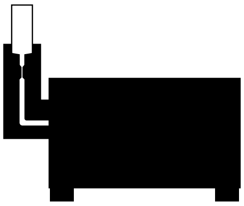
Application Note

Determination of the surface potential and isoelectric point of ion-exchange membranes with a zeta potential analyzer

Ion-exchange membranes are widely used in numerous applications, such as water treatment, chemistry, electrolysis, sensorics and other fields. A good ion transfer selectivity of the ion-exchange membrane is highly important for all of these applications. The charge structure and composition of ion-exchange membranes has a strong influence on the mobility of different ions or molecules and thus governs the selectivity of ion transport processes through the membrane.[1] Therefore, it is of great importance to have a good technique to characterise the charged surface functionalities of ion-exchange membranes. A powerful technique to evaluate charged surface functionalities is the measurement of the zeta potential, that is, the electric potential of solid surfaces in contact with an electrolyte solution. With this information it is possible to better understand the dissociation state of functional groups on the surface, and conclude the electrostatic interactions that will occur with other materials such as charged particles. The new Zeta Potential Analyzer ZPA 20 from DataPhysics Instruments (Fig. 1) measures the zeta potential of fibres, powders and plate shaped surfaces by means of a novel bidirectional oscillating streaming potential or streaming current technique. In this application note, we study the functional groups of different ion-exchange membrane surfaces with the ZPA 20.

Measurement device
Zeta potential analyzer



Measurement method
Oscillating streaming current
Oscillating streaming potential

Measured quantities
Zeta potential
Isoelectric point

Environmental conditions
Room temperature

Samples
Ion exchange membrane

Industries
Ion exchange membrane development
Ion exchange membrane manufacturing

dataphysics

Technique and Method

Solid surfaces in contact with an aqueous solution are in most cases charged – either by dissociation of functional groups or by adsorption of ions and molecules from the solution. Even primarily uncharged surfaces in simple salt solutions usually carry a negative charge due to the adsorption of OH^- ions. If the solution moves with respect to the solid (or vice versa), a shear plane is formed between ions and molecules strongly adsorbed to the surface and the mobile ions in the surrounding solution (Fig. 2). The electrical potential at this shear plane, the so-called zeta potential, is a very sensitive measure for the charge situation on the solid surface. From pH- or concentration-dependent zeta potential measurements, conclusions can be drawn regarding the nature of the functional surface groups and adsorption processes[2].

The Zeta Potential Analyzer ZPA 20 from DataPhysics Instruments uses the streaming potential (Eq. 1) or streaming current (Eq. 2) method to determine the zeta potential. An oscillating flow of an electrolyte solution is pumped either through a thin slit between two flat surfaces or the capillary system formed by a dense fibre or powder package. The solution flow shears off the mobile ion layer near the surface and creates an alternating potential and current in the measuring cell.

From the ratio of the streaming potential U_{str} or current I_{str} and the pressure difference Δp (Fig. 3), the zeta potential ζ is calculated[3][4]:

Fig. 1: The Zeta Potential Analyzer ZPA 20 from DataPhysics Instruments

$$\zeta = \frac{\eta}{\varepsilon_r \cdot \varepsilon_0} \cdot \kappa \cdot \frac{dU_{str}}{d\Delta p} \quad \textit{(Equation 1)}$$

$$\zeta = \frac{\eta}{\varepsilon_r \cdot \varepsilon_0} \cdot \frac{L}{H \cdot W} \cdot \frac{dI_{str}}{d\Delta p} \quad \textit{(Equation 2)}$$

η is the viscosity of the solution, ε_r is the relative permittivity of the solution, ε_0 is the absolute permittivity of vacuum, κ is the electrical conductivity of the solution, L, H and W are the dimensions of the streaming channel between plate-shaped samples.

Data analysis using the streaming current requires knowledge of the dimensions of the streaming channel and the viscosity, can be used for plate shaped solids. The streaming potential method needs the viscosity and the conductivity of the solution and can be used for measurements of fibres, powders, and plate shapes surfaces.

Experiment

In this application note, the zeta potential ζ and the isoelectric point (IEP) of two types of ion-exchange membranes (IEMs), i.e. IEM 1 and IEM 2, were determined by using the ZPA 20 equipped with the MC-ZPA/S plate measuring cell from DataPhysics Instruments (Fig. 4). Streaming current and streaming potential methods were used. To clarify the influence of the sample holder, i.e. stamps, the zeta potential ζ and the isoelectric point of the stamps were determined with the ZPA 20 and the streaming current method as a blank test.

To ensure the cleanliness of the measuring device and MC-ZPA/S measuring cell for plate-shaped materials, the equipment was thoroughly cleaned

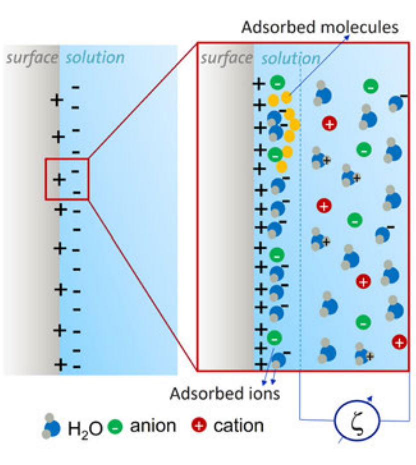


Fig. 2: Charge formation at solid surfaces in aqueous solution

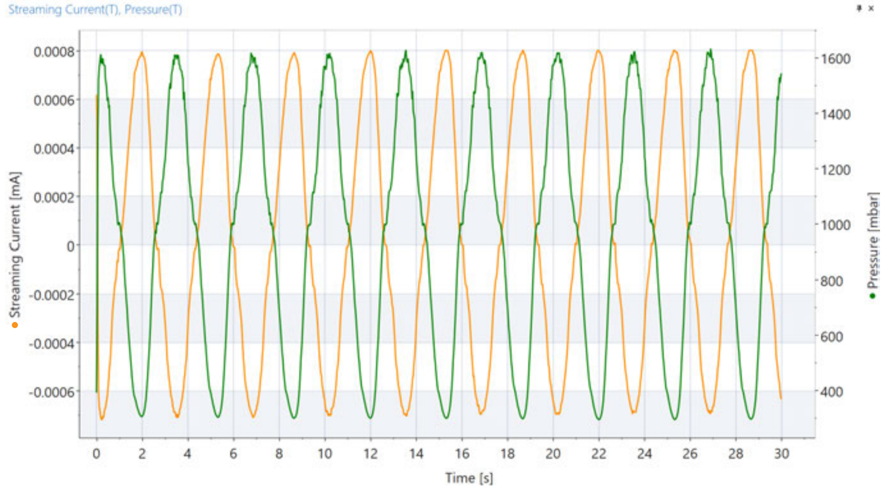


Fig. 3: Oscillating pressure (green) and resulting streaming current (orange) vs. time

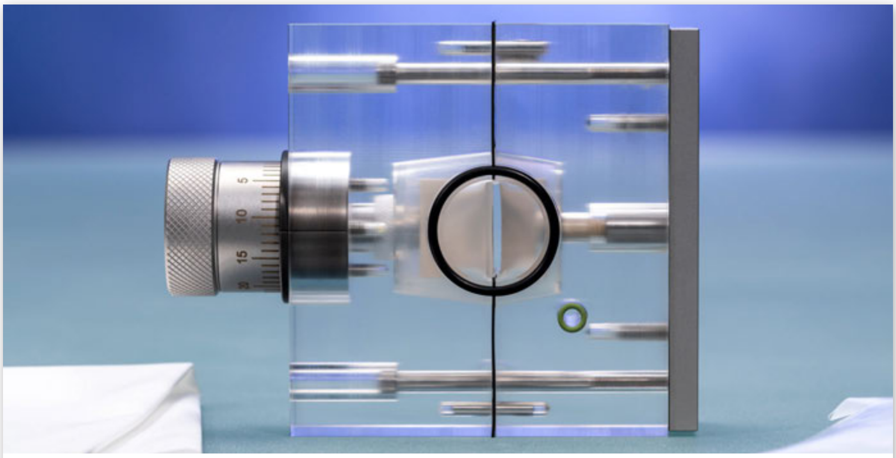


Fig. 4: The MC-ZPA/S measuring cell for zeta potential of plate shaped solids, such as wafers, membranes or plastic sheets.

with ultra-pure water (≤ 0.055 µS/cm) before the ion-exchange membrane samples were mounted into the measuring cell.

IEM samples of 10 mm x 20 mm size were attached to the stamps of the MC-ZPA/S measuring cell by adhesive tape (Fig. 4) and arranged facing towards each other to form a gap of about 150 µm width. Each sample was cut while immersed in a KCl solution. Special caution was taken that the membranes were exposed to the open air for less than 1 minute during the sample preparation process to avoid that the membrane dries out.

After mounting the measurement cell with the membrane sample in the ZPA 20, the storage vessel was filled with KCl solution (1 mmol/L, pH ~6). By using the ‘Bubbles purging’-function of the ZPA 20, possible air bubbles on the sample and in the device were removed before starting the measurement. From the streaming current vs. pressure ramps obtained in several oscillations (Fig. 3), the zeta potential was calculated for the given pH value. For each pH value, a measurement time of only a few seconds is sufficient to generate results with excellent statistical quality underlining the benefits of the new oscillation method. Thanks to the automatic titration function utilising the LDU 25 liquid dosing unit from DataPhysics Instruments (Fig. 5), the zeta potential in a pH range from 2 to 10 was determined fully automatically. Titrations were done once from neutral to the acidic range and once from neutral to the alkaline range. As titrant HCl (0.1 mol/L) and KOH (0.1 mol/L) solutions were used. After the measurement the device and the measuring cell were thoroughly cleaned using ultra-pure water which is especially easy since no pipes are used in the ZPA 20 reducing the surface area and complexity of the wetted parts tremendously.

Results & Discussion

Fig. 6 shows the zeta potential of the ion-exchange membranes and stamp surface as function of the pH value, which is determined with the streaming current method. The curves show the typical decrease of the zeta potential from positive values at low pH values to negative values with increasing pH values. This is partly an effect of the dissociation of functional groups, but also of the pH-dependent adsorption of H_3O^+ and OH^- ions.

An important parameter for the verification of dissociable functional groups is the zero crossing of the zeta potential curves, the so-called isoelectric point (IEP). An IEP below a pH of 4 indicates acidic surface groups, while an IEP above a pH of 5 indicates alkaline groups. As a reference measurement, the IEP of the sample holder tamp was measured (pH 4.39), indicating the presence of functional groups

Table 1: IEP of sample IEM 2 determined with the streaming potential and streaming current methods

Method	pH at IEP
Streaming potential	9.21
Streaming current	9.04

Fig. 5: The LDU 25 liquid dosing unit allows operators to change the concentration inside the solution automatically.

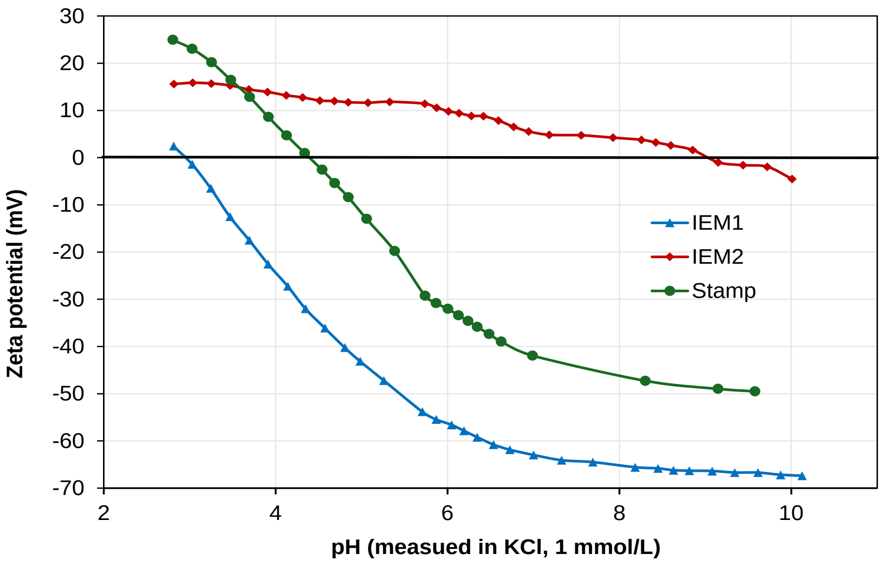


Fig. 6: Zeta potential of IEMs and stamp surfaces as function of the solution’s pH value

with a near to neutral character that have a neglectable influence on the other measurements. The IEP of sample IEM 1 is at a pH value of 2.95, indicating the presence of acidic hydroxyl groups. The IEP of sample IEM 2 is at a pH value of 9.04, which is characteristic for alkaline groups. Additionally, the zeta potential of IEM 2 was also measured by using the streaming potential method. As shown in Table 1, the IEP of sample IEM 2 measured with streaming potential method is at a pH value of 9.21, which is consistent with the IEP value determined by streaming current method. This suggests a high reliability of both measurement methods.

A look at the measurement diagram in Fig. 3 shows that the bidirectional pressure ramps form an even, sinusoidal curve, giving the user a clear indication that the sample was prepared well and homogeneously. In addition, the sinusoidal character of the pressure ramps and also the streaming current show that the IEMs are highly stable during the measurement. In view of the often-challenging preparation of a homogeneous sample layer for zeta potential measurements, the bidirectional approach easily reveals any preparative issues that stay unnoticed with unidirectional measurement techniques.

Summary

The ZPA 20 equipped with the plate measuring cell from DataPhysics Instruments reveals the pH-dependent zeta potential of different flat solid surfaces and helps to identify acidic and alkaline surface functionalities. The results determined with the streaming potential and streaming current methodsare consistent and highly reliable. This was demonstrated by obtaining matching IEPs of sample IEM 2 with both methods. The article furthermore showcases the beneficial effects of the bidirectional measurement principle for the verification of good sample preparation and a quick measurement speed compared to established methods.

In summary, the ZPA 20 from DataPhysics Instruments has been proven to be a powerful tool for the development of new ion-exchange membranes.

References

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AppNote/ZPA 20_IEM_4 – 24-6 – 1.0/En
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