

CHEMICAL EQUILIBRIA BETWEEN THE ION EXCHANGER AND GAS PHASE

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Ion exchange technologies for air purification (fibrous ion exchangers in form of fabrics)

Purification of industrial and agricultural exhaust gases from ionizable or catalytically convertible impurities (i. g. NH_3 , HCl , SO_2 , H_2S , Cl_2 ,...)

Removal malodorous substances from breathing air (organic acids, amines, mercaptanes,...)

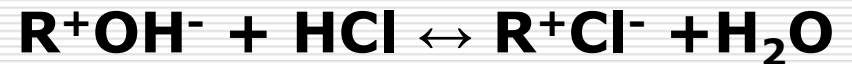
Individual protection means for humans lungs and skin

Deep air purification in clean rooms in production of microchips, precise mechanics, optics, pharmaceuticals...

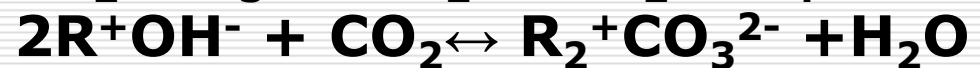
Examples of the sorption processes in systems GAS-ION EXCHANGER

Sorption of ammonia and amines: $R-H^+ + NH_3 \leftrightarrow R-NH_4^+$

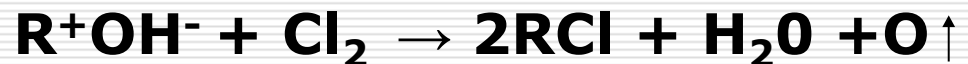
Sorption of acids:



Sorption of anhydrides:



Sorption of neutral
substances :



Features of practically important gaseous processes with ion exchangers

Extremely short contact time of the ion exchanger and air requiring application of the sorbents in form of fibers (fractions of second)

Low concentration of the sorbate in the air (≤ 200 mg/m³)

Plentiful side processes (oxidation the sorbate by atmospheric O₂, sorption competition with CO₂,...)

Extremely strong effect of the air relative humidity on the sorption and catalysis

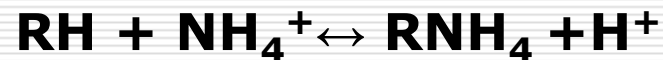
The aim of theory

To calculate sorption of an ionic sorbate, exemplified by NH_3 , by the ion exchanger from its concentration and relative water humidity in the gas phase on the basis of the following information:

1. Exchange capacity of the ion exchanger.
2. The acidity parameters of functional groups pK° and ΔpK (*obtainable from the titration curves*)
3. Parameters of isopiestic curve $W=W(\text{P}/\text{P}_0)$ (*obtainable from the isopiestic data*)
4. Constant of ion exchange equilibrium K^+-NH_4^+ (*obtainable from the experiment on the ion distribution*)

Assumptions:

- 1.** The water in ion exchanger presents in two forms – “free water” and “hydrate water”.
- 2.** Molecular NH_3 is dissolved only in the free water.
- 3.** Distribution of NH_3 between gas phase and the **free water** is controlled by the Henry's law with the same distribution constant as that for the liquid water.
- 4.** Distribution of NH_4^+ between the internal solution and the sorption centers of ion exchanger is controlled by ion exchange reaction



described by the equilibrium coefficient

$$k = [\text{RNH}_4][\text{H}^+] / ([\text{RH}] [\text{NH}_4^+])$$

$$k = k(X)$$

Scheme of theoretical calculation of ammonia sorption

Air containing NH_3 and H_2O + ion exchanger in H^+ -form →

sorption of water, →

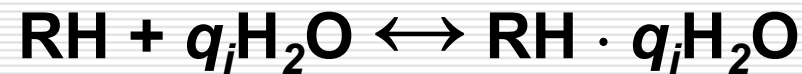
formation of hydrates →

dissolution of ammonia in the **free water, →**

ammonia dissociation →

interaction of ammonia with the functional group

Evaluation of the amount of hydration water in the ion exchanger



$$K_i = \frac{n_{h,i}}{n_{R,i} \cdot \alpha^{q_i}}$$

$$n_h = \sum_i q_i \cdot n_{h,i} = \sum_i \frac{q_i \cdot K_i \cdot \alpha^{q_i}}{1 + K_i \cdot \alpha^{q_i}}$$

q - number of water molecules in hydrate

α – relative humidity P/P_0

n_h and n_R - number of moles of the hydrate and non-hydrated groups

Evaluation of the amount of the free water

We assume in the first approximation the ion exchanger is an ideal mixture of hydrates and **free water** molecules and the system obeys the Rault's law in the following form:

$$a = X_W \cdot f_W / (X_{OW} \cdot f_{OW})$$

where X_W , X_{OW} and f_W , f_{OW} are respectively mole fractions and the rational activity coefficients of **free water** in a partially and completely swollen ion exchanger ($a = 1$):

$$X_W = n_W / (n_W + 1), \quad X_{OW} = n_{OW} / (n_{OW} + 1)$$

n_W is a number of **free water** moles per mole of the functional groups

Evaluation of the amount of the free water

Choosing the reference state as $f_{0W} = 1$ at $X_W = X_{0W}$ we obtain for the amount of **free water** in the ion exchanger:

$$n_W = \frac{\alpha \cdot (W_0 - \sum_i q_i \cdot n_{h,i}) \cdot f_W}{1 + W_0 - \sum_i q_i \cdot n_{h,i} - \alpha \cdot (W_0 - \sum_i q_i \cdot n_{h,i})}$$

$$f_W = \alpha^m$$

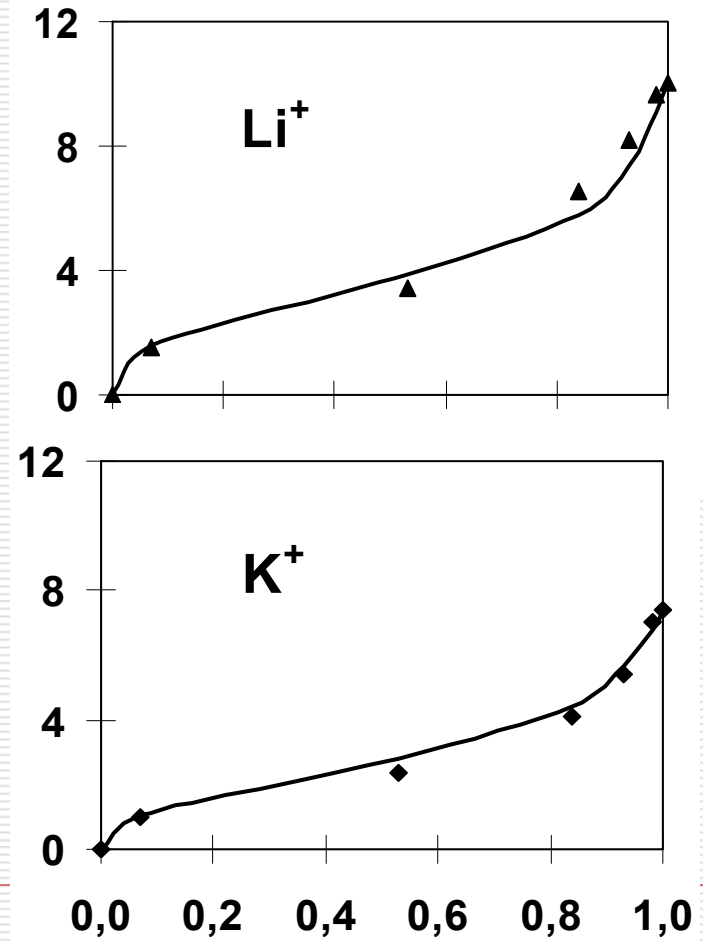
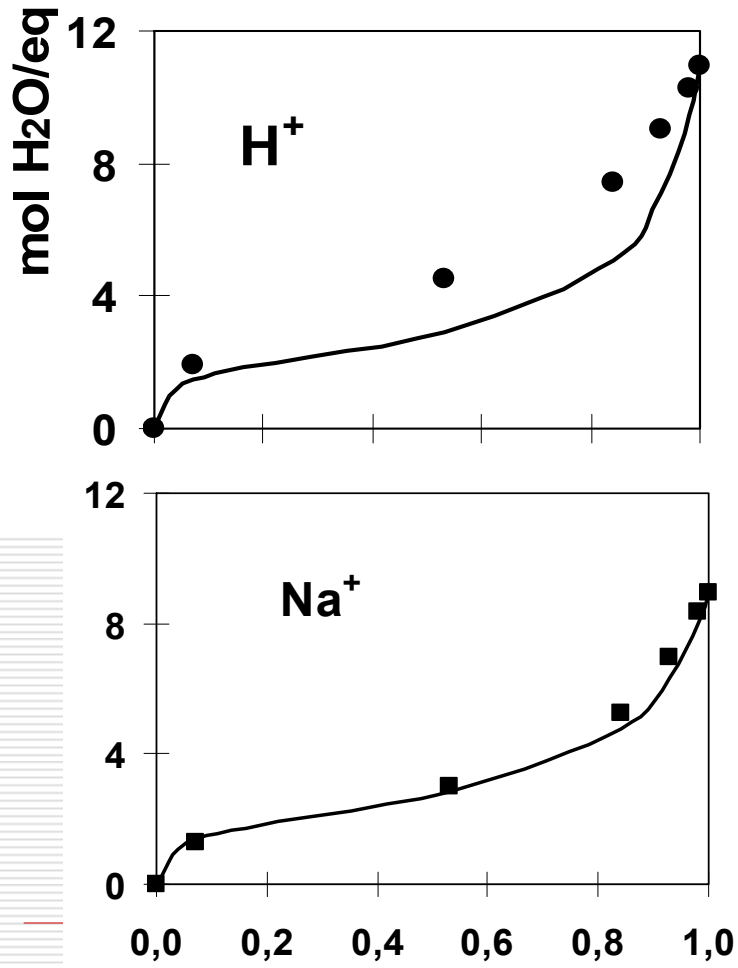
m is empirical constant ≥ 0 , usually equal to 0.

A new equation for the isopiestic curve

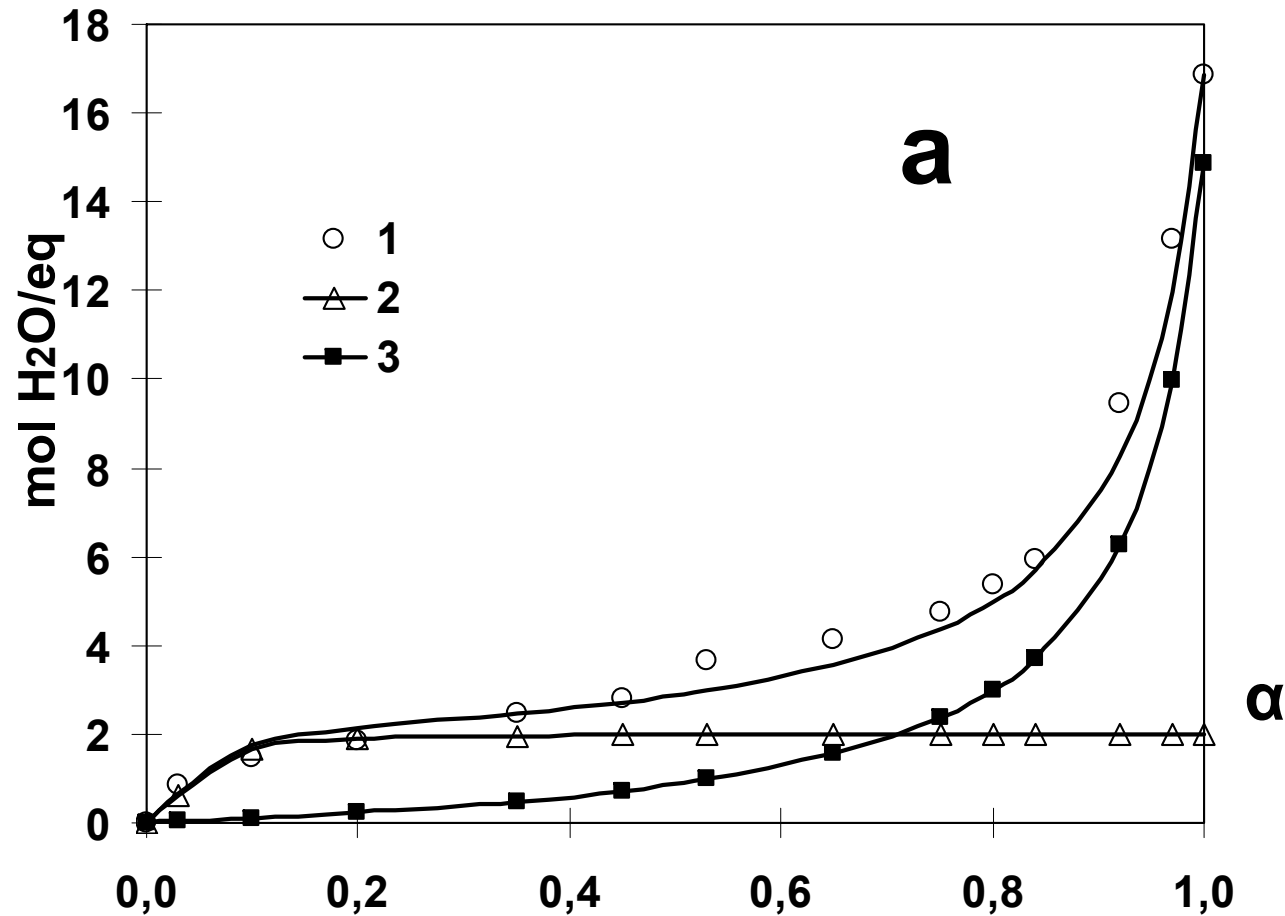
$$W(a) = \sum_i q_i \cdot n_{h,i} + n_W$$

$$W = \sum_i \frac{q_i \cdot K_i \cdot \alpha^{q_i}}{1 + K_i \cdot \alpha^{q_i}} + \frac{\alpha \cdot (W_0 - \sum_i q_i \cdot n_{h,i}) \cdot f_W}{1 + W_0 - \sum_i q_i \cdot n_{h,i} - \alpha \cdot (W_0 - \sum_i q_i \cdot n_{h,i})}$$

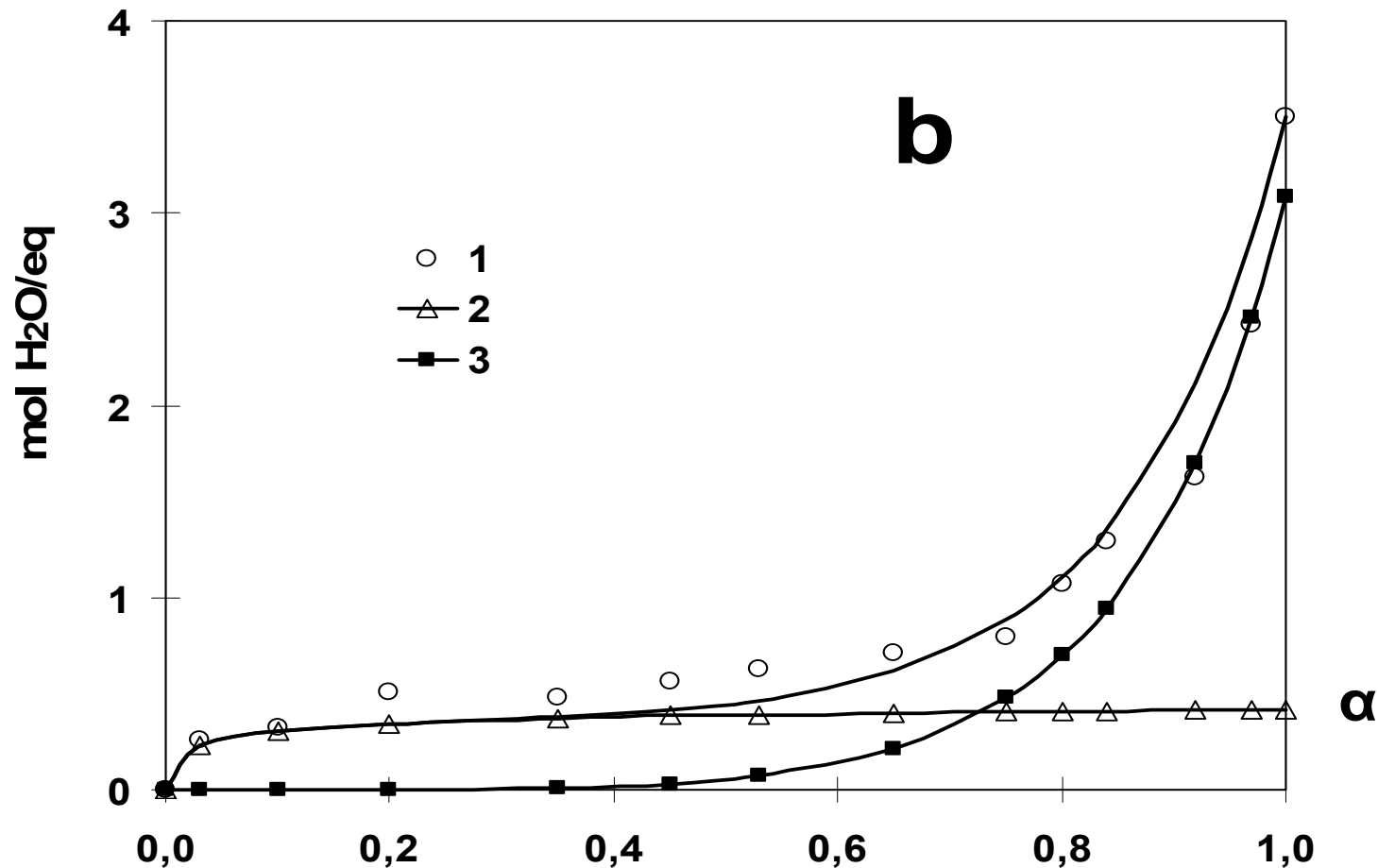
Comparison of experimental data for Dowex-50x8 from Boyd and Soldano with theoretical calculation (lines)



1-isopiestic curve of sulfonic ion exchangers FIBAN K-1, H form. The lines are calculated from the new equation with the following parameters: $q = 2$; $K = 500$; $m = 0$. q -hydration water; 3 – free water



1-isopiestic curve of carboxylic ion exchangers FIBAN K-4.
The lines are calculated from the new equation with the following parameters: $q = \frac{1}{2}$; $K = 5$; $m = 3.5$.
2-hydration water; 3 – free water



Molecular ammonia distribution between the ion exchanger and gas phase

We assume that ammonia gas can dissolve only in **free water** in the phase of ion exchanger. In this assumption Henry's law is formulated as:

$$[\text{NH}_3]_{\text{R}} = K_{\text{H}} \cdot [\text{NH}_3]_{\text{G}} \cdot X_{\text{W}}$$

where $[\text{NH}_3]_{\text{R}}$ is concentration of NH_3 in the internal solution, the mole fraction of **free water** X_{W} is calculated from isopiestic data .

Constant K_{H} is assumed to be the same as that for equilibrium of aqueous solution of ammonia with water solution. It was calculated from the literature data and equaled $7.763 \times 10^{-5} \text{ (mol/kg) / (mg/m}^3\text{)}$.

Determination of amount of RNH_4^+ as a function of x

In order to compute amount of NH_3 bound to the functional groups we apply equation of hydrolysis:



$$k_{hyd}(x) = (1-x) [\text{NH}_4^+] [\text{OH}^-] / (x \cdot [\text{H}_2\text{O}]),$$

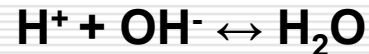
$$X = [\text{RNH}_4] / E, (1-X) = [\text{RH}] / E$$

E – exchange capacity

$k_{hyd}(x)$ depends on degree of hydrolysis $(1-x)$. It can be determined via the acidity parameters of ion exchanger obtainable from the titration curve

The acidity parameters

Titration of the H form of ion exchanger with alkali KtOH is described as equilibria



Dependence of the equilibrium coefficient of ion exchange $\text{Kt}^+ - \text{H}^+$

$$k(x) = X \cdot [\text{H}^+] / ((1 - X) \cdot [\text{Kt}^+])$$

with sufficient accuracy can be described as

$$pk = pK + \Delta pk (X-1/2)$$

K is the thermodynamic constant of ion exchange independent of the degree of ion exchange, Δpk is a constant equal to $pk_{x=1} - pk_{x=0}$.

In our works we use K^+ as a standard cation for determination of the acidity parameters, $\text{Kt}^+ = \text{K}^+$.

Connection between the acidity parameters and RNH_4 hydrolysis equilibrium coefficient

Value pK for the case $\text{Kt}^+ = \text{NH}_4^+$ is obtainable from direct experiment or from combining constants of ion exchange equilibria $\text{H}^+ - \text{K}^+$ and $\text{K}^+ - \text{NH}_4^+$

Combine equations of equilibrium coefficients of hydrolysis and ion exchange with those for water and ammonia dissociation, K_D :

$$pk_{hyd} = 14 - pK - \Delta pk \cdot (X_{\text{RNH}_4^+} - 1/2)$$

$$X_{\text{RNH}_4^+} = [\text{NH}_3]_{\text{R}} \cdot K_D / (k_{hyd} + K_D \cdot [\text{NH}_3]_{\text{R}})$$

Apply the modified Henry's equation:

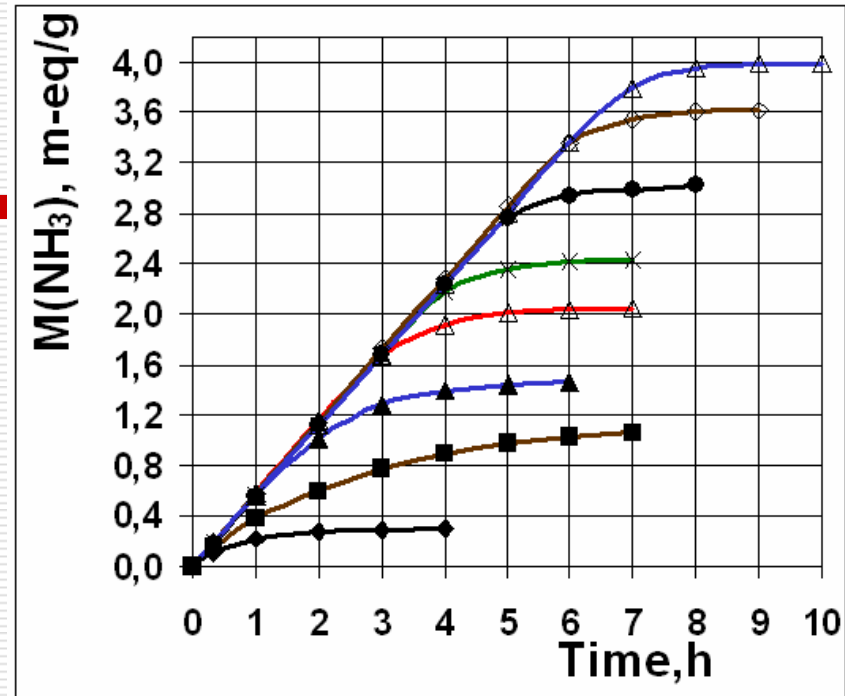
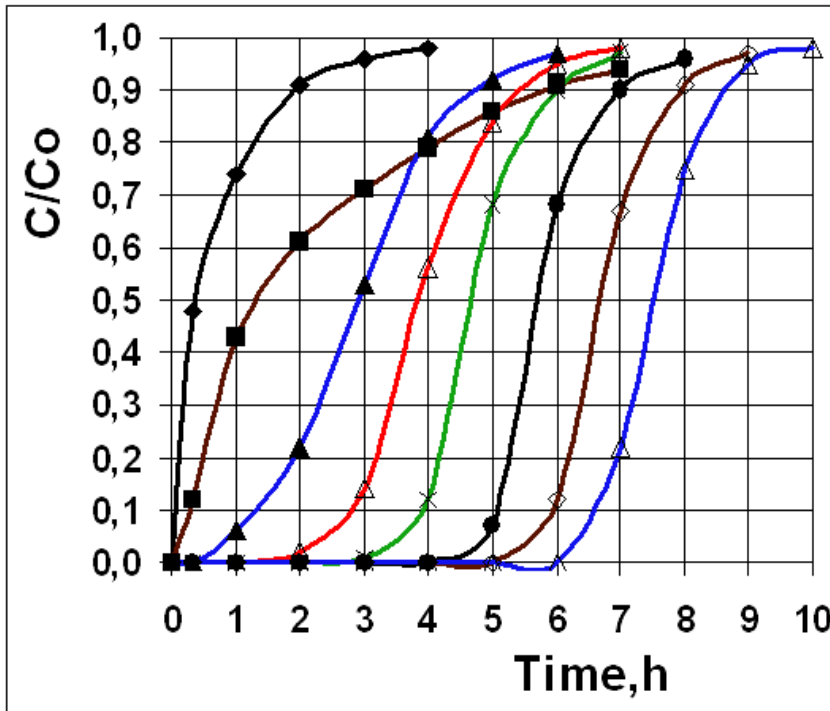
$$X_{\text{RNH}_4^+} = K_H \cdot X_W \cdot [\text{NH}_3]_{\text{G}} \cdot K_D / (k_{hyd} + K_D \cdot K_H \cdot X_W \cdot [\text{NH}_3]_{\text{G}})$$

The information needed for aprioristic calculation of the ionizable sorbate sorption by the ion exchanger

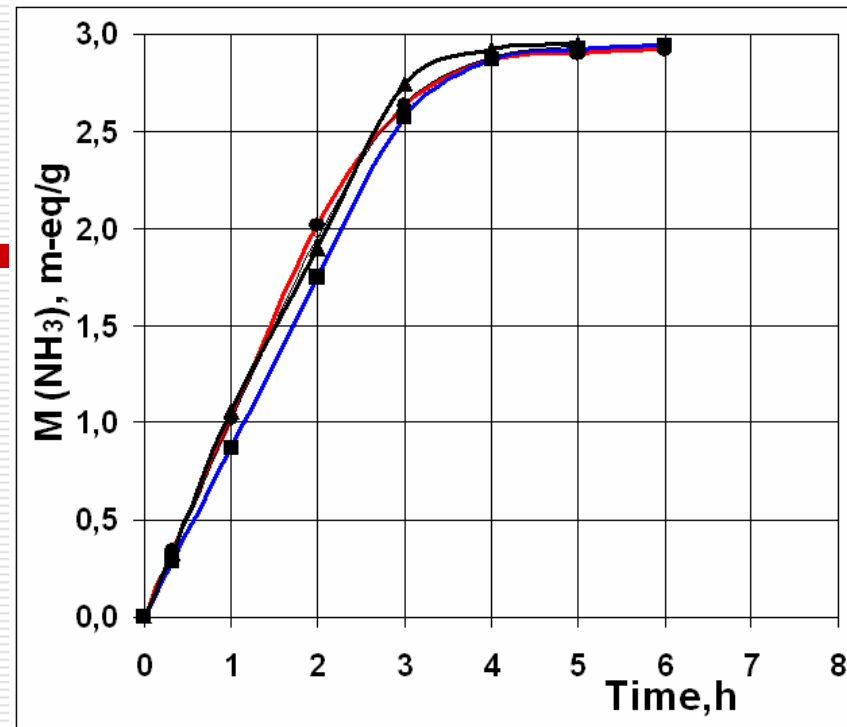
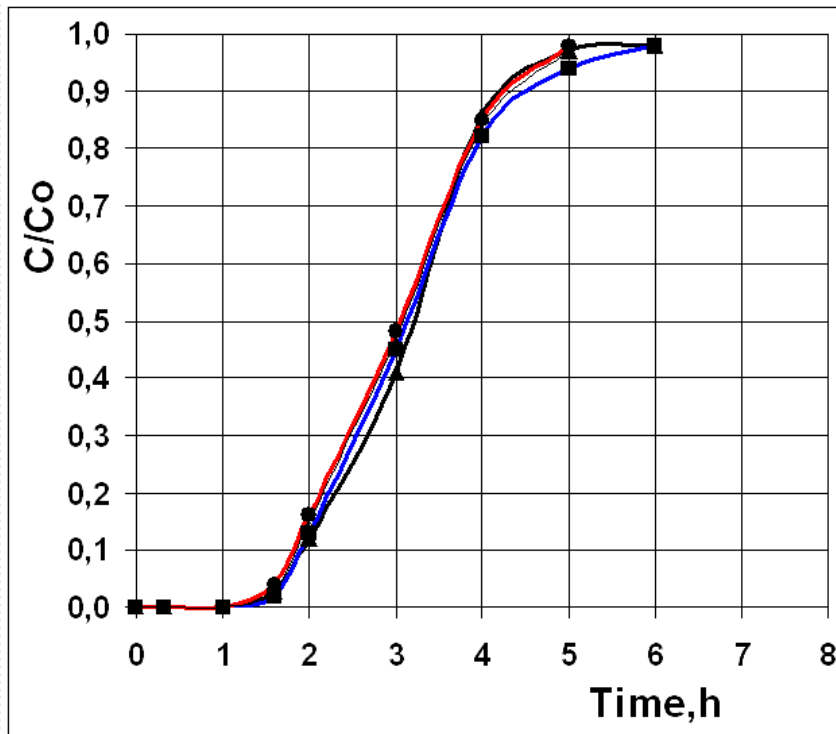
- 1. Dissociation constant of the sorbate**
- 2. The acidity parameters of ion exchanger (obtainable from the titration curves)**
- 3. Isopiestic curve of the ion exchanger in the acid form**
- 4. The constant of Henry's law.**

The pathway for an aprioristic calculation of ammonia sorption by the ion exchanger

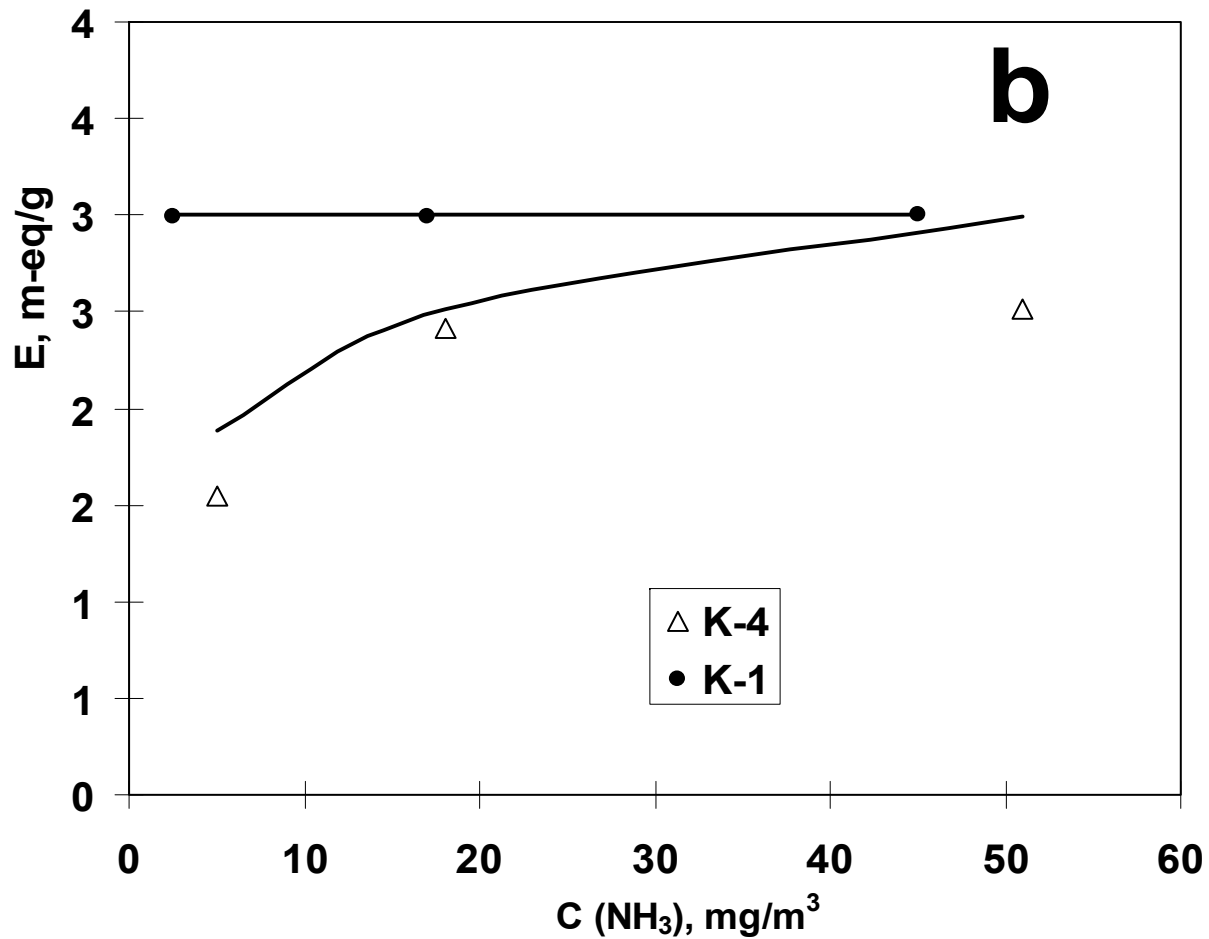
- 1. Fitting the isopiestic data for the ion exchange in H form to the theoretical equation and finding parameters q_i , K_i and m .**
- 2. Finding the mole fraction of **free water** in the ion exchanger, X_w , at a given relative humidity α .**
- 3. Calculation of the relative mole fraction of ammonia in the ion exchanger using the final equation.**



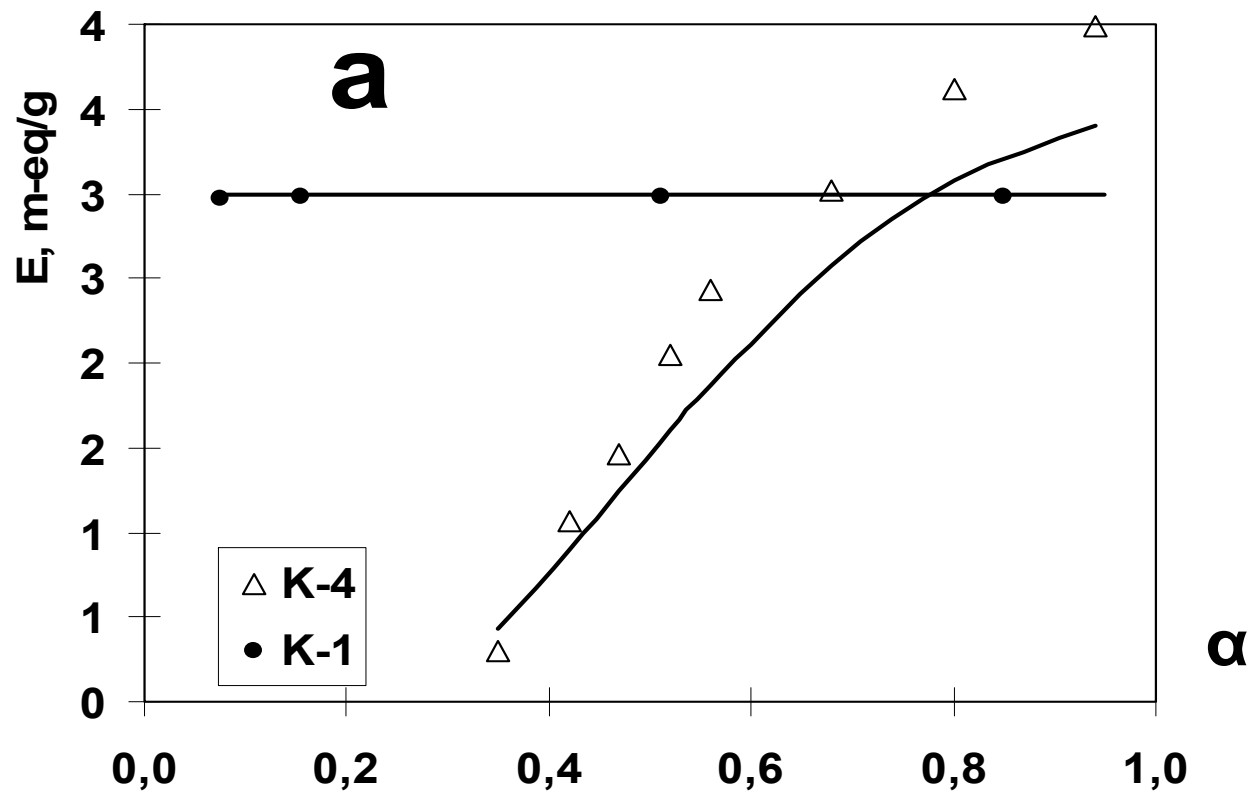
Breakthrough and sorption curves of NH₃ (18 mg/m³) for carboxylic acid fibrous ion exchanger FIBAN K-4 at different relative humidity of the air passing through the layer of ion exchange fabric 6 mm thick with linear flow rate 0.08 m/s
1 – 35%; 2 – 42%; 3 – 47%; 4 – 52%; 5 – 56%; 6 – 68%; 7 – 80%; 8 – 94%.



Breakthrough and sorption curves of NH₃ (18 mg/m³) for sulfonic acid fibrous ion exchanger FIBAN K-1 at different relative humidity of the air passing through the layer of ion exchange fabric 3 mm thick with linear flow rate 0.08 m/s
 $\alpha = 7,5\%, 15,5\%; 51\%, 85\%$.



Ammonia sorption on ion exchangers FIBAN K-1 and K-4 in dependence concentration of ammonia at $\alpha = 0.48$ for K-1 and $\alpha = 0.55$ for K-4. Symbols – experimental data, the curves are computed



Ammonia sorption on ion exchangers FIBAN K-1 and K-4 in dependence of relative air humidity at $[\text{NH}_3]_G = 18 \text{ mg/m}^3$. Symbols – experimental data, the curves are computed.