

Protonation Equilibria on Sephadex C-25

Erik Högfeldt

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

Högfeldt, E., 1988. Protonation Equilibria on Sephadex C-25. – Acta Chem. Scand., Ser. A 42: 304–306.

Recently, Miyajima *et al.*¹ studied the neutralization of Sephadex gels at two ionic strengths at 298 K in order to apply an approach described by Marinsky for treating ion binding in polyelectrolyte gels.^{2–4}

These data can also be used to test a recently developed three-parameter approach for treating thermodynamic and other molar properties of liquid and solid ion exchangers.^{5,6}

This note reports the application of this approach to Sephadex C-25 at an ionic strength of $I = 0.100 \text{ mol dm}^{-3}$ (Na)ClO₄ at 298 K. A treatment comprising also Sephadex C-50 and $I = 0.01$ is published elsewhere.⁷

According to the model, a mixture of A and B is divided into three regions: one corresponding to A only, one corresponding to B only and one with both A and B. The amounts of these regions are given by the number of A-A, B-B and A-B pairs in the mixture. Assuming random distribution of the pairs,⁸ Guggenheim's zero'th approximation yields for the property Y :

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

where y_A, y_B and y_m are the quantity Y in pure A, pure B and the mixture, and x_A, x_B are the stoichiometric mole fractions of A and B in the mixture. When applying eqn. (1) to ion exchange, x_A, x_B are changed to \bar{x}_A, \bar{x}_B , the equivalent fractions of the two ionic forms in the exchanger phase. In ion exchange, data are often plotted against \bar{x}_A or \bar{x}_B . It is then useful to introduce the equation

$$Y = y_A \bar{x}_A + y_B \bar{x}_B + \bar{B} \bar{x}_A \bar{x}_B \quad (2)$$

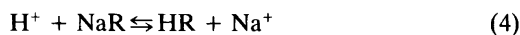
where \bar{B} is an empirical constant. By fitting data $Y(\bar{x})$ by least-squares methods, the parameters y_A and y_B as well as the empirical constant \bar{B} are obtained. With knowledge of these quantities, the parameter y_m is obtained from

$$y_m = \frac{1}{2}(y_A + y_B + \bar{B}) \quad (3)$$

which is derived by setting eqn. (1) equal to eqn. (2) using equivalent fractions in both expressions.

Both differential and integral thermodynamic quantities can be treated by the model.

This note describes application of the model to the ion exchange reaction:



The equilibrium quotient, κ , of reaction (4) is defined by

$$\kappa = \frac{[\text{HR}][\text{Na}^+]}{[\text{NaR}][\text{H}^+]} = \frac{(1-\alpha)[\text{Na}^+]}{\alpha[\text{H}^+]} \quad (5)$$

where α is the fraction of sodium ions

$$\text{in the resin, i.e. } \alpha = \frac{[\text{NaR}]}{[\text{NaR}] + [\text{HR}]} \quad (6)$$

The concentration of sodium ions in the solution is obtained from

$$[\text{Na}^+] = I - 10^{-\text{pH}_c} \quad (7)$$

where $\text{pH}_c = -\log[\text{H}^+]$ i.e. involving the hydrogen ion concentration in the ionic medium used. I is the ionic strength. It is assumed that the activ-

ity coefficient ratio for the two cations in the aqueous phase is kept constant by the ionic medium.

According to the model,

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

$\kappa(\text{Na})$ is the limiting value of κ when $\alpha = 1$, and $\kappa(\text{H})$ is that for $\alpha = 0$.

From eqn. (3) we obtain:

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

Moreover, the integral free energy of reaction (4), expressed as a thermodynamic equilibrium constant, K , is obtained from

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

In Fig. 1, $\log \kappa$ is plotted against α for Sephadex C-25 at 298.2 K and with an ionic strength in the aqueous phase of $I = 0.100 \text{ mol dm}^{-3}$. The curve has been computed from

$$\log \kappa = 3.376\alpha + 2.780(1-\alpha) + 0.090\alpha(1-\alpha) \quad (11)$$

with:

$$\log \kappa(\text{Na}) = 3.376 \log \kappa(\text{H}) = 2.780$$

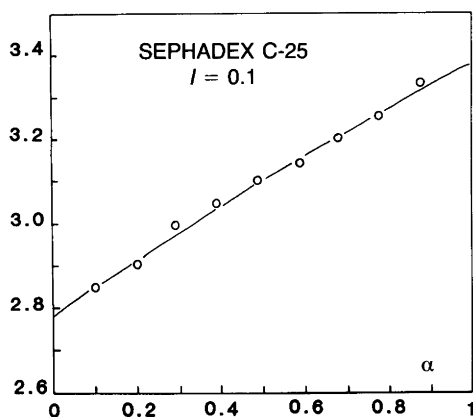


Fig. 1. $\log \kappa$ plotted against α for Sephadex C-25 at 298.2 K and $I = 0.100 \text{ M}$ $(\text{Na})\text{ClO}_4$. The curve is that of eqn. (11).

Table 1. Comparison of experimental and calculated^a pH_c values for the system $\text{H}^+ - \text{Na}^+$ on Sephadex C-25. $T = 298.2 \text{ K}$. $I = 0.100 \text{ mol dm}^{-3}$ $(\text{Na})\text{ClO}_4$.

α	pH_c exp.	pH_c calc.
0.10	2.895	2.899
0.20	3.299	3.314
0.29	3.605	3.583
0.39	3.850	3.840
0.49	4.081	4.078
0.59	4.296	4.311
0.68	4.526	4.532
0.78	4.800	4.810
0.88	5.192	5.179

^aStandard deviation: ± 0.013

$$\log \kappa_m = 3.123 \log K = 3.093$$

obtained by a least-squares fit of eqn. (8) to the data.

In Table 1, experimental and calculated pH_c values are compared. For a chosen α value, $\log \kappa$ is obtained from eqn. (11). pH_c is then calculated from

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

obtained by taking the logarithm of eqn. (5).

From Table 1 it is seen that an excellent fit is obtained, with a standard deviation in pH_c of ± 0.013 . This result shows the advantage of using the Stockholm school definition of pH as the negative logarithm of the hydrogen ion concentration in the ionic medium used, as adopted by oceanographers for the definition of pH in seawater.⁹ That the three-parameter model fits the experimental data so well is a strong argument in its favour.

Acknowledgement. The experimental part of this work received support from the Swedish Natural Science Research Council (NFR).

References

- Miyajima, T., Marinsky, J. A. and Muhammed, M. *To be published.*
- Marinsky, J. A. In: Marinsky, J. A. and Marcus, Y.,

SHORT COMMUNICATION

- Eds., *Ion Exchange and Solvent Extraction*, Dekker, New York 1973, Vol. 4, Chap. 5, pp. 227–243.
3. Slota, P. and Marinsky, J. A. In: *Advances in Chemistry Series, No. 187*, American Chemical Society, Washington D.C. 1980, pp. 311–325.
 4. Marinsky, J. A., Lin, Fu G. and Chung, K. J. *Phys. Chem.* 87 (1983) 3139.
 5. Högfeldt, E. *React. Polym.* 2 (1984) 19.
 6. Högfeldt, E. In: Naden, D. and Streat, M., Eds., *Ion Exchange and Solvent Extraction*, Ellis Horwood, Chichester 1984, pp. 170–178.
 7. Högfeldt, E., Miyajima, T. and Muhammed, M. *To be published*.
 8. Guggenheim, E. A. *Mixtures*, Clarendon Press, Oxford 1952, Chap. 4.
 9. *Convention for Seawater Equilibria*, Group Report, Dahlem Workshop on the Nature of Seawater, Berlin 1975.

Received February 29, 1988.