

## Sodium and Chloride Ion Activities in Polyacrylic Acid— Polyacrylate Solutions at Various Degrees of Ionization

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As part of a study of the polyacrylic acid–polyacrylate system in aqueous solution, sodium and chloride ion activities have been measured at various degrees of dissociation  $\alpha$  in solutions of constant ionic strength. The total concentration of polyacrylic acid was  $0.05 \text{ mol l}^{-1}$  and the sodium ion concentration was maintained at  $0.05 \text{ mol l}^{-1}$  by addition of sodium chloride. The activity coefficient of  $\text{Cl}^-$ ,  $\gamma_{\text{Cl}^-}$ , was equal to 0.86 in all six solutions in which  $\alpha$  varied between 0.1 to 0.8. From  $\alpha = 0.2$ ,  $\gamma_{\text{Na}^+}$  decreases linearly with increasing  $\alpha$ . Values of the fractional charge  $f_z$  of the carboxylate groups uncompensated by associated  $\text{Na}^+$  ions were calculated assuming  $\gamma_{\text{Na}^+} = \gamma_{\text{Cl}^-}$  for free  $\text{Na}^+$  ions and  $\gamma_{\text{Na}^+} = 0$  for associated ions. Calculated values of  $f_z$  indicate pronounced association already at  $\alpha = 0.2$ ; at  $\alpha = 0.3$  and higher, the values are nearly constant and close to 0.35. The results are compared with previously determined proton dissociation enthalpies. Sodium ion activities were also measured in polyacrylic acid solutions ( $0.05 \text{ mol l}^{-1}$ ) neutralized to various  $\alpha$  with NaOH and values of  $f_z$  estimated. In both systems the calculated fractional charges are much lower than those predicted on the basis of Manning's theory for linear polyelectrolytes.

Polyacrylic acid is an inexpensive, well-defined synthetic polycarboxylic acid which is a good model compound for studies of interactions in polyelectrolyte systems. It has been extensively studied and information about various properties of polyacrylic acid–polyacrylate systems has become available.<sup>1,2</sup> However, systematic thermodynamic studies of, e.g., effects of variations in concentration of polymer

and of various counterions and byions at varying degrees of ionization are scarce. Likewise only few studies have been made at temperatures other than 25 °C. Interactions in polyelectrolyte systems are complex and reliable thermodynamic information is essential for the development of quantitative theoretical descriptions. In a previous paper calorimetrically measured differential enthalpies of proton dissociation  $\Delta H_a$  of polyacrylic acid at three temperatures were reported together with a theoretical calculation of  $\Delta H_a$  based on the Poisson-Boltzmann equation.<sup>3</sup> In the present paper are reported results of emf-measurements of sodium and chloride ion activities using ion-selective electrodes in the solutions used for the calorimetric measurements.

### EXPERIMENTAL

Solid polyacrylic acid  $[-\text{CH}_2\text{CH}(\text{COOH})-]_n$  with an average molecular weight of 250 000 and showing a glass transition temperature  $T_g = 106 \text{ °C}$  purchased from Aldrich-Europe was used without further treatment. The purity was checked by acidimetric titration and was found to be better than  $97.0 \pm 0.5 \%$  (by weight).

Sodium chloride (Analar analytical reagent, BDH) and concentrated sodium hydroxide solution (P.-H. Tamm) were used without further treatment.

To prepare the sodium polyacrylate–polyacrylic acid (NaPA-PAH) solutions, aliquots of a stock solution of PAH were neutralized with aqueous NaOH to the desired degree of neutralization and diluted to give a polymer concentration of  $0.0500 \pm 0.001 \text{ mol l}^{-1}$ . In the set of solutions also used in the calorimetric measurements, the total  $\text{Na}^+$  ion concentration was adjusted to  $0.05 \text{ mol l}^{-1}$  by addition of solid NaCl. Solutions were prepared

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Table 1. Results of emf-measurements on solutions containing  $[0.05\alpha \text{ M NaPA} + 0.05(1-\alpha) \text{ M PAH} + 0.05(1-\alpha) \text{ M NaCl}]$ .

$\alpha$	$10^3 c_{\text{Na}^+}$ mol l <sup>-1</sup>	$10^3 c_{\text{Cl}^-}$ mol l <sup>-1</sup>	pH	$E_{\text{Na}^+}$ mV	$E_{\text{Cl}^-}$ mV	$10^3 a_{\text{Na}^+}$	$10^3 a_{\text{Cl}^-}$	$\gamma_{\text{Na}^+}$	$\gamma_{\text{Cl}^-}$
0.104	50.03	45.03	3.84	116.2	67.2	43.0	38.5	0.86	0.86
0.201	50.08	40.08	4.37	112.0	70.0	38.0	34.5	0.76	0.86
0.300	50.05	35.05	4.90	109.6	73.2	35.0	30.6	0.70	0.87
0.400	50.01	30.02	5.28	107.2	77.6	32.1	25.8	0.64	0.86
0.600	49.11	19.11	6.11	101.6	89.4	25.7	16.2	0.52	0.85
0.800	49.99	9.98	7.00	94.2	106.0	19.1	8.52	0.38	0.85

with  $\alpha = c_{\text{PA}^-} / (c_{\text{PA}^-} + c_{\text{PAH}})$  equal to 0.10, 0.20, 0.30, 0.40, 0.60 and 0.80. The uncertainty in  $\alpha$  was less than 0.005.

The ion-selective electrodes used were G502 Sodium Selectrode<sup>®</sup> from Radiometer and the model 94-17 chloride electrode from Orion Research Inc. In addition, the double-junction reference electrode model 90-02 from the latter company was used. The potentials were measured using a high-precision double electrometer which allowed simultaneous measurements on the two ion-selective electrodes.<sup>4</sup> The sodium electrode was kept in 0.1 mol l<sup>-1</sup> NaCl solution for one week before use. All measurements were made at  $25.5 \pm 0.1$  °C in a thermostated 50 ml glass vessel with stirring. The equilibration time was 20 to 40 min after which the emf's of the cells were stable to within  $\pm 0.1$  mV for 2 to 3 h.

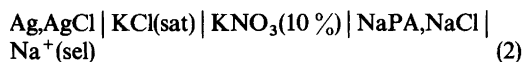
The electrodes were calibrated using sodium chloride solutions of concentrations 0.1 to 0.001 mol l<sup>-1</sup>. The activity coefficient of chloride ion was calculated as recommended<sup>5</sup> from eqn. (1),

$$-\log \gamma_{\text{Cl}^-} = AI^{1/2} / (1 + 1.5I^{1/2}) \quad (1)$$

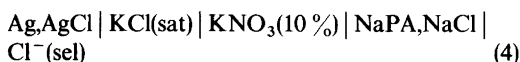
where  $A$  is equal to  $0.512 \text{ mol}^{1/2} \text{ l}^{-1/2}$  and  $I$  denotes the ionic strength. It is assumed that  $\gamma_{\text{Cl}^-} = \gamma_{\text{Na}^+} = \gamma_{\pm}$  in the NaCl solutions used. The Nernst's slope was found to be 57.86 mV for the Na<sup>+</sup> electrode and 59.20 mV for the Cl<sup>-</sup> electrode. The selectivity coefficient indicating the sensitivity of the Na<sup>+</sup> electrode to H<sup>+</sup> was estimated to be about 20 from measurements on NaCl-solutions of various pH adjusted by the addition of tris-buffer.

## RESULTS

Simultaneous measurements of emf of the two cells 2 and 4 were made:



$$E_{\text{Na}^+} = E' + S_{\text{Na}^+} \log a_{\text{Na}^+} \quad (3)$$

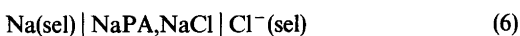


$$E_{\text{Cl}^-} = E'' - S_{\text{Cl}^-} \log a_{\text{Cl}^-} \quad (5)$$

Results of the measurements on the (NaPA-PAH) solutions with added NaCl are summarized in Table 1. The degree of dissociation  $\alpha$  is given in the first column and the Na<sup>+</sup> ion and Cl<sup>-</sup> ion concentrations in the second and third columns. The pH of the solutions is given in column 4. The emf of cells (2) and (4) found from duplicate readings are shown in, respectively, columns 5 and 6. Calculated activities of Na<sup>+</sup> and Cl<sup>-</sup>,  $a_{\text{Na}^+}$  and  $a_{\text{Cl}^-}$ , respectively, are shown in columns 7 and 8. The Na<sup>+</sup> activities have been corrected for interference from H<sup>+</sup>.

In calculating  $a_{\text{Na}^+}$  and  $a_{\text{Cl}^-}$  it is assumed that differences in the liquid junction potential  $E_j$  between the calibration and polyacrylic acid solutions were negligible. It is not possible to evaluate the uncertainty in the calculated values due to this source of error.

However, the cell



$$E = E^\circ - S \log a_{\text{Na}^+} a_{\text{Cl}^-} \quad (7)$$

does not contain any liquid junction and spurious potentials should therefore be minimized. Now (7)=(5)-(3) so that  $E$  can be found from the measured emf's of the cells (2) and (4). In this subtraction the liquid junction potential  $E_j$  included in  $E'$  and  $E''$  cancels and therefore does not affect the product  $a_{\text{Na}^+} a_{\text{Cl}^-}$ .

Values of the activity coefficient of chloride ions,

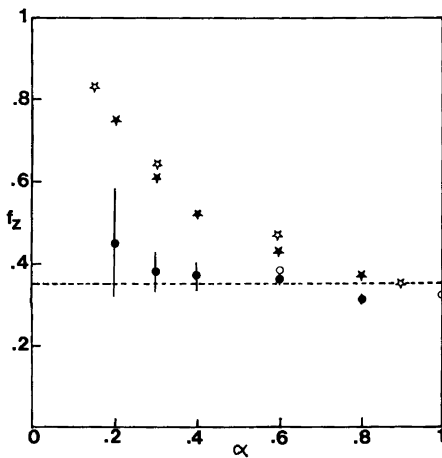


Fig. 1. Charge fraction  $f_z$  of carboxylate groups not neutralized by associated  $\text{Na}^+$  ions. ●, This study  $c_{\text{Na}^+} = 0.05 \text{ mol l}^{-1}$ ; ★, this study  $c_{\text{Na}^+} = \alpha \cdot 0.05 \text{ mol l}^{-1}$ ; ☆, from Ref. 6; ○, from Ref. 7.

$y_{\text{Cl}^-} = a_{\text{Cl}^-} c^{\circ} / c_{\text{Cl}^-}$ , and of sodium ions,  $y_{\text{Na}^+} = a_{\text{Na}^+} c^{\circ} / c_{\text{Na}^+}$ , are shown in Table 1.

The concentration of free  $\text{Na}^+$  ions can be calculated if it is assumed that the activity coefficient is zero for  $\text{Na}^+$  ions strongly associated with the macroion and that  $y_{\text{Na}^+} = y_{\text{Cl}^-}$  for the mobile ions. The fractional charge  $f_z$  on the carboxylate group not neutralized by bound  $\text{Na}^+$  ions can then be estimated from eqn. (8), where  $C_{\text{PAH}}$  is the total

$$f_z = [\alpha C_{\text{PAH}} - (c_{\text{Na}^+} - a_{\text{Na}^+} / y_{\text{Cl}^-})] / (\alpha C_{\text{PAH}}) \quad (8)$$

concentration of polyacrylic acid and  $c_{\text{Na}^+}$  that of sodium ions.

A plot of calculated values of the net charge  $f_z$  against  $\alpha$  is shown in Fig. 1. The vertical bars indicate estimates of the experimental uncertainties.

From measurements using cell (2) on polyacrylic acid solutions neutralized with  $\text{NaOH}$  but without added  $\text{NaCl}$  the following set of activity coefficients  $y_{\text{Na}^+}$  was calculated: 0.88(0.1), 0.71(0.2), 0.56(0.3), 0.47(0.4), 0.38(0.6) and 0.32(0.8). Values of  $\alpha$  in the solutions are given within parentheses. The average number of  $\text{Na}^+$  ions bound per carboxylate group in the macroanion was estimated assuming the activity coefficient of free  $\text{Na}^+$  ions in the polymer solution to be 0.04 higher than  $y_{\pm}$  calculated from eqn. (1), cf. Discussion. The resulting values of  $f_z$  plotted against  $\alpha$  are shown in Fig. 1. Included in the figure are the results found by Wall and

Hill<sup>6</sup> from transference measurements on solutions containing a total polyacrylic acid concentration of  $0.029 \text{ monomol l}^{-1}$  neutralized to various  $\alpha$  with sodium hydroxide. The influence of  $f_z$  of the difference between the polyacid concentrations is small compared to the experimental uncertainties. As can be seen, the agreement is good between the two sets of estimates.

Our results from measurements on solutions with added  $\text{NaCl}$  are in satisfactory agreement at higher  $\alpha$  with results from transference measurements reported by Nagasawa *et al.*<sup>7</sup> while their value for  $\alpha = 0.2$  is higher than ours. However, the difference may be due to experimental uncertainties.

Quite different estimates of the extent of  $\text{Na}^+$  ion association have been derived by Ikegami<sup>8</sup> from measurements of changes in refractive index upon addition of  $\text{NaCl}$  to polyacrylic acid solutions partially neutralized by  $\text{Bu}_4\text{NOH}$ . He found  $f_z \approx 0.95$  at  $\alpha = 0.4$  and  $f_z = 0.6$  at  $\alpha = 0.6$ . The reason for this discrepancy is not clear, one possible cause could be the presence of the butylammonium ions in the solutions he used.

## DISCUSSION

It is noteworthy that the same value of  $y_{\text{Cl}^-} = 0.86 \pm 0.01$  is found in the six different solutions with  $c_{\text{Na}^+} = 0.05 \text{ mol l}^{-1}$  in which the  $\text{Cl}^-$  ion concentration decreases from  $0.045$  to  $0.01 \text{ mol l}^{-1}$  as  $\alpha$  increases from  $0.1$  to  $0.8$ . However, the ionic strength is constant<sup>9</sup> and the constant  $y_{\text{Cl}^-}$  indicates that the chloride ions are not influenced by the increased charge density on the macroion. The observed value is  $0.04$  higher than the activity coefficient of  $\text{Cl}^-$  in a  $\text{NaCl}$  solution of the same ionic strength. The difference may stem from changes in activities due to the polymer or from changes in the liquid junction potential  $E_j$ . However, the found values of  $y_{\text{Cl}^-}$  indicate that possible errors in the single-ion activities from varying  $E_j$  are not serious.

At  $\alpha = 0.1$ ,  $y_{\text{Na}^+} = y_{\text{Cl}^-}$ , indicating that at low  $\alpha$  there is little special interaction between  $\text{Na}^+$  ions and the polyion. At  $\alpha = 0.2$  and higher,  $y_{\text{Na}^+}$  decreases linearly with increasing  $\alpha$ , reflecting an increasing influence on the  $\text{Na}^+$  ions of the increasing charge density on the polyion. Extrapolation of  $y_{\text{Na}^+}$  to  $\alpha = 1$  and zero  $\text{NaCl}$  gives  $y_{\text{Na}^+} = 0.26$ , which is in satisfactory agreement with the value  $0.28$  found from measurements on fully ionized sodium polyacrylate solutions.<sup>10</sup> Ex-

trapolation of  $y_{\text{Na}^+}$  as a function of  $\alpha$  in solutions of partially neutralized polyacrylic acid without NaCl give  $y_{\text{Na}^+}$  of about 0.28 at  $\alpha=1$  which indicates that our two sets of measurements are mutually consistent.

The fractional charge  $f_z$  of the polyelectrolyte charged groups not neutralized by strongly associated counterions is a useful concept when discussing polyion-counterion interactions. According to Manning's theory of counterion condensation,<sup>11</sup> there exists a critical value of the charge density of a linear polyelectrolyte  $\zeta = |z|^{-1}$  where  $z$  is the valence of the counterion. At charge densities below this value there are no associated counterions; at higher values counterions condense on the polyelectrolyte, leaving an uncompensated charge fraction  $f_z = |z|^{-1} \zeta^{-1}$ . The critical charge density is reached in the presence of univalent counterions in water at 25 °C when the distance between the ionized groups is 7.1 Å. At  $\alpha$  about 0.35 this will be the average distance between the ionized groups in polyacrylic acid, and  $f_z$  should then decrease from 1 to 0.35 as  $\alpha$  increases from 0.35 to 1. As can be seen from Fig. 1, Manning's theory is not applicable to partially dissociated polyacrylic acid. Our estimate of  $f_z$  in solutions with added NaCl indicates that the limiting value of  $f_z$  is reached already at  $\alpha$  about 0.3. Also in solutions without added NaCl the observed values of  $f_z$  are lower than predicted. It must be admitted that the identification of the degree of ion association with  $f_z$  as calculated from the result of activity and transference measurements is not free from objections as the procedure of dividing the counterions into free and bound ions is not well-founded. However, the estimated values of  $f_z$  in solutions with  $c_{\text{Na}^+} = 0.05 \text{ mol l}^{-1}$  vary in the same manner as the differential enthalpy changes  $\Delta H_a$  for proton dissociation under the same conditions as determined from calorimetric experiments.<sup>3</sup> The dissociation enthalpy decreases rapidly as  $\alpha$  increases up to about 0.3 but changes only slightly with further increase in  $\alpha$ . The theoretical calculations based on a solution of the Poisson-Boltzmann equation give a qualitatively correct prediction of the variation of  $\Delta H_a$  with  $\alpha$ .

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