Short Communication

Determination of Effective Charge Numbers for a Polydisperse Polyelectrolyte. An Improvement which Shortens the Measuring Time

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Methods for determining ionic diffusion coefficients (D_i) and effective charge numbers (z_i) for a polydisperse polyelectrolyte have been presented previously.[1-3] These methods are based on a convective diffusion process across a porous membrane. The principle of the experimental arrangement is outlined in Fig. 1.

When measuring diffusion coefficients the concentration of the supporting electrolyte in the
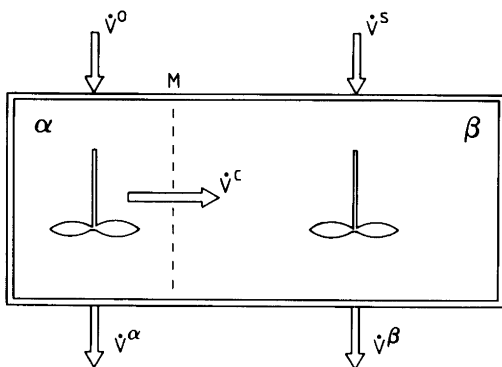

Fig. 1. A schematic drawing of the membrane cell. The system consists of two electrolyte solutions (α and β) separated by a thin membrane (M). The solutions α and β are kept homogeneous by stirring. Inside the membrane the local concentration gradients are determined by the Nernst-Planck equations with constant ionic fluxes. These fluxes can be determined from the concentration in the α compartment, the flow rate $V^{\cdot\alpha}$ and the surface area of the membrane (A) with the aid of the balance equation $J_i A = c^\alpha V^{\cdot\alpha}; i = 1,2,...n$.

feed solution is the same as in the β compartment. When measuring charge numbers pure water is fed to the α compartment. In both cases the trace-ion is added to the β compartment and from its diffusion to the α compartment the diffusion coefficients and effective charge numbers can be determined.

From a practical point of view the α compartment should be as small as possible in order to attain a stationary state as soon as possible, but the stirring requirement puts a limit on its size. Furthermore, the porous membrane must not have too large a surface area so as to ensure an even pressure distribution on the membrane and to achieve a smooth hydrodynamic boundary layer just adjacent to the membrane surface. All these criteria place demands which have led us to the cell described in detail in Ref. 1.

We have already presented an improvement[3] on the original method for measuring the effective charge numbers,[2] but the problem is still the fact that the concentration of polyelectrolyte in the α compartment becomes low (which makes the analytical work difficult) because of the water fed into this compartment. In order to be able to increase the concentration of polyelectrolyte in the α compartment we should decrease the convection ($V^{\cdot c}$). This is, however, possible to only a limited extent, owing to the sensitivity of the method, i.e. there must be measurable differences in the molar mass distribution between the α and β compartments. If the convection is too low these differences cannot be achieved and in

addition, the whole diffusion process becomes slow and labile due to the difficulties involved in maintaining constant boundary layers just adjacent to the membrane surface. It is therefore important to be able to raise the concentration in the α compartment while maintaining the differences in molar mass distributions between the two compartments. If this can be achieved, the measuring time will be considerably shortened because a smaller volume of sample will be sufficient for the gel chromatographic analysis.

In order to be able to raise the concentration of the trace-ion (= polyelectrolyte) in the α compartment we therefore have to change the coupling factor $d\varphi/dx$ in the Nernst-Planck equation. We have found, at first experimentally and subsequently theoretically, that the concentration of the trace-ion in the α compartment at stationary state can be raised by increasing the concentration of supporting electrolyte in this compartment. Such a situation can be achieved by feeding more concentrated supporting electrolyte solution into the α compartment than into the β compartment. The fluxes of the supporting electrolyte and the trace-ion are then:

$$J_i A = -c_i^\alpha V^{\cdot\alpha} \tag{1}$$

$$J A = c^\circ V^{\cdot\circ} - c^\alpha V^{\cdot\alpha} \tag{2}$$

where the subscript i denotes the trace-ion and quantities without subscript denote the supporting electrolyte, J is the flux, A is the surface area of the membrane, $V^{\cdot\alpha}$ is the outflow from and $V^{\cdot\circ}$ the feed rate into the α compartment, c° is the concentration of the supporting electrolyte in the feed solution going into the α compartment, and c^α and c_i^α are the concentrations in the α compartment.

Using the Nernst-Planck equation in the form in which the activity correction has been taken into account as presented previously,[4] an expression can be obtained for the concentration of the supporting electrolyte in the α compartment:

$$c^\alpha = \frac{c^\beta + c^\circ \dfrac{V^{\cdot\circ}}{V^{\cdot c}}\left\{\exp\left(\dfrac{V^{\cdot c}l}{D_m A}\right) - 1\right\}}{\dfrac{V^{\cdot\circ}}{V^{\cdot c}}\exp\left(\dfrac{V^{\cdot c}l}{D_m A}\right) - \dfrac{V^{\cdot\alpha}}{V^{\cdot c}}} \tag{3}$$

where D_m is the diffusion coefficient for the supporting electrolyte and l is the thickness of the membrane.

Using the procedure presented earlier,[2,3,4] the following equation for evaluating the charge numbers is obtained:

$$\frac{c_i^\beta}{c_i^\alpha} = \frac{\exp\left(\dfrac{V^{\cdot c}l}{D_i A}\right)}{\left(\dfrac{c^\beta}{c^\alpha}\right)^{z_i[(D_m/D_+) - \delta]}} \cdot$$

$$\left\{1 + \left(\frac{V^{\cdot\alpha}l}{D_i A}\right)\int_0^1 \left(\frac{c}{c^\alpha}\right)^{z_i[(D_m/D_+) - \delta]} \exp\left(\frac{-V^{\cdot c}l}{D_i A}x\right)dx\right\}$$

$$i = 1, 2, \ldots n \tag{4}$$

where

$$\frac{c}{c^\alpha} = \frac{c^\circ}{c^\alpha}\frac{V^{\cdot\circ}}{V^{\cdot c}} - \frac{V^{\cdot\alpha}}{V^{\cdot c}}$$

$$+ \left(1 - \frac{c^\circ}{c^\alpha}\frac{V^{\cdot\circ}}{V^{\cdot c}} + \frac{V^{\cdot\alpha}}{V^{\cdot c}}\right)\exp\left(\frac{V^{\cdot c}l}{D_m A}x\right),$$

$\delta = (1 + d\ln y_{+-})/(d\ln c)$ and y_{+-} is the mean activity coefficient of the supporting electrolyte. The activity correction δ in this form is valid only for 1:1 electrolytes, which is the case considered here (for unsymmetrical electrolytes see Ref. 4). Thus, when the ratio c_i^β/c_i^α has been determined experimentally we can calculate z_i from eqn. 4 in the same way as presented in Ref. 3, as soon as D_+ has been evaluated (see Ref. 4).

Three different measurements were performed: In each measurement the concentration of the supporting electrolyte (LiCl) was 0.1 M and the mass concentration of the polyelectrolyte (lignosulfonate in this case) was 1 g dm^{-3} in the β compartment. In the first experiment we fed 0.1 M LiCl solution into the α compartment and then calculated the diffusion coefficients for the lignosulfonate as described earlier.[1] In the second experiment we fed pure water into the α compartment and calculated the effective charge numbers for the lignosulfonate using the diffusion coefficients obtained from the first experiment by the method presented in Ref. 3. In the

third experiment we fed 0.15 M LiCl solution into the α compartment and calculated the effective charge numbers by the method presented in this paper. The effective charge numbers calculated from the second and third experiments were very close to each other. The concentrations of the lignosulfonate in the α compartment after a stationary state had been attained were in each experiment:

$c_i^\alpha = $ 60 mg dm^{-3} (first experiment);

$c_i^\alpha = $ 40 mg dm^{-3} (second experiment);

$c_i^\alpha = 125$ mg dm^{-3} (third experiment).

In all of these measurements the convection $V^{\cdot c}$ and the outflow from the α compartment $V^{\cdot \alpha}$ were the same. Since it is primarily the convection which determines the molar mass distribution, it is almost the same in the second and third experiments.

As can be seen, the concentration in the α compartment is almost three times higher in the third experiment than in the second. Thus, the measuring time becomes three times shorter with this improved method.

References

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