REPUBLIC OF UZBEKISTAN
MINISTRY OF HEALTH
TASHKENT PHARMACEUTICAL INSTITUTE
DEPARTMENT OF "*I*norganic, analytic, physic and colloid chemistry"

on physic and colloid chemistry

SELF STUDY

SUBJECT: THE ADSORPTION OF ION EXCHANGE. THE TYPES OF IONITES.

Done by: Mavlyanova Rukhshona I.P. 1/1
Checked by: Rahmatullayeva M.

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PLAN:

1. Ion exchange
2. The types of ionites
3. Organic ionites
4. Inorganic ionites
5. Adsorption

Ion exchange

Ion exchanger

Ion exchange resin beads

Ion exchange column, used for protein purification

Ion exchange is an exchange of ions between two electrolytes or between an electrolyte solution and a complex. In most cases the term is used to denote the processes of purification, separation, and decontamination of aqueous and other ion-containing solutions with solid polymeric or mineralic 'ion exchangers'.

Typical ion exchangers are ion exchange resins (functionalized porous or gel polymer), zeolites, montmorillonite, clay, and soilhumus. Ion exchangers

are either **cation exchangers** that exchange positively charged ions (cations) or **anion exchangers** that exchange negatively charged ions (anions). There are also **amphoteric exchangers** that are able to exchange both cations and anions simultaneously. However, the simultaneous exchange of cations and anions can be more efficiently performed in *mixed beds* that contain a mixture of anion and cation exchange resins, or passing the treated solution through several different ion exchange materials.

Ion exchangers can be unselective or have binding preferences for certain ions or classes of ions, depending on their chemical structure. This can be dependent on the size of the ions, their charge, or their structure. Typical examples of ions that can bind to ion exchangers are:

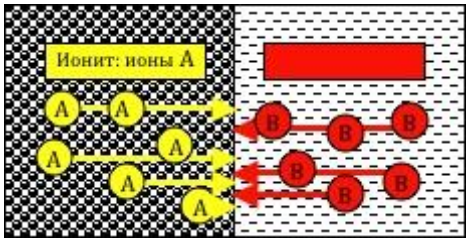
- H^+ (proton) and OH^- (hydroxide)
- Single-charged monatomic ions like Na^+, K^+, and Cl^-
- Double-charged monatomic ions like Ca^{2+} and Mg^{2+}
- Polyatomic inorganic ions like SO_4^{2-} and PO_4^{3-}
- Organic bases, usually molecules containing the amine functional group - NR_2H^+
- Organic acids, often molecules containing -COO^- (carboxylic acid) functional groups
- Biomolecules that can be ionized: amino acids, peptides, proteins, etc.

Along with absorption and adsorption, ion exchange is a form of sorption.

Ion exchange is a reversible process and the ion exchanger can be *regenerated* or *loaded* with desirable ions by washing with an excess of these ions.

Ion Exchange technology

IONIC EXCHANGE is a reversible chemical reaction with exchange of ions between the solid substance (ionite) and electrolyte solution.



In water treatment industry the ionic exchange is used for softening, desalting, selective removal of various ions etc. Water for purification passes through one filter or through the system of filters filled with ionites, selected depending on required problem. Ionites eliminate from water corresponding ions and exchange with water the

equivalent amounts of other ions which originally were in ionite. Exchanging ions are counter-ions. Ionites consist of motionless skeleton - matrix and functional groups - fixed ions which are rigidly attached to the matrix and interact with counter-ions.

Depending on a charge of counter-ions, ionites are divided into cationites and anionites. If counter-ions are charged positively, i.e. are cationes (for example, ions of hydrogen H+ or ions of metals), ionite is named cationite. If counter-ions are charged negatively, i.e. are aniones (for example, hydroxyl ion OH- or the acid residues), ionite is named anionite.

Basic characteristics of ionites are: selectivity, working exchange capacity and kinetics of ion exchange.

Ionite selectivity shows, how ionite can eliminate specific counter-ions at presence of other competing counter-ions. Ionite selectivity depends on the nature of ionite matrix, type of functional groups, counter-ion concentration in the solution, etc. As a rule, ionite selectivity increases with increase in counter-ion charge, and among the ions with the same charge - with increase in nuclear weight. I.e., the more heavy is counter-ion and the higher its charge is, the higher selectivity ionite shows to it. Typical row of selectivity is shown below:

$$Na^{+} < K^{+} < Mg^{2+} < Ca^{2+} < Fe^{2+} < Mn^{2+} < Ba^{2+} < Fe^{3+}$$

Exceptions are the counter-ions which form low dissociating compounds with the fixed groups, for example, low alkaline ionites with weak acids aniones (carbonates), or some zeolites with ammonium. Besides there can be specific interactions based on chelate effect or on screen effect.

The reversion of selectivity can be seen at increase in solution concentration. For example, double-charged counter-ions can be eliminated from ionite by single-charged counter-ions at contact with the solution containing single-charged counter-ions in high concentration. It is defined by the major property of ionites - their ability to regenerate after saturation by ions, eliminated from water, by washing of approximately 5-6% solutions of acids (for cationites) or alkalis (for anionites) or 10-12% solutions of salts. Due to this property it is possible to use ionite filling repeatedly during several years for water purification.

The size of working exchange capacity tells us, for how long ionite can work in these conditions up to the first breakthrough of an absorbed ion into the filtrate, and, hence, shown a resource of work of ionite at water treatment. Usually exchange capacity can be expressed in equivalents per liter of turgid ionite.

Ion exchange kinetics defines the speed of ion exchange reactions and, hence, required speed of filtering. Ionic exchange speed depends on the following factors: availability of the fixed ions inside of the ionite skeleton, size of ionite granules, their temperature and concentration of the solution, etc.

Total speed of ionic exchange process can be shown as a set of processes taking place in a solution (counter-ions diffusion to ionite grain and from the grain) and in the ionite (diffusion of counter-ions from the surface to the center of the ionite grain and in the opposite direction; an exchange of ionite counter-ions by counter-ions from the solution):

In the conditions approximated to the real conditions of water purification, the dominating factor determining the speed of ionic exchange is a diffusion of ions inside the ionite grain. Hence, the speed of ionic exchange, first of all, depends on the size of ionite grain and increases with reduction of the grain size.

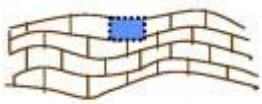
Depending on the matrix nature there are two types of ionites: inorganic and organic.

ORGANIC IONITES

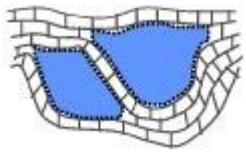
Organic ionites are basically synthetic ion-exchange resins. The organic matrix is made by polycondensation of monomeasured organic molecules, such as styrene, divinylbenzene, acrylamide, etc. This matrix contains chemically introduced ionogenic groups (fixed ions) of acid or alkali type. Traditionally introduced groups of acid type are -COOH; -SO_3H; -PO_4H_2 etc., and the alkali type: ≡ N; =NH; -NH2; -NR3+ etc. Modern ion-exchange resins, as a rule, have high exchange capacity and operational stability.
Ionites can swell in water that is caused by presence of hydrophilic fixed groups capable to hydration. However boundless swelling, i.e. dissolution, is interfered by cross-section connections. The degree of cross-section connectivity is set at ionite synthesis by amount of the introduced cross-linking agent - divinylbenzene (DVB). The standard

resins used for softening, contain 8% DVB. Available resins can contain from 2 up to 20%. As a whole the degree of ionite swelling is determined by amount of DVB cross-linking, concentration of hydrophilic ionogenic groups in the ionote grain and the type of counter-ions in the ionite. Usually singly charged ions, especially ions of hydrogen and hydroxyl, result in the highest swelling; multi charged counter-ions result in some compression and reduction of grains volume.

At present there are two types of ion-exchange resins: gel and macroporous.



Gel resins are homogeneous cross-linked polymers. The fixed ions located with regular intervals in all the volume of the polymer. The small number of links results in high exchange capacity, but in low durability. An increase in the number of links results in increase in durability, but in decrease in swelling and exchange speed.



Macroporous resins have fixed system of pores and channels which is set during synthesis that helps to introduce plenty of DVB for increase in mechanical stability without delay in exchange kinetics. However this results in decrease in exchange capacity, because accessible for exchange are only fixed ions on the walls of the pores - 10-30 % of the entire polymer.

The special attention is paid to monodisperse resins which as against standard polydisperse resins are characterized by constant diameter of granules with deviation of no more than 50 microns (polydispersity of standard resins makes from 0,3 up to 1,2 mm). Monodispersity provides increase in ionic exchange speed, because the time of diffusion of the ions in all the granules is the same that results in increase in working exchange capacity. Besides the special method of synthesis of monodisperse resins provides increase in mechanical durability.

INORGANIC IONITES

Inorganic ionites are mostly ionites of natural origin, which are aluminum silicates, hydroxides and salts of polyvalent metals. The most widespread and widely used for water purification inorganic natural ionites are zeolites.

Zeolites are minerals from the group of water aluminum silicates of alkaline and alkaline-earth elements which have three-dimensional aluminium-silicon-oxygen skeleton forming systems of cavities and channels, which contains alkaline, alkaline-earth cationes and water molecules. Total amount of the system of cavities and channels of zeolite makes up to 50% of zeolite skeleton volume. Cationes and water molecules are poorly connected to the skeleton and can be partially or completely replaced by the way of ionic exchange and dehydration. Ion exchange properties of zeolites are defined by the features of chemical affinity of ions and crystal structure of zeolite. Thus it is necessary to provide conformity of sizes of intake openings in the zeolitic skeleton and replacing ions, since the skeleton of zeolite has rigid crystal structure and as against organic resins cannot swell due with volume change.

Ionic exchange in zeolites helps isolating ions which extraction by other methods is often very complex. Zeolites can adsorb radioactive caesium ions from solutions, eliminate NH_4+,take out Cu, Pb, Zn, Cd, Ba, Co, Ag ions and other metal ions, clear natural gases. Due to ion-screen effect they can adsorb from gas and liquid systems the vapors of nitrogen, CO_2, SO_2, H_2S, Cl_2, NH_3. Besides the zeolites can be used for elimination of dissolved iron, manganese and hardness.
As against organic resins there is a number of zeolites' features. Total mineralization of treated water should be not less than 80 mg/l, because lower contents of salts results in dissolution of silica-alumina skeleton of zeolite. Low pH of treated water - lower than 6 - results in increase in probability of destruction of the crystal lattice.

Dynamic exchange capacity of zeolites is lower than dynamic exchange capacity of organic resins in the same conditions that is connected to slower exchange kinetics for zeolites. Residual hardness of water after zeolites makes about 0,3 mg - equivalent/l, whereas after organic resins - no more than 0,1 mg - equivalent/l.

Table 1. The basic types of modern organic and inorganic ionites, used for water treatment

Trademark	Type	Grain size, mm	Exchange capacity, equivalent/l	Application	Regeneration
Synthetic organic ion-exchange resins					
КУ-2-8 Granion K001-8 Dowex HCR-S Purolite C-100 Amberlite SR Lewatit S-100	Copolymer of styrene and DVB, strong acid cationite with sulfonate groups, gel structure, polydisperse granules	0,3-1,2	1,8-2,2	Softening	NaCl 60-250 g per liter of resin Solution 8-12 %
				Demineralization	HCl 50-150 g per liter of resin Solution 4-8 % H_2SO_4 50-240 g per liter of resin Solution 1-8 %
Dowex Marathon C Dowex Monosphere Lewatit S 1467 Lewatit MonoPlus S100	Copolymer of styrene and DVB, strong acid cationite with sulfonate groups, gel structure, monodisperse granules	0,6±0,05	2,0	Softening	NaCl 60-250 g per liter of resin Solution 8-12 %
				Demineralization	HCl 50-150 g per liter of resin Solution 4-8 % H_2SO_4 50-240 g per liter of resin Solution 1-8 %
КУ-23 Granion D001 Dowex MSC-1 Purolite C-150	Copolymer of styrene and DVB, strong acid cationite with sulfonate groups, macroporous structure, polydisperse granules	0,3-1,2	1,9	Softening, elimination of iron	NaCl 60-250 g per liter of resin Solution 8-12 %
				Demineralization	HCl 50-150 g per liter of resin Solution 4-8 % H2SO4 50-240 g per liter of resin Solution 1-8 %
КУ-2-7П Granion D113-III Dowex MAC-3 Purolite C-105 Lewatit CNP-80	Copolymer of acryl and DVB, weak acid cationite with carboxyl groups, macroporous structure, polydisperse granules	0,3-1,6	4,5	Elimination of bicarbonate alkalinity and softening	HCl 60-80 g per liter of resin Solution 3-6 % H2SO4 60-100 g per liter of resin Solution 0,5-0,8 %
				Elimination of heavy metals	NaCl 60-250 g per liter of resin Solution 8-12 %
Granion D 201 Dowex SBR-P Purolite A-400 Lewatit M-504	Copolymer of styrene and DVB, strong alkaline anionite with quarternary amino groups, gel structure, polydisperse granules	0,3-1,2	1,15- 1,35	Demineralization	NaOH 60-150 g per liter of resin Solution 3-6 %
				Elimination of silicates	

Dowex Marathon A Lewatit MonoPlus M-500 Lewatit MonoPlus M-600	Copolymer of styrene and DVB, strong alkaline anionite with quarternary / tertiary amino groups, gel structure, monodisperse granules	0,6±0,05	1,25	Demineralization	NaOH 60-100 g per liter of resin Solution 3-5 %
Granion D202, D2001 Dowex MSA-1, MSA-2 Purolite A-500, A-510 Lewatit MP-600	Copolymer of styrene and DVB, strong alkaline anionite with quarternary / tertiary amino groups, macroporous structure, polydisperse granules	0,3-1,2	0,75- 1,25	Demineralization	NaOH 60-150 g per liter of resin Solution 3-6 %
Granion D301 Dowex MWA-1, MWA-66 Purolite A-100 Lewatit MP-62, MP-64	Copolymer of styrene and DVB, weak alkaline anionite with tertiary amino groups, macroporous structure, polydisperse granules	0,3-1,2	1,3-1,6	Elimination of organic compounds, including colored humic acids	NaOH 60g per liter of resin Solution 2-3 %
Inorganic ionites					
Zeolite	Aluminum silicate	Fractions in the range 0,3-5,0	0,7-1,5	Elimination of the dissolved iron, hardness, heavy metals	NaCl 60-250 g per liter of zeolite Solution 8-12 %
				Elimination of ammonium	NaCl 60-250 g per liter of zeolite Solution 8-12 % pH = 10-12

Adsorption

Brunauer, Emmett and Teller'smodel of multilayer adsorption is a random distribution of molecules on the material surface.

Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. This process creates a film of the *adsorbate* on the surface of the *adsorbent*. This process differs from absorption, in which a fluid (the *absorbate*)permeates or is dissolved by a liquid or solid (the *absorbent*). Adsorption is a surface-based process while absorption

involves the whole volume of the material. The term *sorption* encompasses both processes, while *desorption* is the reverse of it. Adsorption is a *surface phenomenon*.

Langmuir

Irving Langmuir was the first to derive a scientifically based adsorption isotherm in 1918.[7] The model applies to gases adsorbed on solid surfaces. It is a semi-empirical isotherm with a kinetic basis and was derived based on statistical thermodynamics. It is the most common isotherm equation to use due to its simplicity and its ability to fit a variety of adsorption data. It is based on four assumptions:

1. All of the adsorption sites are equivalent and each site can only accommodate one molecule.
2. The surface is energetically homogeneous and adsorbed molecules do not interact.
3. There are no phase transitions.
4. At the maximum adsorption, only a monolayer is formed. Adsorption only occurs on localized sites on the surface, not with other adsorbates.

These four assumptions are seldom all true: there are always imperfections on the surface, adsorbed molecules are not necessarily inert, and the mechanism is clearly not the same for the very first molecules to adsorb to a surface as for the last. The fourth condition is the most troublesome, as frequently more molecules will adsorb to the monolayer; this problem is addressed by the BET isotherm for relatively flat (non-microporous) surfaces. The Langmuir isotherm is nonetheless the first choice for most models of adsorption, and has many applications in surface kinetics (usually called Langmuir–Hinshelwood kinetics) and thermodynamics.

Langmuir suggested that adsorption takes place through this mechanism: $A_g + S \rightleftharpoons AS$, where A is a gas molecule and S is an adsorption site. The direct and inverse rate constants are k and k_{-1}. If we define surface coverage, θ, as the fraction of the adsorption sites occupied, in the equilibrium we have:

$$K = \frac{k}{k_{-1}} = \frac{\theta}{(1-\theta)P}$$

or

$$\theta = \frac{KP}{1+KP}$$

where P is the partial pressure of the gas or the molar concentration of the solution. For very low pressures $\theta \approx KP$ and for high pressures $\theta \approx 1$

θ is difficult to measure experimentally; usually, the adsorbate is a gas and the quantity adsorbed is given in moles, grams, or gas volumes at standard temperature and pressure (STP) per gram of adsorbent. If we call v_{mon} the STP volume of adsorbate required to form a monolayer on the adsorbent (per gram of adsorbent), $\theta = \frac{v}{v_{\text{mon}}}$ and we obtain an expression for a straight line:

$$\frac{1}{v} = \frac{1}{Kv_{\text{mon}}}\frac{1}{P} + \frac{1}{v_{\text{mon}}}$$

Through its slope and *y*-intercept we can obtain v_{mon} and K, which are constants for each adsorbent/adsorbate pair at a given temperature. v_{mon} is related to the number of adsorption sites through the ideal gas law. If we assume that the number of sites is just the whole area of the solid divided into the cross section of the adsorbate molecules, we can easily calculate the surface area of the adsorbent. The surface area of an adsorbent depends on its structure; the more pores it has, the greater the area, which has a big influence on reactions on surfaces.

If more than one gas adsorbs on the surface, we define θ_E as the fraction of empty sites and we have:

$$\theta_E = \frac{1}{1 + \sum_{i=1}^{n} K_i P_i}$$

Also, we can define θ_j as the fraction of the sites occupied by the *j*-th gas:

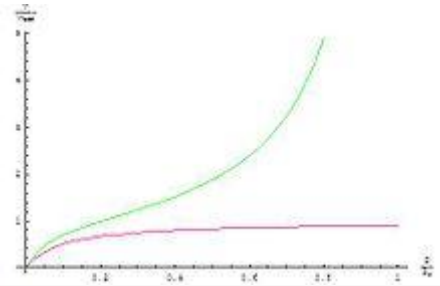
$$\theta_j = \frac{K_j P_j}{1 + \sum_{i=1}^{n} K_i P_i}$$

where *i* is each one of the gases that adsorb.

BET

Often molecules do form multilayers, that is, some are adsorbed on already adsorbed molecules and the Langmuir isotherm is not valid. In 1938 Stephen Brunauer, Paul Emmett, and Edward Teller developed a model isotherm that takes that possibility into account. Their theory is called BET theory, after the initials in their last names. They modified Langmuir's mechanism as follows:

$A_{(g)} + S \rightleftharpoons AS$
$A_{(g)} + AS \rightleftharpoons A_2S$
$A_{(g)} + A_2S \rightleftharpoons A_3S$ and so on



Langmuir isotherm (red) and BET isotherm (green)

The derivation of the formula is more complicated than Langmuir's (see links for complete derivation). We obtain:

$$\frac{x}{v(1-x)} = \frac{1}{v_{\mathrm{mon}}c} + \frac{x(c-1)}{v_{\mathrm{mon}}c}.$$

x is the pressure divided by the vapor pressure for the adsorbate at that temperature (usually denoted P/P_0), *v* is the STP volume of adsorbed adsorbate, v_{mon} is the STP volume of the amount of adsorbate required to form a monolayer and *c* is the equilibrium constant *K* we used in Langmuir isotherm multiplied by the vapor pressure of the adsorbate. The key assumption used in deriving the BET equation that the successive heats of adsorption for all layers except the first are equal to the heat of condensation of the adsorbate.

The Langmuir isotherm is usually better for chemisorption and the BET isotherm works better for physisorption for non-microporous surfaces.