulfonate	500	75
Salicylate	450	65
Citrate	220	23
I^-	175	17
Phenate	110	27
HSO_4^-	85	15
ClO_3^-	74	12
NO_3^-	65	8
Br^-	50	6
CN–	28	3
HSO_3^-	27	3
BrO_3^-	27	3
NO_2^-	24	3
Cl^-	22	2.3
HCO_3^-	6.0	1.2
IO_3^-	5.5	0.5
Formate	4.6	0.5
Acetate	3.2	0.5
Propionate	2.6	0.3
F^-	1.6	0.3
$HSiO_3^-$	< 1.0	< 1.0
$H_2PO_4^-$	5.0	0.5

The reason for mentioning benzene sulfonate in the preceding list is that it is an example of synthetic surfactants frequently found in water. The very strong affinity of the resins for this compound results in a high risk of resin fouling.

WAC resins

The selectivity data is less significant for weak acid cation exchange resins, which operate (in the H^+ form) only with feed water containing alkalinity. In addition, selectivity values are less well documented for these resins. However, approximate data is available as follows, with calcium as the reference ion:

Cation	
Mg^{2+}	0.3
Sr^{2+}	< 1
Ba^{2+}	< 1
Ca^{2+}	1.0
Cd^{2+}	1.0
Ni^{2+}	1.4
Zn^{2+}	1.5
Co^{2+}	1.9
Cu^{2+}	2.0
Pb^{2+}	> 1

It is important to know that weak acid resins do not have a high affinity for strontium and barium, so that in operation, these ions may leak before calcium into the treated water.

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