Short Communication

Application of a Simple Model to Protonation Equilibria of some Weak Acid Resins

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Högfeldt applied a simple three-parameter model to a wide variety of ion exchange equilibria, as illustrated in Refs. 1–3. The model has been found to fit satisfactorily data on weak acid and chelating resins.[4,5] The model takes nonideal behaviour into account in a simple way. With knowledge of the parameters of the model, accurate equilibrium predictions can be made when using the actual resin. Also, temperature and ionic strength dependence can be accommodated by the model.[3] The parameters for different ion exchangers and different experimental conditions are thus of value. The present paper supplies new information on the acrylate resin Wofatit CA-20 and the methacrylate resin Amberlite IRC-50.

Experimental

The resins. Wofatit CA-20 is a macroporous acrylate resin. The degree of crosslinking of the samples used in this study was about 6 % DVB. The capacity is 10.0 meq g^{-1} supplied in the hydrogen form with 40 % humidity. Amberlite IRC-50 is a methacrylate resin. The degree of crosslinking is 5 % DVB. The capacity is 11.1 meq g^{-1} and the samples are supplied with 45 % humidity. The ion-exchanging groups are carboxylate groups in both resins.

Experiments. The batch method was employed. To samples in the hydrogen form containing 1 meq carboxylate groups the required amount of sodium hydroxide was added to ensure the desired fraction of the sodium form in the resin. At the same time 1.00 mol dm^{-3} NaCl autoclaved at either 303 or 343 K was added to make the final volume 100 cm^3. After equilibration for ca. 4 h measurements commenced and continued until no further changes in composition could be observed. Separate tests showed that temperature equilibrium was reached and that the required degree of dissociation, α, was obtained to within a few percent. The glass electrodes were calibrated with standard buffers. The protonation constants are thus mixed constants.

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The model

The experimental data are fitted to eqn. (1) by least-squares procedures using nonlinear regression. From the parameters y_A and y_B and the constant B the third parameter y_m is computed from eqn. (2).

$$Y = y_A x_A + y_B x_B + B x_A x_B \quad (1)$$

$$y_m = 0.5[y_A + y_B + B] \quad (2)$$

Treatment of data

The protonation constant. The protonation reaction can be written as reaction (3), with an equilibrium constant given by eqn. (4).

$$H^+(aq) + R^- \rightleftharpoons RH \quad (3)$$

$$K = \{RH\}/\{R^-\}\{H^+\}_{aq} \quad (4)$$

If concentrations are used in the resin phase, K is replaced by the quantity k. If k is found to vary with composition, the resin behaves nonideally. The use of the model outlined above is thus a simple way to account for this behaviour. In the following k, given by eqn. (5), is fitted to the model. As independent variable the degree of neutralization (α) is used, defined by eqn. (6), and thus $x_B = 1 - \alpha$.

$$k = [RH]/[R^-]\{H^+\} \quad (5)$$

$$\alpha = x_A = [R^-]/([R^-] + [RH]) \quad (6)$$

The boundary value of log k at $\alpha = 0$ is denoted log $k(0)$ and $\alpha = 1$ log k = log $k(1)$. Eqn. (1) can now be written as eqn. (7).

$$\log k = \log k(1)\alpha + \log k(0)(1 - \alpha) + B\alpha(1 - \alpha) \quad (7)$$

Table 1. Parameters of the model obtained by least-squares fitting to eqn. (7). Ionic strength = 1.00 mol dm^{-3} NaCl. System: H^+-Na^+.

Resin	T/K	Constants	log k(0)	log k(1)	log k_m	log K
Wofatit CA-20	303	2	5.34	6.01	5.67	5.67
Wofatit CA-20	303	3	5.30	5.97	5.73	5.67
Wofatit CA-20	343	2	5.96	6.29	6.13	6.13
Wofatit CA-20	343	3	5.87	6.20	6.25	6.11
Amberlite IRC-50	303	2	6.02	6.45	6.24	6.24
Amberlite IRC-50	303	3	5.97	6.41	6.30	6.23
Amberlite IRC-50	343	2	6.36	6.74	6.55	6.55
Amberlite IRC-50	343	3	6.34	6.71	6.58	6.55

By least-squares methods the parameters log $k(1)$ and log $k(0)$ and the constant B are obtained. Then log k_m is computed from eqn. (2). The equilibrium constant K [see eqn. (4)] is computed from eqn. (8). From eqns. (5) and (6) we have eqn. (9).

$$\log K = \int_0^1 \log k(\alpha)\mathrm{d}\alpha = (1/3)[\log k(1) + \log k(0) + \log k_m] \quad (8)$$

$$\mathrm{pH} = \log k - \log [\alpha/(1-\alpha)] \quad (9)$$

Inserting the constants from the least-squares fitting into eqn. (7) gives log k_{calc}, and then this value in eqn. (9) for each α gives pH_{calc}, which can be compared with experimental values.

Results and discussion

The model. In Table 1 parameters of the model are given. In Tables 2 and 3 experimental values of both log k and pH are given, together with those computed from the model. The goodness of fit is illustrated by the fitting to the pH data, i.e. the residual squares sum, U, the standard deviation, s(pH) and the Hamilton R-factor as a percentage, R(%). These quantities are defined by eqns. (10)–(12), where n is the number of experimental points.

Table 2. Comparison between experimental and computed log k and pH values for Wofatit CA-20.

α	Experimental		Computed		
	pH	log k	log k	pH	
T = 303 K, two constants					
0.2	4.88	5.482	5.474	4.872	$U = 7.42\times10^{-3}$
0.4	5.38	5.556	5.608	5.432	
0.5	5.68	5.680	5.675	5.675	s(pH) = ∓0.043
0.6	5.98	5.804	5.742	5.918	
0.8	6.45	5.848	5.876	6.478	R(%) = 0.68
I = 303 K, three constants					
0.2	4.88	5.482	5.463	4.861	$U = 7.16\times10^{-3}$
0.4	5.38	5.556	5.611	5.435	
0.5	5.68	5.680	5.680	5.680	s(pH) = ∓0.042
0.6	5.98	5.804	5.745	5.921	
0.8	6.45	5.848	5.865	6.467	R(%) = 0.66
T = 343 K, two constants					
0.2	5.41	6.012	6.026	5.424	$U = 2.39\times10^{-3}$
0.4	5.91	6.086	6.092	5.916	
0.5	6.16	6.160	6.125	6.125	s(pH) = ∓0.024
0.6	6.35	6.174	6.158	6.334	
0.8	6.80	6.198	6.224	6.826	R(%) = 0.36
T = 343 K, three constants					
0.2	5.41	6.012	6.006	5.404	$U = 7.810\times10^{-4}$
0.4	5.91	6.086	6.108	5.932	
0.5	6.16	6.160	6.145	6.145	s(pH) = ∓0.014
0.6	6.35	6.174	6.174	6.350	
0.8	6.80	6.198	6.204	6.806	R(%) = 0.20

Table 3. Comparison between experimental and computed values for Amberlite IRC-50.

α	Experimental		Computed		
	pH	log k	log k	pH	
T = 303 K, two constants					
0.2	5.50	6.102	6.106	5.504	$U = 1.43\times10^{-3}$
0.4	6.00	6.176	6.192	6.016	
0.5	6.25	6.250	6.235	6.235	s(pH) = ∓0.019
0.6	6.48	6.304	6.278	6.454	
0.8	6.95	6.348	6.364	6.966	R(%) = 0.27
T = 303 K, three constants					
0.2	5.50	6.102	6.095	5.493	$U = 1.02\times10^{-3}$
0.4	6.00	6.176	6.201	6.025	
0.5	6.25	6.250	6.248	6.248	s(pH) = ∓0.016
0.6	6.48	6.304	6.289	6.465	
0.8	6.95	6.348	6.359	6.961	R(%) = 0.23
T = 343 K, two constants					
0.2	5.84	6.442	6.436	5.834	$U = 1.74\times10^{-3}$
0.4	6.31	6.486	6.512	6.336	
0.5	6.56	6.560	6.550	6.550	s(pH) = ∓0.021
0.6	6.79	6.614	6.588	6.764	
0.8	7.25	6.648	7.664	6.266	R(%) = 0.28
T = 343 K, three constants					
0.2	5.84	6.442	6.432	5.830	$U = 1.65\times10^{-3}$
0.4	6.31	6.486	6.514	6.338	
0.5	6.56	6.560	6.553	6.553	s(pH) = ∓0.020
0.6	6.79	6.614	6.588	6.764	
0.8	7.25	6.648	6.654	7.256	R(%) = 0.28

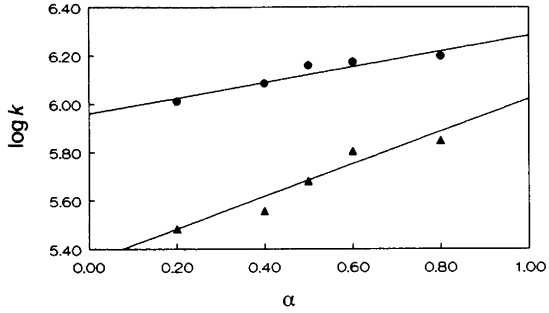

Fig. 1. log k plotted versus α for Wofatit CA-20: (▲) 303 and (●) 343 K. The straight lines have been computed with the parameters given in Table 1.

$$U = \Sigma(\mathrm{pHe}_{xp} - \mathrm{pH}_{calc})^2 \quad (10)$$

$$s(\log k) = \mp [U/(n-k)]^{1/2} \quad (11)$$

$$R(\%) = 100\,[\Sigma(\mathrm{pH}_{exp} - \mathrm{pH}_{calc})^2/(\Sigma \mathrm{pH}_{exp}{}^2)]^{1/2} \quad (12)$$

From Tables 2 and 3 it is evident that straight lines give a satisfactory fit to the experimental data. This is also illustrated in Figs. 1 and 2, where log k is plotted versus α for the two resins and temperatures.

Comparison with the literature. The values for log K found in this paper for the IRC-50 are not directly comparable with those found[3] from the data of Chatterjee and Marinsky,[6] because the latter were obtained at 298 K and low ionic strengths. In Ref. 6 the authors compare the acidity constants for resins with that of the uncrosslinked monomer. It has also been suggested that the intrinsic protonation constant, log K_{int}, should be equal to log $k(0)$, because at α = 0 the Donnan potential is zero. The idea was recently used by Miyajima *et al.*,[7] who used the three-parameter model to estimate log K_{int} rather than using uncertain extrapolations.

Since the present data were obtained at $I = 1.00$ no extrapolation to zero ionic strength is possible, and thus a direct comparison can not be made. However, rough estimates can be made by neglecting ionic strength. From Table 1

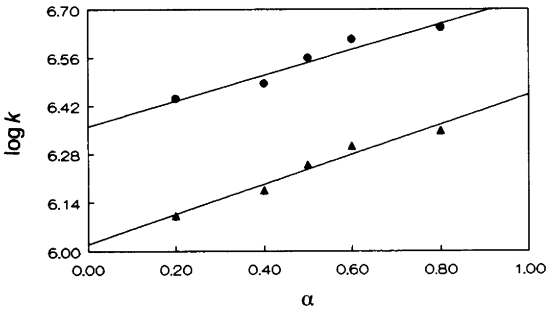

Fig. 2. log k plotted versus α for Amberlite IRC-50: (▲) 303 and (●) 343 K. The straight lines have been computed with the parameters given in Table 1.

Table 4. Estimated free energies of proton transfer at $I = 1.00$.

Resin	T/K	log K	log $k(0)$	log k_H	ΔG_H/kJ
Wofatit CA-20	303	5.67	5.34	0.33	−1.9
Wofatit CA-20	343	6.13	5.96	0.17	−1.1
Amberlite IRC-50	303	6.24	6.02	0.22	−1.3
Amberlite IRC-50	343	6.55	6.36	0.19	−1.3

values for log K_{int} of around 6 are found, with the exception Wofatit CA-20 at 303 K. Chatterjee and Marinsky obtained values ≪5 and a value near 4.9 for the monomer.[6] On the other hand the data obtained by Högfeldt *et al.*[4] at around 396 K were recently used to estimate the intrinsic protonation constant at $I = 0$,[8] giving log $K_{int} = 6.03$, in agreement with the estimates at $I = 1$ in this paper.

Enthalpy of reaction (3). Using the van't Hoff equation (log K vs. $1/T$) the following estimates of ΔH of reaction (3) are found: 22.9 kJ mol^{-1} for Wofatit CA-20 and 15.4 kJ mol^{-1} for Amberlite IRC-50. These values are of the same sign and order of magnitude as ordinary carboxylic acids.

The free energy of proton transfer. From the equilibrium constant defined by eqn. (8) and log $k(0)$ identified as the intrinsic protonation constant an estimate of the equilibrium constant of reaction (13) can be obtained as log k_H = log K − log $k(0)$. In Table 4 these log k_H-values are given

$$H^+_{aq} \rightleftharpoons H^+_{resin} \quad (13)$$

together with the free energy of proton transfer, ΔG_H, computed from them. The values for ΔG are around −1 kJ eq^{-1}.

Concluding remarks

Finally it deserves to be mentioned that a practical use of eqn. (7) is that estimates of pH values near α = 1 are easily obtained while experimental values are difficult to obtain because of hydrolysis of the resin.

References

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