



MULTIPARAMETRIC CURVE FITTING XVI. ANALYSIS OF ACID-BASE TITRATION DATA ON CHELATING RESINS*

MILAN MELOUN¹ and ERIK HÖGFELDT²

¹Department of Analytical Chemistry, The College of Chemical Technology,
 532 10 Pardubice, Czech Republic

²Department of Inorganic Chemistry, The Royal Institute of Technology,
 S-100 44 Stockholm, Sweden

(Received 15 April 1993. Revised 22 July 1993. Accepted 2 August 1993)

Summary—Methods for treating acid–base titration data on chelating resins are described and applied to the computer-assisted regression program IONEX with the regression procedure MINOPT. In this approach nonideal behavior in the exchanger phase is taken into account by the Högfelt three-parameter model. Regression analysis is applied to data on Ligandex-I studied by Szabadka and the results compared with those from a least squares program. The two approaches give identical results. The application of regression analysis program is further illustrated on titration data from a commercial chelate exchanger Iontsorb Salycil 100.

It is of practical importance to be able to characterize ion exchangers by parameters that permit prediction of acid–base and complexation equilibria. In recent years a simple three-parameter model has been shown to fulfil that request. It is applicable to strong acids,^{1–3} strong base³ as well as weak acid and complex forming resins.^{3–6}

In the present paper the model has been incorporated in a regression analysis for evaluating acid–base equilibria on weak acid and chelating resins and applied to data on the resin Ligandex-I studied by Szabadka⁷ as well as commercial chelate exchanger.

EXPERIMENTAL

The experiments on Ligandex-I are reported elsewhere.⁷ On the chelate resin Iontsorb-Salycil 100 (IONTSORB Ltd., Ústí nad Labem) studied the procedure described below was used.

Chemicals and solutions

Perchloric acid, $C = 1.00 \text{ mol/dm}^3$ was prepared by dilution 70% HClO_4 , p.a. quality from MERCK with deionized, twice distilled water and standardized against HgO and KI with a reproducibility of $\pm 0.2\%$.

Sodium hydroxide, $C = 1.00 \text{ mol/dm}^3$ was

prepared from a 50% solution of NaOH stored for several days in a polyethylene bottle. The clear, supernatant solution was siphoned off and diluted with carbon dioxide-free water to give $1.00 \text{ mol/dm}^3 \text{ NaOH}$. This solution was standardized by titration against potassium phthalate using the Gran method.

Apparatus and titration procedure

All emf measurements were carried out at $298.0 \pm 0.1 \text{ K}$ on a digital voltmeter, PHM4 with a glass electrode G202B and a standard SCE electrode K401 all from Radiometer, Copenhagen.

Titration were carried out in a water-jacketed glass vessel of 100 cm^3 volume, closed with a Teflon bung containing the electrodes, argon inlet, thermometer, propeller stirrer and capillary tip from microburette.

During titration a stream of argon was bubbled through the solution. Before entering the titration vessel the argon was passed through pure ionic medium. The burettes were home made syringe microburettes of 1250 and $2500 \mu\text{l}$ capacity with 25.00 mm micrometer screw. The polyethylene capillary tip of the microburette was immersed in solution when adding reagent.

The microburettes were calibrated by weighing water on a Sartorius 1712 MP8 balance with

*Part XV. *Talanta*, 1993, **40**, 279.

a precision of $\pm 0.015\%$ over the volume range covered. Titrant was added with a precision of $\pm 0.1 \mu\text{l}$.

The Stockholm school convention was used for defining pH in terms of hydrogen ion concentration in the medium used, *i.e.*

$$E = E^0 + s \log h$$

$$s = \text{slope (59.16 mV/mol at 298 K)} \quad (1)$$

$$\text{pH} = -\log h \quad (2(a))$$

$$h = [\text{H}^+] \quad (2(b))$$

In emf-titrations data $\{E, \log h\}$ were collected in absence of ion exchanger. E^0 and s were obtained by applying linear regression to equation (1). This procedure is included in the program EKVBOD¹³ used for estimating E^0 and s .

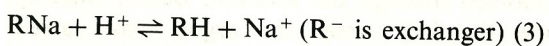
The exchanger was transformed into sodium form by rinsing with 50 cm³ 0.5 mol/dm³ NaOH and washing with 100 cm³ boiled, twice distilled water. After washing the exchanger was separated from solution by centrifuging about 10 min. A quantity of about 1 g exchanger and 25 cm³ 1 mol/dm³ NaClO₄ were transferred to the titration vessel and titrated with 1.00 mol/dm³ HClO₄ and back titrated with 1.00 mol/dm³ NaOH. Each point on the titration curve, $\{v, E\}$ was recorded after equilibrium was established (5–10 min).

TREATMENT OF DATA

Determination of capacity with the Gran method

Gran⁸ devised a method to evaluate the equivalence point of a titration curve by using a linear extrapolation. This method can be adapted for determination of the capacity of an ion exchanger sample. Two cases will be discussed: titration with strong acid and titration with strong base.

(1) *Titration with strong acid.* Consider the reaction



Before:

$m_0 s_0$	cv	0	Iv_0	(millimoles)
-----------	------	---	--------	--------------

After:

0	cv	$m_0 s_0$	$I(v_0 + v_e)$	(millimoles)
	$-m_0 s_0$			

It is assumed that m_0 g ion exchanger with

capacity s_0 milliequivalents/g in v_0 cm³/mol/dm³ NaX ($X = \text{ClO}_4^-, \text{Cl}^-, \text{Br}^-, \text{etc.}$) is titrated with I mol/dm³ HX. In the table above, the points beyond the equivalence point are considered and v_e is the number of millimoles of acid at the equivalence point. In the range considered the expression for the hydrogen ion concentration, h , becomes

$$h = \frac{cv - m_0 s_0}{v_0 + v}$$

If the proton activity, $\{\text{H}^+\}$, is measured and calibrated by standard buffers, the relation becomes

$$h = \frac{\{\text{H}^+\}}{y_{\text{H}^+}} = \frac{10^{-\text{pH}}}{y_{\text{H}^+}} = \frac{cv - m_0 s_0}{v_0 + v}$$

and following variables are introduced:

$$Y = (v_0 + v) \frac{10^{-\text{pH}}}{m_0} = \frac{cv y_{\text{H}^+}}{m_0} - s_0 y_{\text{H}^+}$$

or

$$Y = x y_{\text{H}^+} - s_0 y_{\text{H}^+} \quad (4a)$$

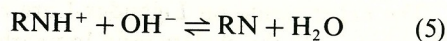
with

$$x = \frac{cv}{m_0} \quad (4b)$$

If a constant ionic medium is used the glass electrode can be calibrated in terms of h and $y_{\text{H}^+} = 1$ in equation (4a). If the electrode is calibrated in terms of proton activity in a constant ionic medium, y_{H^+} is constant and equation (4a) can be treated by linear regression to give s_0 .

If the experiment is carried out as a titration m_0 is constant and can be left out in equation (4a). In batch experiments m_0 must be given for each experimental point.

2. *Titration with strong base.* Consider the reaction



Before: $m_0 s_0$ cv 0 —
(millimoles)

After: 0 $cv - m_0 s_0$ $m_0 s_0$ —
(millimoles)

The notation is the same as for titration with acid. In the range of excess base the expression for $[\text{OH}^-]$ becomes

$$[\text{OH}^-] = \frac{cv - m_0 s_0}{v_0 + v}$$

and

$$[\text{OH}^-] = \frac{\{\text{OH}^-\}}{y_{\text{OH}^-}} = \frac{10^{\text{pH} - \text{p}K_w}}{y_{\text{OH}^-}} = \frac{cv - m_0 s_0}{v_0 + v}$$

where K_w is the ionic product of water and y_{OH^-} is a constant relating hydroxide ion concentration to pOH . This expression is linearized by

$$Y = (v_0 + v) \frac{10^{\text{pH} - \text{p}K_w}}{m_0} = x y_{\text{OH}^-} - s_0 y_{\text{OH}^-} \quad (6)$$

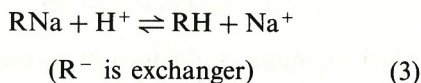
with x defined by equation (4b). If a constant ionic medium is used and pH calibrated in terms of activity y_{OH^-} is constant and s_0 estimated by applying linear regression to equation (6). If the system is calibrated in terms of hydroxyl ion concentration y_{OH^-} is 1 if constant ion medium is used. For m_0 the same remarks apply as for titration with strong acid.

Titration with strong base in presence of excess acid gives

$$Y = (v_0 + v) 10^{-\text{pH}} = c y_{\text{H}^+} (v_e - v) - s_0 y_{\text{H}^+}$$

Determination of α

1. Titration with acid. Return to the reaction



Before: $m_0 s_0 \quad cv \quad 0 \quad Iv_0$
(millimoles)

After: $m_0 s_0 - cv + n_{\text{H}^+} \quad 0 \quad cv - n_{\text{H}^+} \quad Iv_0 + cv - n_{\text{H}^+}$
+
(millimoles)

Here the range beyond the end-point is considered $0 \leq v \leq v_e$. The mass balance condition for protons becomes

$$cv + n_{\text{RH}} + n_{\text{H}^+} \quad (\text{millimoles})$$

n_{H^+} is the number of millimoles of acid in the aqueous phase at equilibrium. At high pH -values this amount is negligible and the expression above reduces to

$$cv = n_{\text{RH}}$$

As independent variable, the fraction of sodium ions RNa in the exchanger, \bar{x}_{RNa} , is given by

$$\bar{x}_{\text{RNa}} = \frac{m_0 s_0 - cv + n_{\text{H}^+}}{m_0 s_0} \quad (7)$$

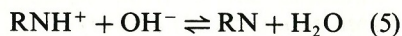
and the fraction of protons in the exchanger, \bar{x}_{H} , is then given by

$$\bar{x}_{\text{H}} = 1 - \bar{x}_{\text{RNa}} = \frac{cv - n_{\text{H}^+}}{m_0 s_0} \quad (8)$$

For simplicity we denote

$$\bar{x}_{\text{Na}} = \alpha \quad (9)$$

2. Titration with base. Return to the reaction



Before: $m_0 s_0 \quad cv \quad 0 \quad -$
(millimoles)

After: $m_0 s_0 - cv + n_{\text{OH}^-} \quad 0 \quad cv - n_{\text{OH}^-} \quad -$
(millimoles)

Again the $0 \leq v \leq v_e$ is considered.

The mass balance condition for hydroxyl ions becomes

$$cv = n_{\text{RN}} + n_{\text{OH}^-} \quad (\text{millimoles})$$

n_{OH^-} is number of millimoles of OH^- present in the aqueous phase at equilibrium. At low pH -values this amount is negligible and the expression above simplifies to

$$cv = n_{\text{RN}}$$

In the literature the quantity α is often defined as

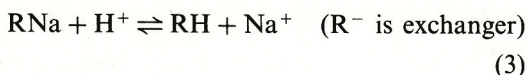
$$\alpha = \frac{cv}{m_0 s_0}$$

i.e. the number of millimoles of base added per milliequivalent of exchanger. However, as above the quantity α will be defined as

$$\alpha = \bar{x}_{\text{RN}} = \frac{cv - n_{\text{OH}^-}}{m_0 s_0} \quad (10)$$

Determination of the equilibrium quotient

1. Titration with acid. Application of the law of mass action to the reaction



gives

$$\kappa_1 = \frac{[\text{RH}][\text{Na}^+]}{[\text{RNa}][\text{H}^+]} \quad (11)$$

Since the ionic strength is assumed to be kept constant by an ionic medium the activity coefficient ratio in the aqueous phase can also be assumed to be constant and included in κ_1 .

By taking the logarithm of equation (11) and rearranging we get

$$\log \kappa_1 = \log \frac{1 - \alpha}{\alpha} + \text{pH} + \log[\text{Na}^+] \quad (12)$$

It is assumed that $\text{pH} = -\log h$, i.e. the Stockholm school convention applied. In the experiments pH is measured and α obtained

from the mass balance condition because n_{H^+} is obtained from

$$n_{H^+} = (v_0 + v)10^{-pH}$$

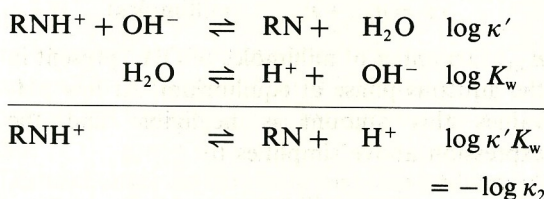
From equations (8) and (9)

$$1 - \alpha = \frac{cv - n_{H^+}}{m_0 s_0}$$

$[Na^+]$ can be computed from

$$[Na^+] = \frac{Iv_0 + cv - n_{H^+}}{v_0 + v}$$

2. *Titration with base.* By combining the two reactions



In order to obtain an expression similar to that for titration with acid the formation of RNH^+ is considered giving

$$\log \kappa_2 = \log \frac{1 - \alpha}{\alpha} + pH \quad (13)$$

α is obtained from equation (10) and n_{OH^-} from

$$n_{OH^-} = (v_0 + v)10^{pH - pK_w} \quad (14)$$

As above the Stockholm school convention is used. K_w is the ionic product of water in the ionic medium used.

Other examples can be constructed for the cases at hand. The two examples given suffice to illustrate the method of obtaining α and κ in media where activity coefficients are kept constant.

Nonideality of the exchanger phase

It is a well-known fact that the equilibrium quotient κ varies with composition for most ion exchange reactions. This can be taken care of by computing the activity coefficients of the two ionic forms. This, however, is rather tedious. A much simpler way is offered by the three-parameter model mentioned in the Introduction.

According to the model a binary mixture of components A and B is considered to be divided into three parts: one corresponding to pure A only, one to B and one containing both A and B. The amount of each part is proportional to the number of A-A pairs, B-B and A-B (or B-A) pairs. If component A is surrounded by A only, any molar property has the same property

as in pure A. This quantity is denoted y_A . Similarly for component B, y_B refers to B surrounded by B only. When surrounded by both A and B the property has the value y_m . Assuming a random distribution of such pairs, the Guggenheim zeroth approximation⁹ yields for any molar property Y

$$Y = y_A x_A^2 + y_B x_B^2 + 2y_m x_A x_B \quad (15)$$

x_A , x_B are stoichiometric mole fractions of A and B; y_A , y_B are the quantities Y in pure A and B, while y_m refers to the mixture. In ion exchange, x_A , x_B are replaced by \bar{x}_A , \bar{x}_B , the equivalent fractions of the two ionic forms in the exchanger.

In ion exchange work data are most often recorded as function of \bar{x} , not of \bar{x}^2 . In that case it is convenient to introduce the equation

$$Y = y_A \bar{x}_A + y_B \bar{x}_B + \bar{B} \bar{x}_A \bar{x}_B \quad (16)$$

By linear regression the parameters y_A , y_B and the empirical constant \bar{B} are estimated. Then the third parameter y_m is now obtained from

$$y_m = \frac{1}{2}(y_A + y_B + \bar{B}) \quad (17)$$

which equation is obtained by setting equation (15) equal to (16) and using the fact that $x_A + x_B = 1$. In this present paper the model is applied to batch data on Ligandex-I by Szabadka⁷ and titration data on a commercial chelate salicylate exchanger. The logarithm of κ is related to the free energy of ion-exchange reaction by

$$\Delta G^0 = RT \ln \kappa = -2.303 RT \log \kappa$$

In the following $\log \kappa$ or $\ln \kappa$ is used for fitting ion exchange data to the model. In these cases expressions (16) and (17) take the form

$$\log \kappa = \log \kappa(1)\alpha + \log \kappa(0)(1 - \alpha) + \bar{B}\alpha(1 - \alpha) \quad (18)$$

The parameter $\log \kappa$ is the limiting value of $\log \kappa$ when $\alpha = 1$. Similarly, $\log \kappa(0)$ is the limiting value of $\log \kappa$ when $\alpha = 0$. These parameters are not directly available experimentally. Equation (18) is fitted by the least-squares methods, given the parameters $\log \kappa(0)$ and $\log \kappa(1)$ together with the empirical constant \bar{B} . Then the third parameter, $\log \kappa_m$, is obtained from (19).

$$\log \kappa_m = \frac{1}{2}[\log \kappa(1) + \log \kappa(0) + \bar{B}] \quad (19)$$

The integral free energy of ion-exchange reac-

tion given as a thermodynamic equilibrium constant K , can be obtained from

$$\log K = \int_0^1 \log \kappa(\alpha) d\alpha \\ = \frac{1}{3}[\log \kappa(0) + \log \kappa(1) + \log \kappa_m] \quad (20)$$

Observe that, for a straight line, $\bar{B} = 0$, equations (19) and (20) give

$$\log \kappa_m = \log K = \frac{1}{2}[\log \kappa(0) + \log \kappa(1)] \quad (21)$$

COMPUTATION

Thermodynamic parameters: $\log \kappa(0)$, $\log \kappa(1)$ and the constant \bar{B} can be estimated by regression analysis (18) using the program IONEX with regression procedure MINOPT from package CHEMSTAT¹⁰ (for details *cf.* previous contribution of this series in Refs 11–12) in combination with the standardization program EKVOD¹³ for determination of E^0 and s .

The data treatment is performed as follows.

- (1) Reading titration data: $\{v \text{ (cm}^3\text{)} \text{ and } E \text{ (mV)}\}$ and transformation of data into normalized data $\{v, -\log h\}$.
- (2) Evaluation of the exchanger capacity, s_0 , by applying the Gran method.
- (3) Transformation of original data $\{v, -\log h\}$ into normalized $[\alpha, \log \kappa]$.
- (4) Application of the nonlinear regression

analysis MINOPT on data $[\alpha, \log \kappa]$ to estimate the parameters in (18) followed by regression diagnostics and goodness-of-fit tests of the reliability of the constants estimated.

In the application of the model to experimental data the model that gives the lowest U value and also fulfils some other statistical criteria of regression analysis is selected as the most plausible (goodness-of-fit test).¹² The residual-squares sum U is defined by

$$U = \sum_{i=1}^n w_i (y_{\text{exp},i} - y_{\text{calc},i})^2 = \sum_{i=1}^n \hat{e}_i^2 \quad (21)$$

where n is number of experimental points, \hat{e}_i is the i th residual and for y either κ or pH can be used. The residuals should be randomly distributed about the predicted regression curve. Systematic departures indicate that the model is not adequate and/or some other parametric estimates are not satisfactory. The residual standard deviation $s(\hat{e})$ or the mean of absolute residuals $E(|\hat{e}|)$ should be close to the instrumental error $s_{\text{inst}}(y)$ of the variable y from which the residuals \hat{e}_i are calculated. For a Gaussian distribution the skewness, $g_1(\hat{e})$, should be close to zero while the kurtosis, $g_2(\hat{e})$, representing "peakedness" of the distribution curve, should be close to 3. Regression rabat, D^2 , in percents expresses percentage of data points which

Table 1. Protonation equilibria of Ligandex-I; $T = 298 \text{ K}$, $I = 1.00M \text{ KCl}$; data from Ref. 7; $\log a_G = -0.215$. From the experimental data below the following average $\log K_i$ values by Szabadka are obtained: $\log K_1 = 1.427 \pm 0.044$, $\log K_2 = 3.169 \pm 0.087$, $\log K_3 = 9.166 \pm 0.043$

Experimental data		Estimation of $\log K_i$ using Szabadka procedure				Estimation of $\log K_i$ using the three-parameter model		
α	pH_{exp}	G	pH	$\log K_i$	\hat{e} in pH	$\log \kappa_{\text{exp}}$	pH_{calc}	\hat{e} in pH
Estimation of K_1								
0.234	0.380	2.485	0.991	1.506	0.078	0.895	0.3777	0.0022
0.447	0.660	2.592	1.289	1.381	-0.046	0.752	0.6673	-0.0074
0.599	0.950	2.526	1.568	1.394	-0.034	0.776	0.9443	0.0057
0.876	1.860	1.550	2.266	1.417	-0.011	1.011	1.8628	-0.0028
0.889	1.950	1.506	2.343	1.440	0.012	1.046	1.9359	0.0141
0.903	2.010	1.460	2.391	1.422	-0.006	1.041	2.0219	-0.0119
Estimation of K_2								
0.204	2.970	1.444	2.595	3.186	0.017	3.561	2.9572	0.0128
0.277	3.120	1.460	2.740	3.157	-0.012	3.537	3.1133	0.0067
0.458	3.400	1.638	2.970	3.043	-0.125	3.473	3.4537	-0.0537
0.582	3.700	1.689	3.257	3.113	-0.055	3.556	3.7035	-0.0035
0.713	4.080	1.760	3.619	3.224	0.055	3.685	4.0208	0.0592
0.933	4.930	1.901	4.436	3.292	0.123	3.786	4.9515	-0.0215
Estimation of K_3								
0.098	8.650	2.032	8.127	9.091	-0.075	9.614	8.6650	-0.0151
0.156	8.940	2.061	8.411	9.144	-0.022	9.673	8.9257	0.0142
0.260	9.260	2.123	8.718	9.172	0.006	9.714	9.2516	0.0083
0.487	9.740	2.230	9.163	9.186	0.033	9.763	9.7566	-0.0166
0.495	9.780	2.294	9.204	9.213	0.047	9.789	9.7723	0.0076
0.937	10.980	2.539	10.360	9.188	0.022	9.808	10.9790	0.0015

Table 2. Goodness-of-fit for pH data of Ligandex-I by the methods of Szabadka and by the Högfeldt's three-parameter model

Parameter estimation	Szabadka procedure			Högfeldt's three-parameter model		
	K_1	K_2	K_3	K_1	K_2	K_3
$\log \kappa(0)$	—	—	—	1.237(35)	3.653(100)	9.573(20)
$\log \kappa(1)$	—	—	—	1.217(13)	3.881(63)	9.797(21)
B	—	—	—	-1.894(112)	-0.928(358)	0.388(92)
$\log \kappa_m$	—	—	—	0.280(59)	3.303(189)	9.879(48)
$\log K_i, i = 1, 2, 3$	1.427(44)	3.169(87)	9.166(43)	0.914(24)	3.612(74)	9.750(19)
Goodness-of-fit test	Residuals in pH					
Residual-square sum, U	9.66×10^{-3}	3.72×10^{-2}	9.93×10^{-3}	4.42×10^{-4}	7.08×10^{-3}	8.39×10^{-4}
Residual standard deviation, $s(\hat{e})$	0.0439	0.0863	0.0445	0.0121	0.0486	0.0167
Mean of absolute values of residuals, $E(\hat{e})$	0.0312	0.0645	0.0342	0.0074	0.0262	0.0106
Skewness, $g_1(\hat{e})$	0.961	-0.049	-0.836	0.237	0.186	-0.415
Kurtosis, $g_2(\hat{e})$	2.869	2.128	2.473	1.974	2.501	1.519
Regression rabat, D^2 [%]	—	—	—	99.983	99.730	99.975
Akaike information criterion, AIC	—	—	—	-51.096	-34.457	-47.252
Mean error of prediction, MEP	—	—	—	6.41×10^{-4}	1.74×10^{-2}	7.32×10^{-3}

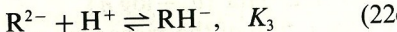
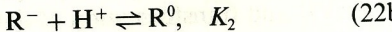
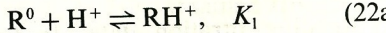
adequately correspond to model fitted. The Akaike information criterion, AIC, serves to distinguish between various models proposed. The best model has the lowest value of AIC. The prediction ability of model proposed can be examined by the mean quadratic error of prediction, MEP. As lower MEP as better prediction ability of a model tested. (For details cf. previous contribution to this series in Refs 11–12.)

RESULTS

The system $H^+ - Na^+$ on Ligandex-I

Szabadka⁷ studied the protonation equilibria of a resin containing iminodiacetic acid groups, which was named Ligandex-I. The resin is protonated in three discrete steps, equations (22a, b, c). At low pH values the resin is an anion exchanger, and at higher pH values it works as a cation exchanger. For each range the water and counter-ion contents in the resin phase were determined, as well as the pH in the

aqueous phase. Szabadka applied ordinary complex chemistry methods to the system. For each step the protonation can be written



These equilibria refer to the resin phase. The pH in the resin phase is related to the pH measured in the aqueous phase by

$\overline{pH} = pH \pm \log G \pm \log a_G \tag{2}$

where, \overline{pH} is pH in the resin phase; G is the concentration of counter-ions in the imbibed water of the resin (mmol/g), and a_G is the activity of counter-ion in the solution. For the quantity the value of $\log a_G = -0.215$ was used corresponding to the mean activity of 1M KCl the ionic medium used. For anion exchange the sign in front of $\log G$ is positive, for cation exchange it is negative. The experimentally

Table 3. Estimation of capacity s_0 of Iontsorb Salycil 100 by Gran method, eqn. (5). Initial volume $v_0 = 26.3 \text{ cm}^{-3}$, $m_0 = 1.0043 \text{ g}$, $c = 0.934 \text{ mol/dm}^3$, $pK_w = 13.90$ at 298 K. Standard deviations of parameters estimated are written in brackets

$v \text{ [cm}^{-3}\text{]}$	pH	$v_0 + v$	x	y
0.81	9.403	27.11	0.7533	0.000683
0.82	9.795	27.12	0.7626	0.001684
0.83	10.002	27.13	0.7719	0.002714
0.84	10.150	27.14	0.7812	0.003817
0.85	10.264	27.15	0.7905	0.004965
0.90	10.607	27.20	0.8370	0.010957
0.95	10.815	27.25	0.8835	0.017722
Intercept			-0.09841(0.000302)	
Slope			0.131072(0.002641)	
Capacity of resin, s_0			0.75081(0.0153)	

Table 4. Search of best model by the least-squares of titration data of Iontsorb Salycil 100 applying three-parameter model

Experimental data		Normalized data		Analysis of residuals for Model I		Analysis of residuals for Model II	
$V[\text{ml}]$	pH_{exp}	α	$\log \kappa_{\text{exp}}$	e in $\log \kappa$	e in pH	e in $\log \kappa$	e in pH
0.660	2.546	0.1608	3.2631	0.0171	0.0176	0.0373	0.0371
0.670	2.623	0.1923	3.2467	-0.0081	-0.0086	0.0055	0.0044
0.680	2.718	0.2238	3.5282	-0.0062	-0.0063	-0.0021	0.0009
0.690	2.811	0.2659	3.2522	-0.0259	-0.0261	-0.0250	-0.0257
0.700	2.933	0.3069	3.2865	-0.0061	-0.0058	-0.0108	-0.0110
0.710	3.066	0.3555	3.3247	0.0134	0.0131	0.0036	0.0029
0.720	3.195	0.4137	3.3462	0.0105	0.0108	-0.0034	-0.0034
0.730	3.347	0.4753	3.3898	0.0259	0.0261	0.0101	0.0100
0.740	3.487	0.5440	3.4106	0.0122	0.0120	-0.0027	-0.0031
0.750	3.631	0.6162	3.4253	-0.0123	-0.0125	-0.0234	-0.0233
0.760	3.796	0.6903	3.4484	-0.0338	-0.0342	-0.0365	-0.0369
0.770	4.037	0.7651	3.5237	-0.0068	-0.0063	0.0022	0.0028
0.780	4.332	0.8423	3.6046	0.0204	0.0202	0.0452	0.0453

terminated quantities α , pH and G have been taken from Table 1 in Ref. 7 and are given in Table 1. The pH was obtained from equation (23), and finally $\log K_i$ was calculated from

$$\log K_i = \overline{\text{pH}} + \log \frac{1 - \alpha}{\alpha} \quad (24)$$

From the data in Table 1, the average $\log K_i$ values have been taken for use in calculating pH from (24) and then the pH from (23).

The data in Table 1 have also been used in regression analysis of program IONEX to compute $\log \kappa$ for each pH region using (12). These data were then fitted to the model (18), (19), (20) and (21), giving parameters in Table 2. and residuals \hat{e} are expressed in $\log \kappa$. Combining (12) (or (13)) and (18) the model $\text{pH} = f(\alpha)$ can also be fitted and residuals \hat{e} are expressed in pH units. In Table 2 the goodness-of-fit in pH

obtained by the two methods, Szabadka and Högfeltdt procedures, is given. The three-parameter model by Högfeltdt procedure gives the best fit, as is to be expected with three parameters instead of one for each region. In spite of that the Szabadka method works surprisingly well.

The system $\text{H}^+ - \text{Na}^+$ on Iontsorb Salycil 100

Iontsorb Salycil 100 is selective chelate resin containing in molecule salycil acid. Concentration of the selective group in chelate resin is 0.4 mmol/g at least and content of water is 66–86%.

The quantity of 1.0043 g Iontsorb Salycil 100, 25.00 ml 1 mol/dm³ sodium perchlorate and 0.800 cm³ 1 mol/dm³ perchloric acid were transferred to the titration vessel and titrated with 0.9340 mol/dm³ sodium hydroxide. Capacity s_0 of chelate resin was calculated using (5)

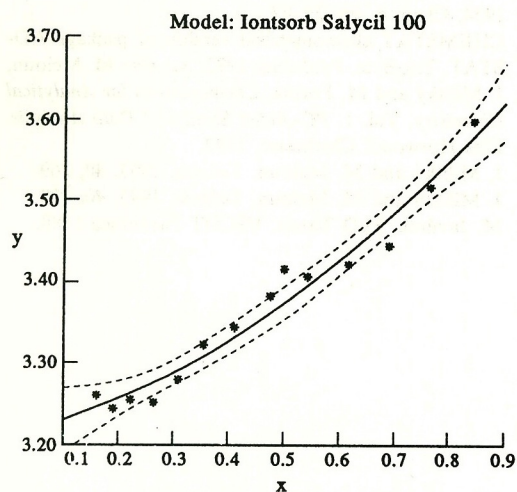


Fig. 1. Multiparametric curve fitting of data $\{\alpha, \kappa\}$ for a dependence $\log \kappa = f(\alpha)$ for Iontsorb Salycil 100.

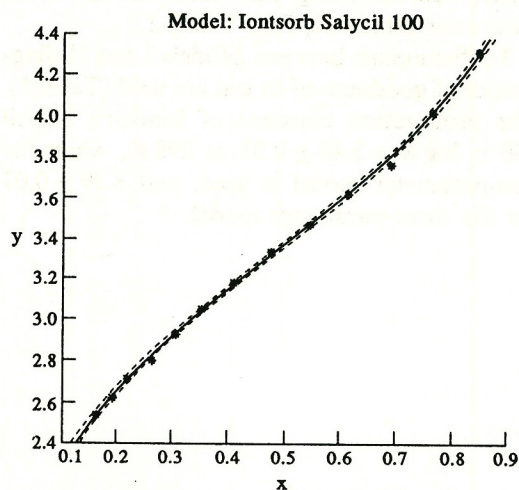


Fig. 2. Multiparametric curve fitting of data $\{\alpha, \text{pH}\}$ for a dependence $\text{pH} = f(\alpha)$ for Iontsorb Salycil 100.

Table 5. Search of best model and parameters estimation by the least-squares of titration data of Iontsorb Salycil 100

Parameter estimation	Model I		Model II	
	\hat{e} in log κ	\hat{e} in pH	\hat{e} in log k	e in pH
log $\kappa(0)$	3.211(29)	3.211(29)	3.637(18)	3.636(18)
log $\kappa(1)$	3.706(33)	3.706(33)	3.147(15)	3.148(15)
\bar{B}	-0.330(138)	-0.331(139)	0	0
log κ_m	3.293(73)	3.293(73)	3.392(71)	3.392(71)
log K	3.404(28)	3.404(28)	3.392(71)	3.392(71)
Diagnostics of goodness-of-fit test	\hat{e} in log κ	\hat{e} in pH	\hat{e} in log κ	e in pH
Residual-square sum, U	3.98×10^{-3}	4.02×10^{-3}	6.24×10^{-3}	6.28×10^{-3}
Residual standard deviation, $s(\hat{e})$	0.0199	0.0200	0.0238	0.0239
Mean of absolute values of residuals, $E(\hat{e})$	0.0153	0.0153	0.0160	0.0159
Skewness, $g_1(\hat{e})$	-0.330	-0.346	0.494	0.463
Kurtosis, $g_2(\hat{e})$	2.103	2.130	2.885	2.882
Regression rabat, D^2 [%]	97.39	99.89	95.93	99.83
Akaike information criterion, AIC	-99.190	-99.047	-95.345	-95.256
Mean error of prediction, MEP	6.34×10^{-4}	6.37×10^{-4}	8.18×10^{-4}	8.22×10^{-4}
Conclusion of diagnostics: Proposed model is	Accepted	Accepted	Rejected	Rejected

and (6), $s_0 = 0.75081$ milliequivalent/g with standard deviation 0.0153 milliequivalent/g (Table 3). The fraction of sodium ions RNa in resin, \bar{x}_{RNa} , denoted here as α was calculated by (7) and (9) while the equilibrium quotient κ by (13) (Table 4). In search for parameters of the best model (18), two models were tested, Model I (with $\bar{B} \neq 0$) and Model II (with $\bar{B} = 0$). For the residual square-sum function U , (21), residuals were formulated in log κ when $\log \kappa = f(\alpha)$ (18) was analyzed or in pH when $\text{pH} = f(\alpha)$ given by

$$\begin{aligned} \text{pH} = & \log \kappa(1)\alpha + \log \kappa(0)(1 - \alpha) \\ & + \bar{B}\alpha(1 - \alpha) + \log \frac{\alpha}{1 - \alpha} \end{aligned}$$

was analyzed. Statistical analysis of residuals shows that both dependencies lead to good quality curve fitting and also to the same parameter estimates, Figs 1 and 2.

To distinguish between Models I and II diagnostics of goodness-of-fit test are used (Table 5). The protonation constant of Iontsorb Salycil 100 is $\log K = 3.40 \pm 0.03$ at 298 K, when the two-parameter model is used, and 3.39 ± 0.07 for the three-parameter model.

CONCLUSION

The great advantage of computer-assisted regression treatment of the three-parameter model is that in data it requires only α calculated in the resin phase and pH measured in the aqueous phase.

REFERENCES

1. E. Högfelt and V. S. Soldatov, *J. Inorg. Nucl. Chem.*, 1979, **41**, 575.
2. E. Högfelt, in *Ion Exchange Technology*, D. Naden and M. Streat (eds). Ellis Horwood, Chichester, 1984, pp. 170–178.
3. E. Högfelt, *Reactive Polymers*, 1984, **2**, 19.
4. E. Högfelt, *Reactive Polymers*, 1989, **11**, 199.
5. E. Högfelt, *Reactive Polymers*, 1987, **7**, 81.
6. E. Högfelt, *J. Phys. Chem.*, 1988, **92**, 6475.
7. Ö. Szabadka, *Talanta*, 1982, **29**, 183.
8. G. Gran, *Analyst (London)*, 1952, **77**, 661.
9. E. A. Guggenheim, *Mixtures*. Clarendon Press, Oxford, 1954, Chap. 4, pp. 29–87.
10. CHEMSTAT chemometrical version of package AD-STAT, TrioByte, Pardubice 1992. See also M. Meloun, J. Militký and M. Forina, *Chemometrics for Analytical Chemistry*, Vol. 1. *PC-Aided Statistical Data Analysis*. Ellis Horwood, Chichester, 1992.
11. J. Militký and M. Meloun, *Talanta*, 1993, **40**, 269.
12. J. Militký and M. Meloun, *Talanta*, 1993, **40**, 279.
13. M. Javůrek, PhD Thesis, VŠCHT Pardubice 1988.