

Application of a Simple Three-Parameter Model to Titration Data for Some Linear Polyelectrolytes

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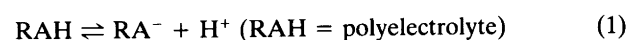
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In recent years a simple three-parameter model has proved useful in summarizing both thermodynamic and water uptake data for liquid and solid ion exchangers, both organic and inorganic.¹⁻⁵ In the present paper the model is applied to linear polyelectrolytes, i.e. one-phase systems. The data selected are α , pH values from titrations on linear carboxymethyl-dextran, C_mD_x , by Miyajima, and similar data for linear polyacrylic acid by Nagasawa *et al.*⁶

Application of the model to cross linked carboxymethyl-dextran (Sephadex C-25 and C-50) has been published elsewhere.⁷

The model

Consider the reaction



The law of mass action gives for reaction (1)

$$pK_a = pH + \log \left(\frac{1-\alpha}{\alpha} \right) \quad (2)$$

where

$$\alpha = \frac{[RA^-]}{[RAH] + [RA^-]} \quad (3)$$

Application of the three-parameter model gives

$$pK_a = pK_a(1)\alpha^2 + pK_a(0)(1-\alpha)^2 + 2 pK_{am}\alpha(1-\alpha) \quad (4)$$

It is convenient to use the equation

$$pK_a = pK_a(1)\alpha + pK_a(0)(1-\alpha) + B\alpha(1-\alpha) \quad (5)$$

The experimental data can be fitted to eqn. (5) by least-squares methods. The third parameter pK_{am} is then obtained from

$$pK_{am} = \frac{1}{2}[pK_a(0) + pK_a(1) + B] \quad (6)$$

$pK_a(0)$ and $pK_a(1)$ are the limiting values of pK_a for $\alpha = 0$ and $\alpha = 1$.

The integral free energy of reaction (1) expressed as a thermodynamic equilibrium constant $p\bar{K}_a$ is obtained from

$$p\bar{K}_a = \int_0^1 pK(\alpha) d\alpha = \frac{1}{3}[pK_a(0) + pK_a(1) + pK_{am}] \quad (7)$$

Experimental

The titrations were carried out as emf titrations of C_mD_x of two different degrees of substitution, DS . This quantity is related to the distance between the carboxylate groups, i.e. the charge density.

The ionic strength was kept at 0.100 M (Na)Cl and the temperature at 298 ± 1 K. The concentration of C_mD_x was 1.00 mM.

For defining pH, Miyajima used the Stockholm school definition with $pH = -\log[H^+]$ and the glass electrode calibrated in terms of hydrogen ion concentration in the ionic medium used.

Nagasawa *et al.* defined $pH = -\log\{H^+\}$ using standard buffers. Their work was carried out at 288 ± 2 K and with ionic strengths ranging from 0.005 to 0.100 M (NaCl). The concentration of polyacrylic acid varied between 0.00829 M and 0.0419 M. α , pH data were read from Fig. 4 in Ref. 6.

Results

Carboxymethyl-dextran. In Table 1 experimental and computed pK_a values are compared. Some statistical quantities are also given in order to give an idea of the fit obtained.

In Fig. 1, pK_a is plotted against α for the two degrees of substitution. The parameters obtained by least-squares fit-

Table 1. Comparison between experimental and calculated pK_a values for linear carboxymethyldextran. $T = 298 \pm 1$ K, $I = 0.100$ M (Na)ClO₄.

α	pK_a exp	pK_a calc	Some statistical quantities	
DS = 0.96				
0.20	3.478	3.483	Residual squares sum	= $1.738 \cdot 10^{-3}$
0.30	3.563	3.562	Mean residual	= 0.0110
0.40	3.645	3.634	Standard deviation	= 0.0186
0.50	3.714	3.701	Hamilton R factor/%	= 0.396
0.60	3.727	3.762		
0.70	3.825	3.816		
0.80	3.874	3.864		
0.90	3.903	3.907		
DS = 1.26				
0.10	3.430	3.445	Residual squares sum	= $6.880 \cdot 10^{-4}$
0.20	3.572	3.558	Mean residual	= 0.0078
0.30	3.668	3.660	Standard deviation	= 0.0107
0.40	3.753	3.749	Hamilton R factor/%	= 0.231
0.50	3.820	3.827		
0.60	3.884	3.892		
0.70	3.943	3.946		
0.80	3.984	3.988		
0.90	4.025	4.018		

ting to eqn. (5) and use of eqns. (6) and (7) to obtain pK_{am} and \overline{pK}_a are given in Table 3. From Table 1 it is evident that a satisfactory fit has been obtained.

Polyacrylic acid. First, data for each ionic strength were fitted individually according to the model. Each parameter was fitted by the expression

$$pK_a = a + bI^{1/2} + cI$$

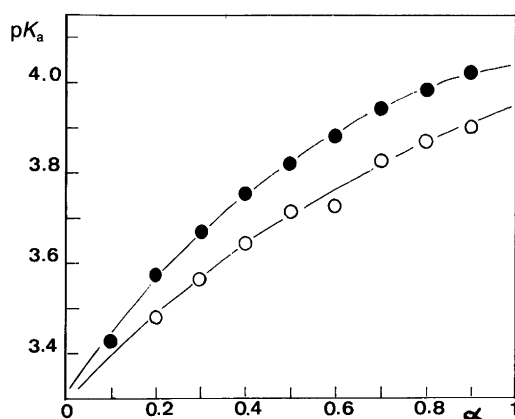


Fig. 1. pK_a vs. α for carboxymethyldextran. \circ : $DS = 0.96$. \bullet : $DS = 1.26$. The curves were calculated from the model with the parameters given in Table 3.

giving

$$pK_a(0) = 5.1466 - 4.4692I^{1/2} + 7.1480I$$

$$pK_a(1) = 7.9302 - 8.8565I^{1/2} + 12.3311I$$

$$pK_{am} = 7.2171 - 9.4919I^{1/2} + 12.0023I \quad (8a-c)$$

In this way 15 parameters were reduced to 9. In Table 2, experimental and computed pK_a values are compared. As seen, a rather satisfactory fit is obtained. The parameters obtained from eqns (8a-c) are given in Table 3, together with \overline{pK}_a from eqn. (7).

Concluding remarks

The fit obtained shows that the three-parameter model applies also to non-crosslinked polymers. The model has been found to apply to liquid cation exchangers,⁸⁻¹¹ solid cation resins,¹⁻⁴ anion resins,¹² and inorganic cation and anion exchangers.^{5,13}

That one and the same model can be applied to such a wide variety of substances implies that the variation in excess free energy is a site effect dependent mainly upon nearest-neighbour interactions as indicated by the model. The model provides a good way of summarizing data as well as predicting titrations, and is a useful alternative to more sophisticated models.¹⁴⁻¹⁶

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Table 2. Comparison between experimental and calculated pK_a values for polyacrylic acid. $T = 288 \pm 2$ K. Data from Ref. 6.

α	pK_a exp	pK_a calc	Some statistical criteria	
<i>I</i> = 0.005 M (Na)Cl				
0.1	5.18	5.204	Residual squares sum	= $1.0281 \cdot 10^{-2}$
0.2	5.56	5.523	Mean residual	= 0.0294
0.3	5.87	5.822	Standard deviation	= 0.0414
0.4	6.12	6.101	Hamilton <i>R</i> factor/%	= 0.534
0.5	6.35	6.361		
0.6	6.59	6.601		
0.7	6.76	6.822		
0.8	7.04	7.023		
0.9	7.24	7.204		
<i>I</i> = 0.01 M (Na)Cl				
0.1	5.00	5.086	Residual squares sum	= $1.478 \cdot 10^{-2}$
0.2	5.41	5.384	Mean residual	= 0.0316
0.3	5.72	5.666	Standard deviation	= 0.0496
0.4	5.94	5.931	Hamilton <i>R</i> factor/%	= 0.658
0.5	6.18	6.179		
0.6	6.40	6.410		
0.7	6.58	6.625		
0.8	6.84	6.823		
0.9	7.04	7.004		
<i>I</i> = 0.02 M (Na)Cl				
0.1	4.90	4.943	Residual squares sum	= $1.454 \cdot 10^{-2}$
0.2	5.24	5.215	Mean residual	= 0.0342
0.3	5.53	5.474	Standard deviation	= 0.0492
0.4	5.70	5.720	Hamilton <i>R</i> factor/%	= 0.679
0.5	5.94	5.953		
0.6	6.15	6.173		
0.7	6.31	6.380		
0.8	6.52	6.574		
0.9	6.76	6.756		
<i>I</i> = 0.05 M (Na)Cl				
0.1	4.71	4.740	Residual squares sum	= $1.080 \cdot 10^{-2}$
0.2	5.00	4.968	Mean residual	= 0.0304
0.3	5.24	5.190	Standard deviation	= 0.0424
0.4	5.41	5.406	Hamilton <i>R</i> factor/%	= 0.615
0.5	5.61	5.615		
0.6	5.84	5.818		
0.7	5.97	6.015		
0.8	6.24	6.205		
0.9	6.44	6.389		
<i>I</i> = 0.10 M (Na)Cl				
0.1	4.63	4.641	Residual squares sum	= $5.279 \cdot 10^{-3}$
0.2	4.81	4.834	Mean residual	= 0.0188
0.3	5.06	5.027	Standard deviation	= 0.0297
0.4	5.24	5.219	Hamilton <i>R</i> factor/%	= 0.446
0.5	5.41	5.411		
0.6	5.59	5.602		
0.7	5.74	5.793		
0.8	5.99	5.983		
0.9	6.16	6.173		

Table 3. Parameters obtained by least-squares fitting of experimental data by eqn. (5), and using eqns. (6) and (7).

DS	T/K	l	pK _a (0)	pK _a (1)	pK _{am}	pK _a
0.96	298±1	0.100	3.307	3.943	3.777	3.676
1.26	298±1	0.100	3.320	4.036	3.975	3.777
–	288±2	0.005	4.866	7.366	6.606	6.279
–	288±2	0.01	4.771	7.168	6.388	6.109
–	288±2	0.02	4.658	6.924	6.115	5.899
–	288±2	0.05	4.505	6.566	5.695	5.589
–	288±2	0.10	4.448	6.363	5.416	5.409

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