

A Useful Method for Summarizing Data in Ion Exchange. 3. Application to the System $H^+ - Na^+$ on a Carboxylate Resin. Influence of Ionic Strength

Erik Högfeldt^a and Larissa V. Novitskaya^b

^aDepartment of Inorganic Chemistry, the Royal Institute of Technology, S-100 44 Stockholm, Sweden and

^bInstitute of Physico-Organic Chemistry, Academy of Sciences, BSSR, Minsk 220603, The Soviet Union

Högfeldt, E. and Novitskaya, L. V., 1988. A Useful Method for Summarizing Data in Ion Exchange. 3. Application to the System $H^+ - Na^+$ on a Carboxylate Resin. Influence of Ionic Strength. – Acta Chem. Scand., Ser. A 42: 298–300.

Recently the three-parameter model introduced for fitting equilibrium data for strongly acidic (strongly basic) solid and liquid ion exchangers^{1,2} was extended to weakly acidic (basic) and complex-forming resins.³ The present paper deals with the influence of ionic strength on the parameters of this model, and for this purpose the study by Soldatov and Novitskaya on the Soviet weak acid resin KB-4 containing carboxylate groups was chosen.⁴ The measurements were carried out at four ionic strengths ranging from 0.02 to 2.5 mol dm⁻³ in the aqueous phase.

Experimental

Samples were shaken to equilibrium at 295–297 K. After phase separation pH was measured in the aqueous phase, while the resin was titrated

Table 1. Parameters in eqns. (8) and (9) for the system $H^+ - Na^+$ on KB-4 resin calculated from eqns. (11a–c). $T = 296 \pm 1$ K. $\log K$ from eqn. (10) is also given.

$I/\text{mol dm}^{-3}$	$\log x(H)$	$\log x(Na)$	$\log x_m$	$\log K$
0.02	4.52	5.75	5.53	5.27
0.10	4.57	5.75	5.61	5.31
0.50	4.69	5.75	5.77	5.40
2.50	4.97	5.75	6.15	5.62

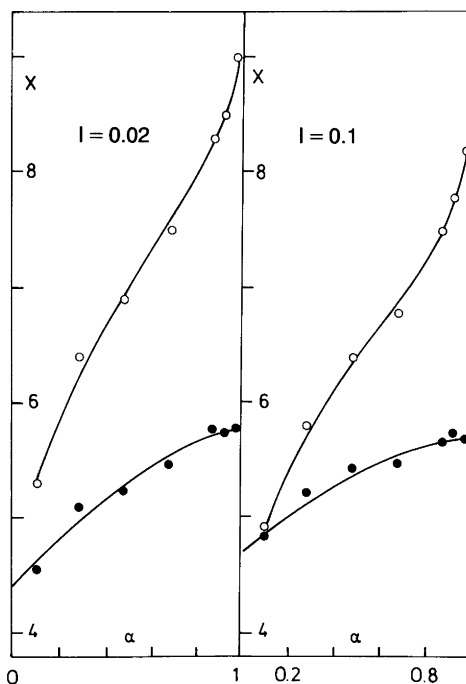


Fig. 1. $\log x$ (●) and pH (○) plotted against α for the two ionic strengths: $I = 0.02$ and $I = 0.10$ mol dm⁻³. The curves have been calculated from the model with the parameters given in Table 1.

with standard alkali to determine the amount of acid in that phase. The pH was measured with a glass electrode calibrated against standard buffers.

The model

The model has been described elsewhere (see Refs. 1-3). According to the model any molar property Y can be expressed by:

$$Y = y_A x_A^2 + y_B x_B^2 + 2y_m x_A x_B \quad (1)$$

where y_A, y_B and y_m are the quantity Y in pure A, in pure B and in the mixture, respectively. x_A, x_B are the equivalent fractions of the two components in the resin.

In ion exchange, data are often plotted against x_A or x_B . It is then useful to introduce the equation:

$$Y = y_A x_A + y_B x_B + \bar{B} x_A x_B \quad (2)$$

in which \bar{B} is an empirical constant. By fitting data $Y = f(x)$ to eqn. (2) by least-squares methods the parameters y_A and y_B as well as the empirical constant \bar{B} are obtained. With a knowledge of these quantities, the parameter y_m is obtained from:

$$y_m = \frac{1}{2}(y_A + y_B + \bar{B}). \quad (3) \quad \text{H}^+ + \text{NaR} \rightleftharpoons \text{HR} + \text{Na}^+ \quad (4)$$

Application to ion exchange equilibria

Consider the reaction:

The equilibrium quotient, κ , for reaction (4) is given by

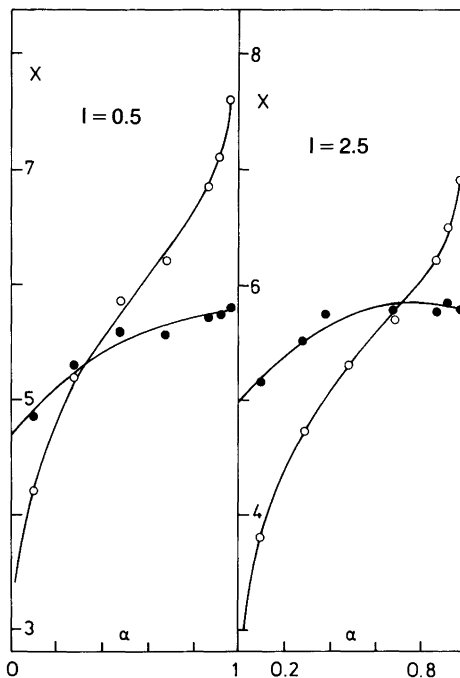


Fig. 2. $\log \kappa$ (●) and pH (○) plotted against α for the two ionic strengths: $I = 0.50$ and $I = 2.50 \text{ mol dm}^{-3}$. The curves have been calculated from the model with the parameters given in Table 1.

Table 2. Comparison between experimental and calculated pH values for the system $\text{H}^+ - \text{Na}^+$ on KB-4 resin at different ionic strengths. $T = 296 \pm 1 \text{ K}$. Data obtained by interpolation of Fig. 1 in Ref. 4.

α	$I = 0.02$		$I = 0.10$		$I = 0.50$		$I = 2.50$	
	pH exp	pH calc	pH exp	pH calc	pH exp	pH calc	pH exp	pH calc
	0.10	5.30	5.46	4.90	4.82	4.20	4.25	3.80
0.28	6.40	6.31	5.80	5.67	5.20	5.10	4.70	4.70
0.48	6.90	6.98	6.40	6.33	5.85	5.74	5.30	5.31
0.68	7.50	7.56	6.80	6.90	6.20	6.28	5.70	5.77
0.87	8.30	8.21	7.50	7.53	6.85	6.87	6.20	6.26
0.92	8.50	8.47	7.80	7.78	7.10	7.11	6.50	6.46
0.97	9.00	8.95	8.20	8.25	7.60	7.56	6.90	6.88
	s(pH) = ± 0.10		s(pH) = ± 0.08		s(pH) = ± 0.07		s(pH) = ± 0.05	

$$\kappa = x_{\text{HR}}[\text{Na}^+]/x_{\text{NaR}}[\text{H}^+]. \quad (5)$$

The ratio between the activity coefficients for the two cations is expected to be kept constant by the ionic medium used and can thus be included in κ . In the following expression:

$$\alpha = n_{\text{OH}^-}/S_0 \approx x_{\text{NaR}} \quad (6)$$

α is the number of millimoles of OH^- added, n_{OH^-} , divided by the capacity of the sample, S_0 , expressed in mequiv. In the pH range covered in the present study α can be set equal to x_{NaR} . From eqn. (5) we obtain:

$$\log \kappa = \log \left(\frac{1-\alpha}{\alpha} \right) + \text{pH} + \log I. \quad (7)$$

From experimental data $\alpha(\text{pH})$, $\log \kappa$ can be obtained from eqn. (7). When these data have been fitted to the model, pH can be calculated from eqn. (7) for chosen α values. In the pH range studied $[\text{Na}^+] = I$.

From eqns. (2) and (3) we then have:

$$\log \kappa = \log \kappa(\text{Na})\alpha + \log \kappa(\text{H})(1-\alpha) + \bar{B}\alpha(1-\alpha) \quad (8)$$

$$\log \kappa_m = \frac{1}{2}[\log \kappa(\text{Na}) + \log \kappa(\text{H}) + \bar{B}]. \quad (9)$$

$\kappa(\text{Na})$ is the limiting value of κ when $\alpha = 1$ and $\kappa(\text{H})$ that for $\alpha = 0$. The integral free energy of reaction (4) given as a thermodynamic equilibrium constant, K , is obtained from:

$$\log K = \int_0^1 \log \kappa d\alpha = \frac{1}{2}[\log \kappa(\text{Na}) + \log \kappa(\text{H}) + \log \kappa_m]. \quad (10)$$

Results

By fitting eqn. (8) to the experimental data by least-squares methods the parameters of the model were obtained for each ionic strength. Each parameter was then studied as a function of $I^{1/2}$. By linear regression the following expressions were obtained:

$$\log \kappa(\text{H}) = 4.47 + 0.31\sqrt{I}$$

$$\log \kappa(\text{Na}) = 5.75 \pm 0.04$$

$$\log \kappa_m = 5.47 + 0.43\sqrt{I}. \quad (11a-c)$$

In Table 1 the parameters from eqns. (11a-c) are given together with $\log K$, calculated from eqn. (10).

In Figs. 1 and 2, $\log \kappa$ and pH are plotted against α for the four ionic strengths studied. The curves were calculated from the model using the parameters in Table 1. In Table 2 experimental and calculated pH values are compared.

The standard deviation in pH, $s(\text{pH})$, is used as a measure of the goodness of fit, and is given in Table 2 for each ionic strength. From Table 2 it is evident that the fit in pH is about ± 0.10 for $I = 0.02$ and decreases to ± 0.05 for $I = 2.5$.

The experimental data in Table 2 were obtained by reading from a graph, with an estimated accuracy of 0.05 and 0.10. This shows that the 5 parameters in eqns. (11a-c) instead of the maximum of 12 give a satisfactory fit both with regard to composition and ionic strength.

Acknowledgements. This work is part of a program supported by the Academies of Sciences in the USSR and Sweden. It is a pleasure to acknowledge the cooperation of Professor Vladimir S. Soldatov in this project and we thank him for useful discussions and comments on the manuscript.

References

1. Högfeldt, E. *Acta Chem. Scand., Ser. A* 33 (1979) 557.
2. Högfeldt, E. and Soldatov, V. S. *J. Inorg. Nucl. Chem.* 41 (1979) 575.
3. Högfeldt, E. *Reac. Polym.* 7 (1988) 81.
4. Soldatov, V. S. and Novitskaya, L. V. *Zh. Fiz. Khim.* 39 (1965) 2720.

Received December 11, 1987.