Salt-specific effects observed in calorimetric studies of alkali and tetraalkylammonium salt solutions of poly(thiophen-3-ylacetic acid)

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ELECTRONIC SUPPLEMENTARY INFORMATION

An estimate of the heat effect, $\Delta H_{\rm h}$, due to hydrolysis

Upon dilution of salts of weak carboxylic acids a small portion of carboxylate groups $-COO^-$ is converted into the non-ionized form -COOH

$$R - COO^{-} + M^{+} + H_2O \rightleftharpoons R - COOH + M^{+} + OH^{-},$$

where M⁺ represents alkali cation. The process is called hydrolysis and includes protonation of carboxylate group and concomitant dissociation of one water molecule per one obtained carboxyl group. Both processes involve heat ex-

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change. The protonation of carboxylate groups in most cases requires enthalpy of protonation up to 6 kJ/mole (mostly heat consumption, seldom release)[1, 2], while the ionization enthalpy of water $\Delta H_{\rm ion}$ is around 55 kJ/mol. In this approximate calculation of the heat effect caused by hydrolysis, $\Delta H_{\rm h}$, only the contribution due to the ionization of water molecules, $\Delta H_{\rm ion}$, is taken into account.

The extent of hydrolysis upon dilution depends on the initial (c_p^i) and final (c_p^f) concentrations of the carboxylic salt as well as on the dissociation constant of the carboxylic acid in question. The concentrations of all species in their initial and final states can be calculated from the equations that take into account:

i) conservation of the total concentration (c_{total}) of carboxylic groups

$$c_{\text{total}} = c_{\text{COO-}} + c_{\text{COOH}},\tag{1}$$

where $c_{\text{COO}-}$ and c_{COOH} denote concentrations of carboxylate and carboxyl groups, respectively.

ii) electroneutrality of the solution

$$c_{\rm M^+} + c_{\rm H^+} = c_{\rm COO^-} + c_{\rm OH^-} \tag{2}$$

where c_{M^+} is the concentration of monovalent counterions (in our case alkali cations). Taking that neutralization is practically complete, c_{M^+} is assumed to be equal to c_{total} .

iii) dissociation constant $K_{\rm a}$ of the acid

$$K_{\rm a} = \frac{a_{\rm H} + a_{\rm COO^-}}{a_{\rm COOH}} \tag{3}$$

where a_{H^+} , a_{COO^-} , and a_{COOH} stand for activities of H_3O^+ ions, carboxylate, and carboxyl groups, respectively. This equation is often simplified by replacing activities with concentrations of the given species:

$$K_{\rm a} \approx \frac{c_{\rm H} + c_{\rm COO^-}}{c_{\rm COOH}}$$
 (4)

Further, according to Katchalsky and Gillis[3]

$$K_{\rm a} \approx K_0 e^{\frac{-\Delta G(\alpha)}{kT}} \tag{5}$$

where K_0 represents the ionization constant of the carboxyl group on the uncharged polyacid, α is the degree of ionization and $\Delta G(\alpha)$ the work required for removing the dissociated proton from the electric field of the carboxylate group of the polymeric molecule to the bulk of solution. In case of a weak polyacid with the high enough number of ionized groups, the $\Delta G(\alpha)$ is not significantly changed by ionization/protonation of an additional carboxyl group.

iv) the ionization product of water

$$K_{\rm w} \approx c_{\rm H^+} \cdot c_{\rm OH^-} \tag{6}$$

The four above mentioned relations (Eqs. 1,2,4, and 6) can be combined into a single equation containing known values of c_{total} , K_{w} , and K_{a} , from which the concentration of OH⁻ ions (c_{OH^-}) needed in further calculation can be obtained:

$$K_{\rm a} \cdot c_{\rm OH^{-}}^3 + K_{\rm w} \cdot c_{\rm OH^{-}}^2 - K_{\rm w} \cdot (c_{\rm total} + K_{\rm a}) \cdot c_{\rm OH^{-}} - K_{\rm w}^2 = 0$$
(7)

Upon dilution a given volume of water is added to the original solution. As a consequence the number of moles of OH^- ions is increased by $\Delta n_{OH^-}(c_p^i \to c_p^f)$. The increased amount of OH^- ions is equal to the amount of water molecules ionized upon the dilution. The contribution of hydrolysis to the enthalpy of dilution accordingly reads:

$$\Delta H_{\rm h}(c_{\rm p}^{\rm i} \to c_{\rm p}^{\rm f}) = \Delta n_{\rm OH^-}(c_{\rm p}^{\rm i} \to c_{\rm p}^{\rm f}) \frac{\Delta H_{\rm ion}}{n_{\rm total}}$$
(8)

where n_{total} is the total number of moles of carboxyl groups $(n_{\text{COO}^-} + n_{\text{COOH}})$.

In numerical calculations the value of $K_{\rm a}$ has been chosen to be the same as found before for poly(metacrylic acid)[4]. Further, in view of the unknown temperature dependence of $K_{\rm a}$ of carboxylic acids, the latter one was assumed to be temperature independent in the interval from 5 °C to 45 °C and equal to $4.00 \cdot 10^{-8}$ [1]. Using this value, the calculated pH at the equivalent point is slightly higher (around 0.5 pH) than determined by titration (see Ref. 25). The choice of K_a has crucial influence on estimated enthalpy of hydrolysis $\Delta H_{\rm h}$. By increasing $K_{\rm a}$ ten times (from $4 \cdot 10^{-8}$ to $4 \cdot 10^{-7}$) $\Delta H_{\rm h}$ decreases to about one third of the original value. While this value of $K_{\rm a}$ reproduces the experimental pH very well, it very likely underestimates the hydrolysis effect.

The $K_{\rm w}$ values are taken from the literature[5]: $K_{\rm w}(5 \ ^{\circ}{\rm C}) = 1.87 \cdot 10^{-15}$, $K_{\rm w}(25 \ ^{\circ}{\rm C}) = 1.01 \cdot 10^{-14}$, and $K_{\rm w}(45 \ ^{\circ}{\rm C}) = 3.93 \cdot 10^{-14}$.



Figure 1: Calculated enthalpy of hydrolysis, $\Delta H_{\rm h}$, as a function of the polyelectrolyte concentration ($c_p = c_{\rm p}^{\rm i}, c_{\rm p}^{\rm f} = 2 \cdot 10^{-3} \text{ monomol/dm}^3$) at various temperatures (5 °C, 25 °C, and 45 °C) and for two $K_{\rm a}$ values (continuous lines: $K_{\rm a} = 4 \cdot 10^{-8}$; dashed lines: $K_{\rm a} = 4 \cdot 10^{-7}$).

In Fig. 1 we present the results for $\Delta H_{\rm h}(c_{\rm p}^{\rm i} \rightarrow c_{\rm p}^{\rm f})$ at various temperatures. The final (diluted) concentration of carboxyl groups is $c_{\rm p}^{\rm f} = 2.0 \cdot 10^{-3}$ monomol/dm⁻³. We demonstrate in this figure that the effect of hydrolysis is endothermic and more pronounced at higher temperatures. This finding is in qualitative agreement with the experimental results for the enthalpy of dilution of this polyacid presented in the main part of the paper.

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