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ACID–BASE PROPERTIES OF CARBOXYLIC CATION EXCHANGERS

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SUMMARY

The acid–base properties of a series of methacrylic acid cation-exchange resins prepared by the direct one-step suspension technique were measured in sodium chloride solutions. The pH values were compared with those calculated from known models. The Gustafson equation, which is based on the Katchalsky–Lifson theory of polyelectrolytes, gave the best fit. Differences in the structure of the resins studied did not influence their acid–base properties.

INTRODUCTION

The excess free energy due to interactions between ionized carboxylic groups in aqueous solutions of linear polyelectrolytes and in swollen carboxylic cation exchangers has a considerable influence on the acid–base properties of these systems.

In general, the pH of a solution in equilibrium with a polyelectrolyte is given by the Henderson–Hasselbach formula with the additional ΔpH term¹:

$$\text{pH} = \text{p}K_0 - \log[(1 - \alpha)/\alpha] + \Delta\text{pH} \quad (1)$$

In earlier papers one may also find an empirical relation in which ΔpH is split into two parameters to give²:

$$\text{pH} = \text{p}K - n \log[(1 - \alpha)/\alpha] \quad (2)$$

In the above equations, K_0 and K are the intrinsic and apparent dissociation constants of the carboxylic groups, respectively, α is the degree of neutralization and n assumes values ranging from 1 to 2. Eqn. 2 is of rather limited use as both K and n are dependent on the system.

For gels, ΔpH of eqn. 1 usually contains a term which takes into account interactions between ionized carboxylic groups and another term which describes the equilibrium distribution of ions between the solution inside and outside the gel, since ΔpH measurements are performed in the external solution.

In this work the acid–base properties of a series of carboxylic cation exchangers

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measured in sodium chloride solution are compared with values calculated according to two models. All equations used by us are essentially the same as those used previously by other authors^{1,3-7}.

EXPERIMENTAL

The carboxylic cation exchangers were prepared by suspension copolymerization of methacrylic acid and divinylbenzene as described previously^{8,9}. The commercial divinylbenzene contained 60.7 wt.-% of *m*- and *p*-isomers. The compositions of the monomer mixtures and the properties of the products are listed in Table I.

TABLE I

COMPOSITIONS AND PROPERTIES OF CROSSLINKED METHACRYLIC ACID GELS

MA = methacrylic acid. *m*- and *p*-DVB content: 5.0 wt.-% of the monomer mixture; the rest up to 100%, styrene and ethylstyrenes. The properties are referred to the dry resins (H⁺-form). $Q = 1/d_0 - 1/d$; d = true copolymer density (1.33–1.37 g/cm³).

Sample	Monomer mixture		Apparent density, d_0 (g/cm ³)	Pore volume, Q (cm ³ /g)	Water regain (g/g)	Ion-exchange capacity (mequiv./g)
	MA (wt.-%)	Inert diluent				
I	91.8	—	1.16	0.12	1.06	10.6
II	85.0	—	1.16	0.12	1.01	10.2
III	85.0	Toluene	1.04	0.22	1.21	10.1
IV	85.0	<i>n</i> -Octane	0.96	0.30	1.29	10.1

The resins (H⁺-form) placed into polyethylene bottles were pre-swollen with deionized water and neutralized to the desired degree with a calculated amount of carbonate-free 2 *N* sodium hydroxide solution. They were kept in an air thermostat at 25°C for at least 1 month and were occasionally shaken. Then they were transferred into plastic tubes terminated by fine polyamide nets, freed from excess of solution by centrifugation and divided into several parts which, after weighing, were again placed into bottles containing a large excess of sodium chloride solution. After another 2 weeks for equilibration, the pH values of the solution above the gels were measured with a combined glass-calomel electrode.

The equilibrium amount of chloride ions within the gels was determined by elution of centrifuged samples with 1 *N* nitric acid followed by potentiometric titration with silver nitrate. A correction for the solution left on the surface of the ion-exchange beads, after centrifugation, was calculated according to the procedure described by Fricke *et al.*¹⁰.

The specific volumes of swollen resins at different neutralization degrees were measured pycnometrically in *n*-heptane saturated with water^{11,12}.

A more detailed description of the procedures may be found elsewhere⁹.

RESULTS AND DISCUSSION

The values of *pK* and *n* occurring in eqn. 2 are given in Table II. The *pK* values decrease with increasing sodium chloride concentration and with increasing

TABLE II

 VALUES OF n AND pK FOR CARBOXYLIC CATION EXCHANGERS AT DIFFERENT CONCENTRATIONS OF SODIUM CHLORIDE SOLUTIONS

Sample	NaCl concn. (mol/dm ³)							
	0.1		0.3		1.0		3.0	
	n	pK	n	pK	n	pK	n	pK
I	1.56	6.69	1.58	6.29	1.58	5.85	1.63	5.48
II	1.48	6.91	1.53	6.58	1.56	6.03	1.63	5.66
III	1.34	6.80	1.37	6.51	1.50	6.02	1.45	5.68
IV	1.66	6.77	1.46	6.38	1.52	5.97	1.59	6.68

swelling ratio of the resins (decreasing concentration of methacrylic acid units). Similar behaviour of various carboxylic cation exchangers was reported by Fisher and Kunin². At a high concentration of external solution (3 moles/dm³), the values of pK seem to become independent of swelling for resins containing the same fraction of methacrylic acid units (samples II–IV). This concentration is close to the total concentration of ions within the swollen gels.

Katchalsky and Michaeli^{3,4} based their description of the acid–base properties of poly(methacrylic acid) gels swollen in salt solution on the Katchalsky and Lifson¹³ theory of polyelectrolytes. In this theory, only the intra-chain interactions between ionized groups are taken into account. The effect of these interactions on the pH of a solution in equilibrium with a gel was expressed by two equations which differed in the method of calculating the distribution of small ions in the gel–solution system (Donnan equilibrium). The terms describing ΔpH are

$$\Delta pH = 2.646 \frac{Z^{1/2}}{q^{1/3}} \log(1 + \chi) + \frac{1}{2} \log \frac{p + a}{p - a} \quad (3)$$

$$\Delta pH = 2.646 \frac{Z^{1/2}}{q^{1/3}} \log(1 + \chi) + \log \frac{x_-}{\bar{x}_-} \quad (4)$$

where Z is the number average of methacrylic acid units in a chain (between crosslinks), q is the reciprocal molar fraction of methacrylic acid units in the swollen gel calculated according to⁴

$$q = 3.67 V/V_0 \quad (5)$$

where V and V_0 are the volumes of the swollen gel and the gel in the reference state, respectively;

$$\chi = 0.3 q^{5/6} / (Z \cdot p)^{1/2} \quad (6)$$

where p is the number of low-molecular-weight ion species per methacrylic acid unit in the gel, and x_- and \bar{x}_- are the molar fractions of monovalent co-ions in the solution and the gel, respectively.

The values of pH calculated according to eqns. 3 and 4 are presented in Table III. The calculations were based on measured specific volumes of swollen gels in equilibrium with 1 *N* NaCl (*cf.* ref. 12). The reference volume was chosen to be the

TABLE III
 VALUES OF pH CALCULATED FROM THE KATCHALSKY AND MICHAELI EQUATIONS
 Concentration of NaCl 1.0 mol/dm³.

Sample	α	$pK - \log \frac{I - \alpha}{\alpha}$	$\frac{Z^{1/2}}{q^{1/3}} \log(I + \chi)$	$\log \frac{p + \alpha}{p - \alpha}$	$\log \frac{x_-}{\bar{x}_-}$	$pH_{calc.}$ eqn. 3	$pH_{exp.}$ eqn. 4
I	0.200	4.26	1.05	0.389	0.431	5.70	5.74
	0.350	4.59	0.89	0.471	0.460	5.95	5.94
	0.493	4.85	0.82	0.548	0.569	6.22	6.23
	0.641	5.11	0.78	0.605	0.663	6.49	6.56
	0.797	5.45	0.73	0.605	0.649	6.79	6.84
II	0.199	4.26	1.05	0.389	0.397	5.60	5.70
	0.350	4.59	0.90	0.454	0.471	5.94	5.96
	0.500	4.86	0.84	0.509	0.478	6.21	6.18
	0.616	5.07	0.98	0.552	0.557	6.38	6.39
	0.800	5.46	0.89	0.607	0.604	6.77	6.77
III	0.200	4.26	1.00	0.316	0.398	5.58	5.66
	0.350	4.59	0.87	0.402	0.430	5.86	5.89
	0.500	4.86	0.77	0.474	0.479	6.10	6.11
	0.650	5.13	0.74	0.502	0.513	6.37	6.38
	0.800	5.46	0.69	0.529	0.522	6.68	6.67
IV	0.197	4.25	0.95	0.261	0.297	5.46	5.50
	0.345	4.58	0.85	0.353	0.363	5.78	5.79
	0.492	4.85	0.78	0.402	0.399	6.03	6.03
	0.640	5.11	0.73	0.444	0.425	6.28	6.26
	0.788	5.43	0.68	0.486	0.459	6.60	6.57

volume of the swollen resins (H^+ -form) rather than of the dry resins, following the reasoning of Michaeli and Katchalsky⁴. When the dry state was taken as the reference one, the agreement with experiment was worse, giving values higher than those presented in Table III by a factor of 0.2–0.3 pH units.

The greatest error introduced into calculations is connected with the values resulting from the first term of eqns. 3 and 4. This term, introduced by Katchalsky and Michaeli, was designed to take into account the effect of swelling both on electrostatic repulsions between groups and on the resulting change of activity coefficient of small ions inside the gel. For moderately crosslinked polyelectrolytes, the dependence of swelling ratio on the neutralization degree is much less pronounced than the similar dependence of coil expansion for linear chains. Since the swelling-dependent quantity $q^{1/3}$ appears in the numerator, the whole term overestimates the effect of swelling, especially at low values of α .

Marinsky and Chatterjee^{5,6} and Gustafson¹ calculated values of pK_0 of commercial carboxylic cation exchangers in equilibrium with salt solutions following essentially the model of Katchalsky and Michaeli, but they used activity coefficients of low-molecular-weight electrolytes inside the gels based on experimental data rather than on the original theory.

Gustafson expressed ΔpH from eqn. 1 in the form

$$\Delta pH = \log \frac{m_-}{\bar{m}_-} \gamma_{\pm} - \log \bar{\gamma}_{\pm}^* + \frac{0.4343}{RT} \left(\frac{\partial F_{e1}}{\partial \alpha} \right)_{\kappa} \quad (7)$$

where m_- and \bar{m}_- are the molarities of chloride ions in the solution and in the gel, respectively, γ_{\pm} is the activity coefficient of the NaCl solution and $\bar{\gamma}_{\pm}^*$ is the mean experimental activity coefficient of the low-molecular-weight electrolyte inside the gel

$$\bar{\gamma}_{\pm}^* = \left(\frac{m_+ m_-}{\bar{m}_+ \bar{m}_-} \gamma_{\pm}^2 \right)^{1/2} \quad (8)$$

where molarities of cations (subscript +) and anions (subscript -) in the gel are distinguished from those in the solution by the upper bar.

The last term in eqn. 7 describes the effect of the potential of the polyon on the activity of hydrogen ions. According to the Katchalsky–Lifson theory¹³

$$\left(\frac{\partial F_{e1}}{\partial \alpha} \right)_{\kappa} = \frac{2\alpha Z e^2}{Dh} \ln \left(1 + \frac{6h}{\kappa h^2} \right) \quad (9)$$

where F_{e1} is the excess free energy due to interactions between ionized groups in the polyelectrolyte, κ is the reciprocal Debye radius of ions inside the gel, D is the dielectric constant, e is the unit charge and h and h_0 are the root-mean-square end-to-end distances of the polyelectrolyte chains, containing on average Z methacrylic acid units, in the system and the reference state, respectively. The reciprocal Debye radius and h are functions of the degree of swelling

$$\kappa^2 = \frac{4\pi e^2}{DkT} \frac{\sum n_i}{v} \quad (10)$$

where n_i is the number of low-molecular-weight ions present in the volume v occupied by a single polyelectrolyte chain, and

$$h = h_0(V/V_0)^{1/3} = (Zsb^2)^{1/2}(V/V_0)^{1/3} \quad (11)$$

where s is the number of units in a statistical segment of hydrodynamic length b in an equivalent freely rotating chain.

In calculations Z was determined from stoichiometric considerations (values of Z were slightly higher than 10 which corresponded to one statistical segment, since we assumed the same numerical values of b and s as Michaeli and Katchalsky⁴), and pK_0 was assumed to be 4.86 as for isobutyric acid¹.

Values of pH calculated from eqn. 7 are presented in Table IV. Agreement with experimental pH values is good for resin I. For other cation exchangers the calculated pH values are slightly lower than the measured values, still the agreement is fairly good. The results show that the acid-base properties of carboxylic cation exchangers are rather insensitive to differences in their structure. Different degrees of chain coiling, due to solvent present during the gel preparation, possibly in voids, in swollen resins have negligible effects on the logarithmic term appearing in eqn. 7. Nevertheless, the Katchalsky-Lifson theory in the form adopted by Gustafson seems to be suitable for description of the acid-base properties of carboxylic cation exchangers.

Mathieson and Shet⁷ calculated the intrinsic dissociation constant of carboxylic groups in weakly swelling polyamide fibres using an equation of similar form to eqn. 1 in which

$$\Delta \text{pH} = 0.4343 \frac{\chi_{el} F}{RT} = 0.4343 \operatorname{arcsinh} \frac{c_f}{2c_s} \quad (12)$$

TABLE IV

VALUES OF pH CALCULATED FROM EQN. 7 OF GUSTAFSON AND EQN. 12 OF MATHIESON-WHEWELL

Concentration of NaCl 1.0 mol/dm³.

Sample	α	$\log \frac{m_- \gamma_{\pm}}{\bar{m}_-}$	$-\log \bar{\gamma}_{\pm}^{\pm}$	$\frac{0.4343}{RT} \left(\frac{\partial F_{el}}{\partial \alpha} \right)_{\kappa}$	$0.4343 \frac{\chi_{el} F}{RT}$	$\frac{pH_{calc.}}{eqn. 7}$	$\frac{pH_{exp.}}{eqn. 12}$	$pH_{exp.}$
I	0.200	0.250	0.142	0.249	0.372	4.90	4.63	4.87
	0.350	0.279	0.192	0.388	0.493	5.45	5.08	5.47
	0.493	0.278	0.170	0.525	0.553	5.92	5.40	5.82
	0.641	0.482	0.124	0.655	0.569	6.38	5.68	6.26
	0.797	0.468	0.138	0.804	0.584	6.86	6.04	6.78
II	0.199	0.216	0.140	0.243	0.340	4.86	4.60	5.05
	0.350	0.290	0.165	0.389	0.454	5.44	5.05	5.63
	0.500	0.297	0.161	0.541	0.528	5.86	5.39	6.08
	0.616	0.376	0.177	0.623	0.563	6.24	5.63	6.39
	0.800	0.423	0.184	0.765	0.626	6.83	6.09	6.89
III	0.200	0.217	0.100	0.223	0.278	4.80	4.54	5.05
	0.350	0.249	0.139	0.322	0.383	5.30	4.97	5.62
	0.500	0.298	0.176	0.555	0.485	5.89	5.35	6.06
	0.650	0.332	0.169	0.681	0.505	6.31	5.63	6.44
	0.800	0.341	0.188	0.804	0.549	6.80	6.01	6.91
IV	0.197	0.116	0.146	0.249	0.252	4.76	4.50	4.98
	0.345	0.182	0.171	0.402	0.358	5.34	4.94	5.61
	0.492	0.218	0.185	0.546	0.418	5.80	5.26	5.97
	0.640	0.244	0.205	0.678	0.473	6.24	5.58	6.37
	0.788	0.278	0.208	0.796	0.529	6.71	5.96	6.80

where χ_{el} is the electrostatic potential generated by ionized carboxylic groups, F is the Faraday constant, c_f is the concentration of ionized groups (roughly proportional to the neutralization degree) and c_s is the concentration of the external solution. Eqn. 12 resulted from averaging the effect of ionized groups throughout the gel volume¹⁴ and neglecting the term describing the distribution of counterions between the gel and the solution. The results of calculations performed using eqn. 12 are listed in Table IV. They are considerably smaller than the measured pH values. The dependence of pH on α is also different from the experimental one.

Neither the Katchalsky–Lifson theory nor the Mathieson–Whewell approach take into consideration many other effects known to exist in swollen polyelectrolyte gels¹⁵, for example formation of ion-pairs. Probably these effects balance each other and appear only through the activity coefficients which one may estimate experimentally. This may also be true of the effect of the structure of crosslinked polyelectrolytes on their acid–base behaviour.

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