ION EXCHANGE RESINS

Ion exchange resin is a cross-linked porous polymer substance containing functional (ionogenic) groups with mobile ions, which may be replaced with ions of the same charge dissolved in the surrounding liquid media.

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Structure of ion exchange resins

The polymer base of most of ion exchange resins is styrene-divinylbenzene copolymer.
The molecular structure of the copolymer presents a network of high-weight polystyrene molecules cross-linked by the molecules of divinylbenzene (DVB).
Cross-linking provides toughness and insolubility of the resin.
The amount of the cross-linking agent (divinylbenzene) may vary within the range 2%-16%.

The functional groups are attached to the styrene rings.

The chemical formulas of some ion exchanging resins:

- $R\text{-}SO_3H$
- $R\text{-}SO_3Na$
- R-COOH
- $R\text{-}NH_3OH$

Ion exchange resins may differ in their porous structure: microporous (gel) resins and macroporous resins.
Gel resins are most widely used. Gel resins have higher ion capacity.
Macroporous resins are used for treating severely contaminated solutions due to their ability to elute foulants.

Ion exchange equilibrium

The general chemical reaction of ion exchange:

Cation exchange
$nRA + B^{n+} = R_nB^{n+} + nA^+$
or
Anion exchange
$nRA + B^{n-} = R_nB^{n-} + nA^-$

Where:
R - ionized resin molecule with an attached functional group;
A^+ / A^- - exchangeable ion;
B^{n+} / B^{n-} - cation/anion dissolved in the liquid;
n+ /n- - electrical charge of the ion B.

The equilibrium constant of the reaction (**selectivity coefficient**):
$K = [A]^n[R_nB]/[RA]^n[B]$

Where $[A], [R_nB], [RA], [B]$ - concentrations of A, R_nB, RA and **B**.

Selectivity coefficient indicates the degree of the ions (A and B) exchanging. The higher the selectivity coefficient the higher fraction of the ion B is replaced with the ion A.
Selectivity coefficient also determines a preference of an ion to another ion. The ions with higher selectivity coefficient will replace the ions with lower selectivity coefficient in the resin molecules.

The values of the selectivity coefficients for various cations in strong cation exchangers are arranged as follows (decreasing order):
Fe^{3+}, Al^{3+}, Pb^{2+}, Sr^{2+}, Ca^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Mg^{2+}, Mn^{2+}, Ag^+, Cs^+, Cd^+, K^+, NH_4^+, Na^+, H^+, Li^+, Hg^{2+}

The values of the selectivity coefficients for various anions in amino base anion exchangers are arranged as follows (decreasing order):
SO_4^{2-}, CrO_4^{2-}, PO_4^{3-}, HSO_4^-, NO_3^-, Br^-, Cl^-, HCO_3^-, F^-, OH^-

Properties of ion exchange resins

- **Swelling**. Ion exchange resins are hygroscopic. The amount of moisture hydrated by a resin is determined by the cross-linking and the type of functional group. Low cross-linking gel resins with functional groups of sulfonic acid or quaternary ammonium contain large amounts of water resulting in swelling. Frequent swelling and contraction reduce the resin life.
- **Capacity**. Capacity is a number of chemical equivalents of ions that can be taken up by a unit amount of the resin (dry weight/wet weight/wet volume). Cross-linking decreases the capacity measured on the dry basis (fewer functional groups may be attached to highly cross-linked polymer molecules). However cross-linking also decreases hydration of the resin therefore the capacity measured on the wet basis increases with an increase of the cross-linking level.

- **Particle size**. Ion exchange resins are available in different particle (bed) size. Common ion exchange resins are manufactured in form of polydispersed spherical beds with the size distributed within the range 0.01-0.05” (0.25-1.25mm) or in form of uniform particle size (UPS). Smaller particles improve the kinetics of the ion exchanging reaction but cause increase of the water pressure drop and decrease of the flow rate.
- **Stability**. Mechanical (physical) stability of ion exchange resins is determined mainly by the toughness of the polymer structure (cross-linking) and by the frequency of swelling-contraction cycles. Chemical degradation of ion exchange resins may be caused by fouling the resin pores by precipitates (e.g., iron hydroxide), breaking polymer structure, loss of ion exchange capacity due to a modification of the functional groups.

Strong Acid Cation resins

Strong Acid Cation (SAC) resins behave similar to strong acids.
Strong Acid Cation resins are available in two forms: hydrogen ($R-SO_3H$) or sodium ($R-SO_3Na$).

The typical strong acid cation exchange reaction:
$2(R-SO_3Na) + CaCl_2 = (R-SO_3)_2Ca + 2NaCl$

Cross-linking level of the Strong Acid Cation resins is 8-10%.
The ion exchange capacity of Strong Acid Cation resins does not depend on the solution PH.
Strong Acid Cation resins are used for water softening and demineralization.
The exhausted Strong Acid Cation resins may be regenerated.
Regeneration in hydrogen (acid) form is performed by a strong acid (e.g., HCL). Regeneration in sodium (salt) form is performed by sodium chloride solution (NaCl).

Weak Acid Cation resins

Weak Acid Cation (WAC) resins behave similar to weak acids.
Weak Acid Cation resins are available in hydrogen form (R-COOH).
Weak Acid Cation resins have high affinity for hydrogen ions therefore they are easily regenerated by stoichiometric amount of acid.
The ion exchange capacity of Weak Acid Cation resins increases with an increase of the solution PH.
WAC resins are not used for treatment acidic (PH<6) solutions.
Weak Acid Cation resins are used for demineralization and dealkalization of water.

Strong Base Anion resins

Strong Base Anion (SBA) resins behave similar to strong bases.
Strong Base Anion resins are available in hydroxide form: ($R-NH_3OH$).

The typical strong base anion exchange reaction:
$R-NH_3OH + HNO_3 = R-NH_3NO_3 + H_2O$

Strong Base Anion resins are used for demineralization and dealkalization of water.
The exhausted Strong Base Anion resins may be regenerated by concentrated sodium hydroxide (NaOH).

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Weak Base Anion resins

Weak Base Anion (WBA)resins behave similar to weak bases.

The typical weak base anion exchange reaction:
$R-NH_2 + HNO_3 = R-NH_3NO_3$

The ion exchange capacity of Weak Base Anion resins increases with a decrease of the solution PH.
WBA resins are not used for treatment basic (PH>6) solutions.
Weak Base Anion resins sorb only anions of strong acids (chlorides, nitrates, sulfates).
Weak Base Anion are easily regenerated by small amounts of weak bases (such as ammonia or sodium carbonate), which neutralize the acid taken up by the resin.

Water treatment with ion exchange resins

Ion exchange resins are used for two types of water treatment:

- **Water softening**. Hard water contains ions of calcium (Ca^{2+}) and magnesium (Mg^{2+}). Sodium type Strong Acid Cation resins (e.g., $R-SO_3Na$) are used for water softening. The ions of calcium and magnesium dissolved in water are bound by the resin exchanging the equivalent amount of sodium ions (Na^+), which are released from the resin to water. PH of water does not change in softening process. Anions are not removed in the process therefore anion base resins are not used. The exhausted resin is regularly regenerated. The regeneration process includes the following stages:
  - Removing suspended hard particles by reverse flow of water.
  - Passing a solution containing high concentration of sodium ions (commonly a strong solution of NaCl) for replacing the calcium and magnesium ions with fresh sodium ions.
  - Rinsing the resin with water in order to remove the regenerating solution.
- **Demineralization (deionization) of water**. Both types of ions cations and anions are removed from the water in the demineralization process. Therefore two resin types are used: Strong Acid Cation resins and Strong Base Anion resins. The cation resins are used in hydrogen form (e.g., $R-SO_3H$), the anion resins are used in hydroxide form (e.g., $R-NH_3OH$). The water first passes through the acid cation resin where the dissolved cations are bound by the resin and replaced by the equivalent amount of ions of hydrogen (H^+). The water becomes slightly acidic. Then the water passes through

the base anion resin where the dissolved anions are replaced with the hydroxide ions, which are released to the water. Hydroxide and hydrogen ions react and form neutral water. The hydrogen type strong acid cation resin is regenerated by solutions of strong acids (hydrochloric or sulfuric). The strong base anion resin is regenerated by solutions of sodium hydroxide (NaOH).

Properties of some ion exchange resins

- Strong Cation Exchange Resin in sodium form
- Strong Cation Exchange Resin in hydrogen form
- Weak Cation Exchange Resin
- Strong Anion Exchange Resin in chloride form
- Strong Anion Exchange Resin in hydroxide form
- Weak Base Anion Exchange Resin

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