

## The Characteristic Calculation of Carboxylic Ion Exchanger

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A method for calculating the main characteristics of a potentiometric titration curve in a carboxylic ion exchanger has been investigated. The potentiometric titration curves of simple electrolyte and ion exchangers (polyelectrolytes) showed a great difference between them. The acidity parameters of the ion exchangers, the thermodynamic constant ( $pK^{\ominus}$ ), apparent equilibrium constant ( $\bar{K}$ ), and correction for the apparent equilibrium constant ( $b$ ), were introduced and used to express the characteristics of the carboxylic ion exchanger. A characteristic equation related to the acidity parameters of the ion exchangers systems was derived. A fibrous carboxylic cation exchanger was used and potentiometric titration curves at different concentrations of the supporting electrolyte were obtained. To prove the validity of the characteristic equation, the theoretical and experimental potentiometric titration data were fitted for a Fiban K-4 ion exchanger as the concentration of the supporting electrolyte was varied. In the present study, good agreement between the data points and the fitted curves was found in all the cases. The  $g$  (number of moles of alkali to 1 g of ion exchanger) of carboxylic ion exchanger was calculated from the concentration of supporting electrolyte ( $C$ ), pH of the solution, and degree of neutralization of ion exchanger ( $\bar{\chi}$ ).

**Keywords :** Ion exchanger, Polyelectrolytes, Carboxylic ion exchanger, Potentiometric titration, Equilibrium constant.

### Introduction

Recently, the removal of toxic heavy metal ions from sewage and industrial and mining wastewater has received much attention. Consequently, there is growing demand for materials to treat wastewater. Toxic heavy metal can be separated easily from wastewater by ion exchange resin.

The traditional precipitation process using zeolite and clay does not always provide a removal rate that meets the pollution control limit. However, ion exchange resin can be used for various functions, such as waste treatment, separation of rare earth metals and heavy metals, separation of amino acids, purification, sorption of toxic gases, drying agents, and bleaching agents.<sup>1</sup> Especially, ion exchange resin can separate metal ions from industrial wastewater selectively with simple equipment and low energy.

The separation and refining of materials had been carried out by distillation and recrystallization in chemical industry, requiring large amount of thermal energy. The separation of metal ions with ion exchange resin saves resources and energy because it uses mechanical pressure, and there is no change in phase. Sequential separation is also possible, so many kinds of ion exchange resins have been studied and used in industry. They have been used to recycle heavy metal in wastewater through adsorption, separation, and recovery because of their metal ion selectivity.<sup>2</sup>

The electrolytes are divided commonly into nonpolymeric and polymeric electrolytes. An ion exchanger is considered

as a kind of polymeric electrolyte. It is recognized that potentiometric titration is one of the most important methods for the investigation and characterization of ion exchangers. At the same time, a great discrepancy between theory and practice as applied ion exchangers exists.<sup>3</sup>

On one hand, there is a good understanding of the physical nature of the main processes that occur during the neutralization of ion exchangers. Current theoretical models can provide sufficient interpretation for the phenomena observed in the potentiometric titration of ion exchangers.<sup>4,6</sup>

On the other hand, researchers applying potentiometric titration for the characterization of ion exchangers use the most simple, if not to say primitive, method of expressing the properties of ion exchanger *via* some ersatz dissociation constant through analogy with nonpolymeric acids and bases. While the imperfection of expressing information of ion exchangers in such a way is well understood, there is no better practical way. It seemed impossible to use ion exchanger parameters in theoretical work for practical characterizations of ion exchangers since the determination requires additional experimental data and assumptions. Also the parameters physical meaning and further applicability has been somewhat uncertain.

As a result, we do not have at present an accepted method for expressing acidic and basic properties of ion exchangers. The quantities used for that purpose in specific work are often different.<sup>7,8</sup>

It is a challenge to attempt to reduce the gap between the

theory and practice of potentiometric titration of ion exchangers, an effort made in the present work.

Analyzing the main theoretical concepts and experimental work on the potentiometric titration of ion exchangers, we came to the conclusion that the concept involving the neutralization of ion exchangers as a specific case of an ion exchanger can provide a simple and non-contradictory way to express acidic-basic properties of ion exchangers as a set of parameters with clear physical meaning.

In the present work, a method for computing the main characteristics of a potentiometric titration curve in ion exchanger/solution systems was taken into consideration. The acidity parameters of ion exchangers, such as the thermodynamic constant ( $pK^0$ ), apparent equilibrium constant, and correction for the apparent equilibrium constant ( $b$ ), were used to express the characteristics of a carboxylic ion exchanger. A carboxylic cation exchanger of a fibrous type was used for the experiment on potentiometric titration, and potentiometric titration curves at different concentrations of the supporting electrolyte were obtained. From the results, characteristic equations related to the acidity parameters of ion exchangers systems were obtained. The characteristic parameters, such as solution pH, supporting electrolyte concentration ( $C$ ), and degree of neutralization of ion exchanger ( $\bar{\chi}$ ), were calculated from  $g$  (number of moles of alkali to 1 g of ion exchanger).

### Experimental Section

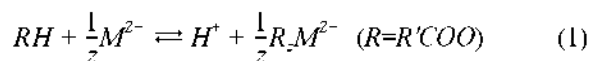
**Materials.** Fiban K-4 was purchased from Ecofil-Deco Ltd. (Minsk). Fiban K-4 is a fibrous carboxylic acid ion exchanger obtained by radioactive grafting of polyacrylic acid onto polypropylene fibers. The ion exchange capacity is 4.90 meq/g and the swollen weight ratio in water is 0.81 [(the weight of swollen ion exchange resin in water minus the weight of dry ion exchange resin)/(the weight of dry ion exchange resin)]. HCl and NaOH aqueous solutions were used as 0.1 N standard solutions. NaCl, buffer solution, and other chemical reagents were reagent grade and used without further purification.

**Potentiometric Titration.** The potentiometric titration curves were obtained by using an automatic titration instrument (Model 761 DMS Titrimo; Metrohm Ltd.). To measure the capacity of ion exchange, Fiban K-4 was transformed into the H-form by slow treatment with 0.5 N aqueous HNO<sub>3</sub> solution, and washed to neutral pH with distilled water. Subsequently Fiban K-4 (1 g) was added in 100 mL of aqueous NaCl solution (1 M) with various NaOH concentrations, and was allowed to stand for 3 days at 20 ± 1 °C. From the supernatant liquid in the flask, 10 mL of the solution were titrated with 0.1 N of HCl standard solution against phenolphthalein.

To determine the effect of supporting electrolytes the concentration of electrolytes was varied in the range of 1.0-1.0<sup>-4</sup> M of NaCl. The pH of the supernatant liquid in the flask was measured by a pH meter (Model HI 8417; Hanna Instruments Co.).

### Theoretical discussion.

**Calculation of the acidity function:** When a cation exchanger with H-form (acidic form) is placed in contact with a solution of alkali M(OH)<sub>z</sub>, ion exchange H<sup>+</sup>-M<sup>z+</sup> followed by the neutralization reaction occurs. This can be formulated as



The relative equilibrium constant is given as follows:

$$K = \frac{\bar{a}_M^{1/z} \cdot a_H}{\bar{a}_H \cdot a_M^{1/z}} \quad (2)$$

where  $a$  is the activity of the species in the subscript,  $z$  is the charge of the counter-ion and  $\bar{a}$  is the activity in the ion exchanger. However, it is practically impossible to determine  $\bar{a}_M$  and  $\bar{a}_H$ .  $K$  is expressed by the equation of the apparent equilibrium constant ( $\bar{K}$ ), which can be calculated from experimental data on the equilibrium from the following equation.

$$\bar{K} = \frac{\bar{C}_M^{1/z} \cdot a_H}{\bar{C}_H \cdot a_M^{1/z}} = K \frac{\bar{f}_H}{\bar{f}_M^{1/z}} \quad (3)$$

where  $\bar{C}$  is the concentration, and  $\bar{f}$  is the activity coefficient of the species in the ion exchanger. It is convenient to express the apparent equilibrium coefficient *via* relative equivalent fractions of the counterions in the phase of the ion exchanger,  $\bar{\chi}$

$$\bar{\chi} = \frac{z\bar{C}_M}{z\bar{C}_M + \bar{C}_H} \quad (4)$$

where the values of  $\bar{C}_M$  and  $\bar{C}_H$  are concentrations of the metal and hydrogen form of the ion exchanger, which are dependent on the degree of neutralization. The  $\bar{K}$  obtained from Eq. (3) and (4) is given as follows:

$$\bar{K} = \frac{\bar{\chi}^{1/z} \cdot a_H}{(1 - \bar{\chi}) \cdot a_M^{1/z}} \cdot z^{-1/z} \cdot (z\bar{C}_M + \bar{C}_H)^{\left(\frac{1}{z} - 1\right)} \quad (5)$$

After taking the logarithm of Eq. (5) and rearranging the terms, the rearranged equation is given as below:

$$\log \frac{\bar{\chi}^{1/z}}{(1 - \bar{\chi})} - pH - \frac{1}{z} \log a_M - \frac{1}{z} \log z + \left(\frac{1}{z} - 1\right) \log(z\bar{C}_M + \bar{C}_H) + p\bar{K}(\bar{\chi}, C_M) = 0 \quad (6)$$

$p\bar{K}(\bar{\chi}, C_M)$  means  $-\log \bar{K}(\bar{\chi}, C_M)$ .  $C_M$  and is the concentration of the supporting electrolyte. This equation is related to the most important properties of our system, that is, the acidity parameters: pH of the solution, degree of neutralization of the ion exchanger (*i.e.* the counterion sorption value), and the concentration of a supporting electrolyte. The acidity parameters can be used to describe the ionic equilibrium in an ion exchanger-solution containing H<sup>+</sup> and counterions M<sup>z+</sup>.

**Calculation of the Apparent Equilibrium Constant ( $\bar{K}$ ):**

An equation for  $\bar{\chi}$  dependency on  $\log \bar{K}$  has been derived in Soldatov's model in the following equation.<sup>9,11</sup>

$$\log \bar{K} = \sum_{j=0}^{i-1} \frac{i!}{(i-j)!j!} \cdot y(i-j, j) \cdot (1-\bar{\chi})^{i-j} \cdot \bar{\chi}^j \quad (7)$$

where  $i$ ,  $j$ , and  $y(i-j, j)$  are the Soldatov's model constants. Their physical meaning is as follows:  $i$  is a maximum number of neighboring exchange group in the microenvironment of any selected exchange group in the ion exchanger. The nearest neighbors are those groups that affect the energy of interaction of counterion ( $M^{2+}$ ) with a selected exchange group. The  $j$  is a number of neighboring exchange groups occupied with counterion ( $M^+$ ), and  $y(i-j, j)$  is constant. In an actual case the  $i$  is not larger than 3, and the  $y(i-j, j)$  is constant on the same order of magnitude as  $\log \bar{K}$ .

The pH of the equilibrated solution depends on the concentration of acid or base. The potentiometric titration curve of ion exchanger is not a simple physico-chemical characteristic since it depends on the ratio of quantities of the ion exchanger and the solution in the system undergoing potentiometric titration.

It is important to foresee the influence of the conditions of the potentiometric titration of ion exchangers on the shape of the potentiometric titration curve and the best conditions for titration and different factors in determining the shape and position of the curve. Therefore, the potentiometric titration curves,  $\text{pH} = f(g, \text{mmol/g})$ , can be computed by values of the solution pH and  $\bar{\chi}$  to find the  $g$  with  $E$  (exchange capacity) in a volume  $V$ .<sup>12,13</sup> The equation expressing  $g$  in the potentiometric titration curve is given as follows:

$$g = \frac{1}{z}(E\bar{\chi} + VC_{OH} - VC_H) \quad (8)$$

Equations (6), (7), and (8) can be used to express the potentiometric titration curve of the ion exchanger.

**Results and Discussion**

Figure 1 shows the theoretical and experimental data of the  $p\bar{K} = -f(\bar{\chi})$  dependencies in 0.01 M of NaCl electrolyte. As Figure 1(a) shows, the experimental data were fitted with a third-order polynomial. To achieve sufficient accuracy from Equation (7), the third-order polynomial needs at least  $\bar{\chi}^3$  and four parameters ( $y(3,0)$ ,  $y(2,1)$ ,  $y(1,2)$  and  $y(0,3)$ ).

$$p\bar{K} = -y(3,0)(1-\bar{\chi})^3 - 3y(2,1)(1-\bar{\chi})^2\bar{\chi} - 3y(1,2)(1-\bar{\chi})\bar{\chi}^2 - y(0,3)\bar{\chi}^3 \quad (9)$$

where the constants of  $y(3,0)$ ,  $y(2,1)$ ,  $y(1,2)$  and  $y(0,3)$  are 3.13, 5.61, 3.71, and 6.02, respectively, and their mean error is 0.08. It can be rewritten as follows:

$$pK = +3.13 + 7.44\bar{\chi} - 13.13\bar{\chi}^2 + 9.59\bar{\chi}^3 \quad (10)$$

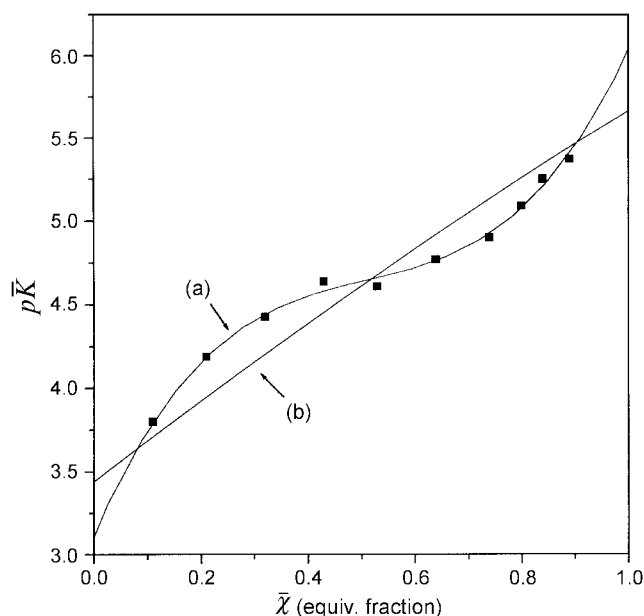


Figure 1. An example of  $p\bar{K} = f(\bar{\chi})$  ( $C_{NaCl} = 0.01 \text{ mol/L}$ ) dependency fitted with different interpolation. The points are experimental data.

The experimental data were fitted by the first-order polynomial to minimize the parameters in Figure 1(b). The linear regression needs at least two parameters. The  $p\bar{K}$  is given as follows:

$$p\bar{K} = -y(1,0)(1-\bar{\chi}) - y(0,1)\bar{\chi} \quad (11)$$

where the constants of  $y(1,0)$  and  $y(0,1)$  are 3.76 and 5.47, respectively, and their mean error is 0.17. Substituting these values into Equation (11) produces the following equation:

$$p\bar{K} = +3.76 + 1.71\bar{\chi} \quad (12)$$

The Equation (12) was used to calculate the apparent equilibrium constant ( $\bar{K}$ ). The ( $p\bar{K}$ ) values for various  $\bar{\chi}$  can be calculated from Equations (10) and (12). Because the concentration of the supporting electrolyte (NaCl) was 0.01 M and the ion charge ( $z$ ) was 1, the equation (6) can be rewritten as follows:

$$\log \frac{\bar{\chi}}{1-\bar{\chi}} - \text{pH} - \log a_M + p\bar{K}(\bar{\chi}, C_M = 0.01) = 0 \quad (13)$$

where, because  $a_M$  is the activity of the counterion,  $C_M$  practically coincides with the concentration of the supporting electrolyte. Therefore, the concentration  $C_M$  was used in place of activity  $a_M$  in Equation (13). Substituting this condition into Equation (13) produced the following equations:

$$\log \frac{\bar{\chi}}{1-\bar{\chi}} - \text{pH} - \log C_M + p\bar{K}(\bar{\chi}, C_M = 0.01) = 0 \quad (14)$$

$$\log \frac{\bar{\chi}}{1-\bar{\chi}} - \text{pH} + 2 + p\bar{K}(\bar{\chi}, C_M = 0.01) = 0 \quad (15)$$

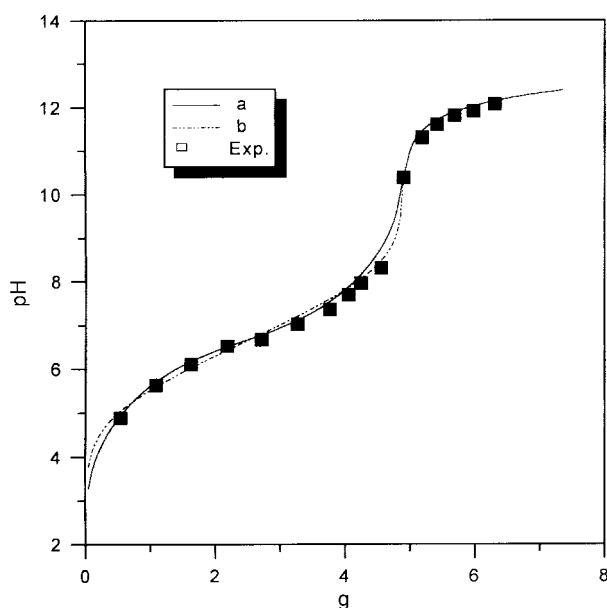


Figure 2. Comparison of experimental data with computed data obtained by using different interpolation in Figure 1.

The pH for various  $\bar{\chi}$  can be calculated from Equation (15). Because the ion charge ( $z$ ) is 1, Equation (8) can be rewritten as follows:

$$g = E\bar{\chi} + V(10^{pH-14} - 10^{-pH}) \quad (16)$$

From Equation (16), the  $g$  values for various  $\bar{\chi}$  can be calculated. Therefore, the  $g$  values for pH were calculated and the experimental data in the potentiometric titration curve were fitted with third-order and first-order polynomials, as in Figure 1.

In the case of linear regression, the fitting deviated significantly from the experimental data points in comparison with third-order fitting. However, in Figure 2, it is shown that the potentiometric titration curves obtained from linear regression and non-linear regression were well coincident with the potentiometric titration curve obtained from the experimental data. Using the higher terms for  $p\bar{K} = -f(\bar{\chi})$  can certainly improve the accuracy in the description of characteristic behavior of ion exchangers, but also lead to much more complicated calculations, and require more parameters and more information for their determination. Therefore, it was found that the  $p\bar{K} = -f(\bar{\chi})$  dependency could be expressed by linear regression with sufficient accuracy.

The  $p\bar{K} = -f(\bar{\chi})$  dependencies of Fiban K-4 at different concentrations of supporting electrolyte are presented in Figure 3. The data points were experimental data and the straight lines were drawn by using linear regression. As shown in Figure 3, the  $\bar{\chi}$  dependencies of  $-p\bar{K}$  decrease with decreasing concentration of supporting electrolyte, and the straight lines with almost the same slope were obtained.

In Figure 4, the experimental data points in the potentiometric titration curves of Fiban K-4 ion exchanger for vari-

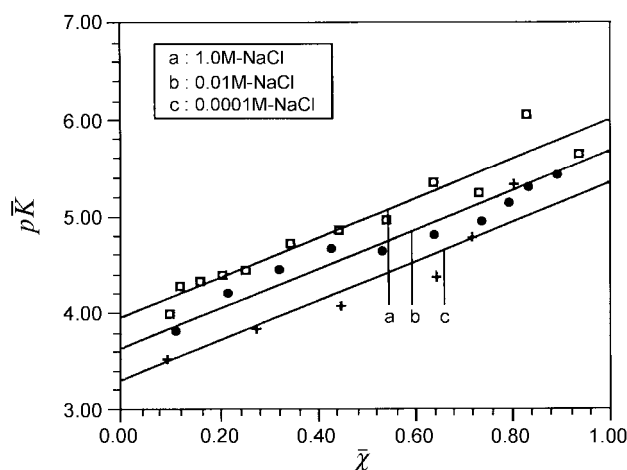


Figure 3. Straight lines represent  $p\bar{K} = f(\bar{\chi})$  dependencies calculated from Eq. (16) with coefficients given in Table 1 for ion exchanger Fiban K-4.

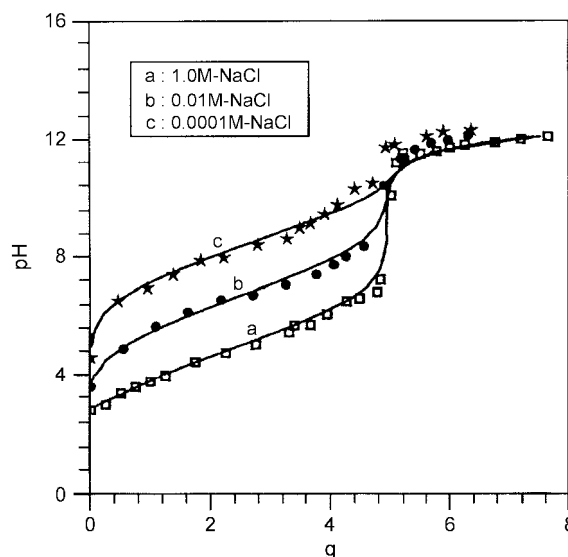


Figure 4. Potentiometric titration curves for ion exchanger Fiban K-4 at various concentrations of supporting electrolyte. The points are experimental data.

ous concentrations of supporting electrolyte were fitted with pH values versus  $g$  from Equation (7). A good agreement between the data points and the fitted curves is attained in all cases. However, the fitted curve deviated from experimental data in the case of the low concentration of supporting electrolyte. Because the degree of dissociation of  $H^+$  ion of carboxylic acid groups decreased compared with the amount of NaOH added in the low concentration solution of supporting electrolyte, the relatively high pH value caused the deviation from the fitted curve. Therefore, it was found that the potentiometric titration curve of the ion exchanger was closely related to the concentration of supporting electrolyte and the pH of the equilibrated solution.

**Acidity Parameters.** The correlation between  $p\bar{K}$  and the degree of neutralization ( $\bar{\chi}$ ) for the ion exchanger can be expressed by the following equation obtained from an

empirical equation.<sup>14,15</sup>

$$p\bar{K}(\bar{\chi}, \text{const.}) = pK^0 + \Delta p\bar{K}(\bar{\chi} - 1/2) \quad (17)$$

Because the  $pK^0$  is the thermodynamic equilibrium constant of the ion exchange between a  $H^+$  ion of functional groups and a counterion  $M^{z-}$ , it can be expressed as follows:

$$pK^0 = \int_0^1 p\bar{K}d\chi \quad (18)$$

Equation (18) is equal to the arithmetic average of  $p\bar{K}$  and can be rewritten as follows:

$$pK^0 = \frac{1}{2}(p\bar{K}_{\bar{\chi}=1} + p\bar{K}_{\bar{\chi}=0}) = p\bar{K}_{\bar{\chi}=1/2} \quad (19)$$

Constant  $\Delta p\bar{K}$  is the difference between  $p\bar{K}$  at complete ( $\bar{\chi}=1$ ) and zero ( $\bar{\chi}=0$ ) neutralization of the ion exchanger.

$$\Delta p\bar{K} = p\bar{K}_{\bar{\chi}=1} - p\bar{K}_{\bar{\chi}=0} \quad (20)$$

Figure 5 shows the plot of  $p\bar{K}$  versus  $\log C$  for Fiban K-4 ion exchanger at specific  $\bar{\chi}$ . This empirical equation can be expressed as follows:

$$p\bar{K}(\bar{\chi}, \text{const.}, C_M) = pK^0 + b \log C_M \quad (21)$$

where constant  $b$  was the correction value of  $p\bar{K}$  for various concentrations  $C_M$ . The constant  $b$  can be obtained from the slope of the linear equation at any fixed  $\bar{\chi}$ . The more precise approximations may be used, but usually they are not practically needed. The  $p\bar{K}(\bar{\chi}, C_M)=0$  can be expressed as follows:

$$p\bar{K}(\bar{\chi}, C_M) = pK^0 + \Delta p\bar{K}(\bar{\chi} - 1/2) + b \log C_M \quad (22)$$

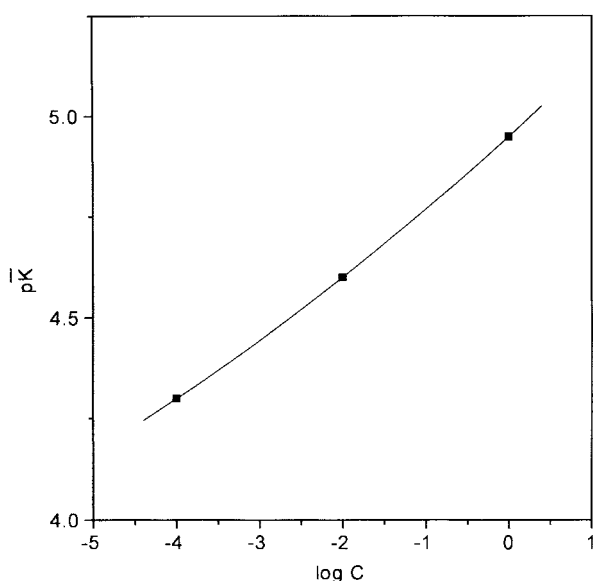


Figure 5. The dependency of  $p\bar{K}$  on concentrations of supporting electrolytes (NaCl) for ion exchanger Fiban K-4.

Table 1. Acidity Parameters of carboxylic ion exchangers

Ion Exchanger	$pK^0$	$\Delta p\bar{K}$	$b$
Fiban K-4	4.85	1.97	0.16

where the  $pK^0$ ,  $\Delta p\bar{K}$ , and  $b$  are related to the acid-base strength of the ion exchanger. A linear regression for  $p\bar{K}(\bar{\chi}, C_M)=0$  provides sufficient accuracy in the description of properties of ion exchange systems under neutralization. The obtained constants ( $pK^0$ ,  $\Delta p\bar{K}$ , and  $b$ ) are related to the properties of the ion exchanger. The acidity parameters of Fiban K-4 ion exchanger are listed in Table 1. The  $p\bar{K}$ ,  $\bar{\chi}$ , and  $C_M$  can be calculated from a straight line in Figure 3. The Equations (6), (7), (8), and (22) were used to obtain the potentiometric titration curves for various concentrations of a supporting electrolyte.

Therefore, the equations (6), (7), (8) and (22) are used to compute the parameters (pH,  $C_M$  and  $\bar{\chi}$  or g) or express the characteristics of a potentiometric titration curve of an ion exchanger. The dependency of pH,  $C_M$  and  $\bar{\chi}$  or g allows the predetermination of the characteristics of an ion exchanger in the system "ion exchanger-solution". If pH,  $C_M$  and  $\bar{\chi}$  or g are given, the capacity of the ion exchanger, the charge of the co-ion and counterion, and the affinity between the counterion and ion exchanger could be explained by the above equations. We can predetermine the properties of the ion exchanger without a potentiometric titration curve. There is no need to determine an entire set of potentiometric curves, and three experimental values (pH- $\bar{\chi}$ - $\log C_M$ ) are needed to determine  $pK^0$ ,  $\Delta p\bar{K}$ , and  $b$  if the exchange capacity ( $E$ ) of the ion exchanger is known. In the characterization of new ion exchangers, however, the capacity should be determined from the potentiometric titration curve. Therefore, it is necessary to have at least one potentiometric titration curve at a sufficiently high concentration of a supporting electrolyte (to determine  $E$ ,  $pK^0$  and  $\Delta p\bar{K}$ ) and one point on a potentiometric titration curve at another concentration of supporting electrolyte (to determine  $pK^0$ , and  $b$ ). This method can be used for an algorithm to determine the acidity parameters from minimum experimental data and the properties of new practical ion exchangers.

## Conclusions

A method to obtain a characteristic equation related to the acidity parameters in the system "ion exchanger-solution" has been investigated. Because it was impossible to describe the process of the neutralization of the ion exchanger with true dissociation constant, we introduced a suitable apparent equilibrium constant for the property of the ion exchanger. Also the deviation between theory and practice of potentiometric titration curves for ion exchangers could be decreased if potentiometric titrations were considered a specific case of the ion exchange between  $H^+$  ion and the counterion of a titrant. The theoretical and experimental potentiometric titration curves for Fiban K-4 ion exchanger were plotted as the concentration of a supporting electrolyte varied. Good

agreement was found in all the cases between the theoretical and experimental potentiometric titration curves. It was concluded that the potentiometric titration curve of the ion exchanger was closely related to the concentration of a supporting electrolyte and the pH of the equilibrated solution. Therefore, this method can be used for an algorithm to determine the acidity parameters with minimum experimental values and the properties of new practical ion exchangers.

### List of Symbols

$a$	: activity
$b$	: correction for the apparent constant shift with changing supporting electrolyte
$C$	: concentration of supporting electrolyte (mol/L)
$f$	: activity coefficient
$i, j$	: constant
$g$	: number of moles of alkali to 1 g of ion exchanger
$E$	: exchange capacity (meq/g)
$K$	: equilibrium constant
$\bar{K}$	: apparent equilibrium constant
$pK^0$	: thermodynamic constant of the ion exchanger
$\Delta p\bar{K}$	: difference of the apparent equilibrium constant at complete and zero neutralization of the ion exchanger
$V$	: solution volume, mL/g of the ion exchanger
$\bar{\chi}$	: equivalent fraction
$z$	: ion charge

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