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Investigation on overall charged behavior of polyamide nanofiltration membranes by electrokinetic method

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ABSTRACT

In this paper, the overall charged behavior of polyamide nanofiltration membranes, including their skin-layer and support-layer, was explored by electrokinetic method. Based on trans-membrane streaming potentials of two polyamide nanofiltration membranes (NF90 and NF) measured in a given series of electrolyte solutions (NaCl, KCl, $CaCl_2$, Na_2SO_4 and $MgSO_4$), respectively, the corresponding zeta potential and charge density were estimated by means of the Helmholtz–Smoluchowski equation and the Gouy–Chapmann double-electric layer theory. The experimental results show that the factors, such as concentration of electrolyte solution, type and valence of ions, have an important influence on the charged behavior of polyamide nanofiltration membranes. Furthermore, it was also found that the relationship between the charge densities and the feed solution concentration agreed well with Freundlich adsorption isotherms under certain testing conditions. Furthermore, it was confirmed that charge formation of polyamide nanofiltration should be attributed to the specific adsorption of ions.

Keywords: Polyamide nanofiltration membrane; Electrokinetic method; Specific adsorption; Charge densities

1. Introduction

It was widely accepted that a nanofiltration membrane will acquire charges in aqueous phase resulting from specific adsorption and/or functional group dissociation [1–4]. It is the charged properties that play a remarkable role in relevant separation performance. Therefore, from the academic and technological points of view, there has been a wide interest in exploring charged behavior of nanofiltration membranes. For examples, Afonso et al. [5] assessed the tangential streaming potential of nanofiltration membranes (Desal G-10 and Desal G-20) in several electrolyte solutions and found the existence of a relationship of a Freundlich adsorption isotherm between the membrane surface charge and the feed solution concentration. Peeters [6] surveyed the tangential streaming potential of two nanofiltration membranes in several electrolyte solutions and found that the formation of surface charge resulted from anion adsorption and charge densities could be described by Freundlich isotherms. Hall et al. [7] explored charge formation in cellulose acetate reverse osmosis membranes by assuming the membrane charges varying with the electrolyte concentration resulting from cation site-binding. Ariza et al. [8] investigated the tangential streaming potential along the surface of polysulfone membranes and also assumed a heterogeneous specific adsorption of anions

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on the membrane surface (Freundlich isotherms). Obviously, the above mentioned studies all placed emphasis on the charged behavior of the membrane surface which played an important role in separation performance by the tangential electrokinetic method.

Actually, the separation performance of nanofiltration membranes should also be influenced by the charged behavior of pore surface to a certain extent, including membrane skin-layer as well as membrane supported-layer. Consequently, it is necessary to grasp the overall charged behavior of nanofiltration membrane in relevant separation systems. In this work, nanofiltration membrane was viewed as an array of charged pores and its overall charged behavior was evaluated tentatively by means of the trans-membrane electrokinetic method. Obviously, for a nanofiltration membrane, there are some potential problems to limit the use of the trans-membrane mode such as the possible appearance of an electrical double layer overlapping in pores and diffusion potential resulting from salt retention. Accordingly, in this work, the electrolyte solution with relatively high concentration was adopted, which corresponds to the relatively small Debye length. Furthermore, according to the cursory estimation, the contribution of the diffusion potential ($\Delta E_d = (RT/F)\ [(t^+/z^+) + (t^-/z^-)]\ \ln (C'/C'')$) to the overall potential difference was no more than 5% for the nanofiltration membranes characterized by NaCl in the preliminary experiments. Therefore, it may be acceptable in this study to take advantage of the trans-membrane mode to investigate the overall charged behavior of the nanofiltration membranes.

2. Experimental

2.1. Membranes and solutions

In order to investigate the charged behavior of polyamide nanofiltration membranes, two commercial composite membranes were selected, whose main characteristics are shown in Table 1.

Experiments were carried out at a constant temperature (25±0.5°C) and at natural pH (6.5±0.1). Electrolyte solutions were prepared by dissolving NaCl, KCl, $CaCl_2$, Na_2SO_4 and $MgSO_4$ (analytical grade) in deionized water produced by reverse osmosis (RO) followed by electrodeionisation (EDI). The range of concentration of the solutions was from 0.01 mol·L^{-1} to 0.30 mol·L^{-1}.

2.2. Experimental equipment and procedure

Fig. 1 is a schematic view of the experimental setup used for the streaming potential measurement. The membrane was equilibrated in the test solution for about 12 h and mounted in the cell. Each compartment was filled with 260 ml electrolyte solution stirred vigorously by a magnetic stirrer in order to lessen the concentration polarization. The trans-membrane pressure was adjusted from 0.05 to 0.45 MPa by regulating the volume of nitrogen gas. Generally, the streaming potential would result when the electrolyte solution was forced through membrane pores. The cell was equipped with two commercial Hg/Hg_2Cl_2 electrodes (Rex, Shanghai Precision and Scientific Instrument Co., Ltd.) which were placed on each side of the membrane sample and linked with a multimeter (Victor, model VC890D) to measure the corresponding streaming potential (ΔE). The impendence of the multimeter is 10 MΩ. In this work, with respect to every specific experimental system, all the measurements were carried out three times at least.

The zeta potential (ζ), the electrokinetic potential at the hydrodynamic plane of shear, is an important and reliable indicator for the distribution of the membrane surface charge. Relevant information is beneficial for the design and operation of membrane processes [9–12]. Usually, the

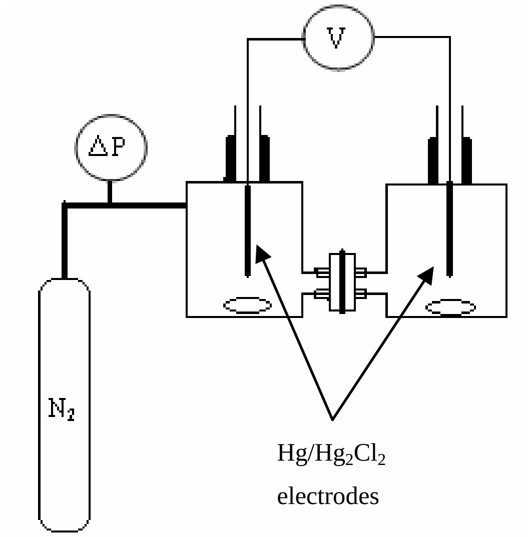

Fig. 1. Apparatus for transmembrane streaming potential measurements.

Table 1
Overview of studied membrane samples

Membrane	Manufacture	Membrane material		MWCO (estimated)
		Skin layer	Support layer	
NF90	DOW Filmtech	Polyamide	PSF	300
NF	DOW Filmtech	Polypiperazineamide	PSF	400

ζ potential can be correlated with the streaming potential through the Helmholtz–Smoluchowski equation [13,14]:

$$\zeta = \frac{\dfrac{d(\Delta E)}{d(\Delta P)}\mu\kappa}{\varepsilon_0\varepsilon_r} \tag{1}$$

where ε is the dielectric constant of water (78.5 at 25°C); ε_o is the vacuum permittivity (8.854×10^{-12} C/m·V); μ is the solution viscosity (kg/m·s); κ is the electrolyte solution conductivity (s/m); ΔE is the streaming potential (V); P is the applied pressure (Pa).

The membrane volume charge density is determined according to the Gouy–Chapmann double-electric layer theory [3,15]:

$$\sigma = \left\{2\varepsilon_r\varepsilon_0\kappa_B T\sum_i C_i N_A\left[\exp\left(-\frac{z_i e\zeta}{k_B T}\right)-1\right]\right\}^{0.5} \tag{2}$$

where σ is the electrical charge density on the membrane/electrolyte interface (C·m^{-2}); κ_B is the Boltzmann constant (1.3806×10^{-23} J·K^{-1}); C_i is the concentration of ion i in the salt solution (mol·L^{-1}); N_A is the Avogadro constant (6.022×10^{23} mol^{-1}); z_i is the valence of ion i (± eq/mol); e is the electronic charge (1.6022×10^{-19} C); T is the absolute temperature (K).

3. Results and discussion

3.1. Variation of streaming potential with concentration

As shown in Figs. 2 and 3, the streaming potential (ΔE) was almost directly proportional to the hydraulic pressure difference (ΔP) across the membrane in any single salt solution with a certain concentration. From the slopes of the lines ($\Delta E \sim \Delta P$), it could be concluded that the membranes were apt to be negatively charged in the electrolyte solution except some special electrolytes (for example, $CaCl_2$). Moreover, according to the slopes displayed in a given series of salt solutions with the same salt type and different concentrations from 0.01 mol·L^{-1} to 0.30 mol·L^{-1}, it was also found that the streaming potential decreased when the electrolyte concentration increased. Generally, a higher electrolyte concentration was propitious to the presence of counter-ions in the compact layer where ions bind to the surface. So, surface charges were screened in part, which resulted in a relatively weak streaming potential. Whereas at a lower electrolyte concentration, the pore surface charge was less neutralized and resulted in the existence of more counter-ions in the diffuse layer and then a relatively high streaming potential came into being [16]. Similarly, the phenomena mentioned above had also been observed by others [10,17]. In the case of

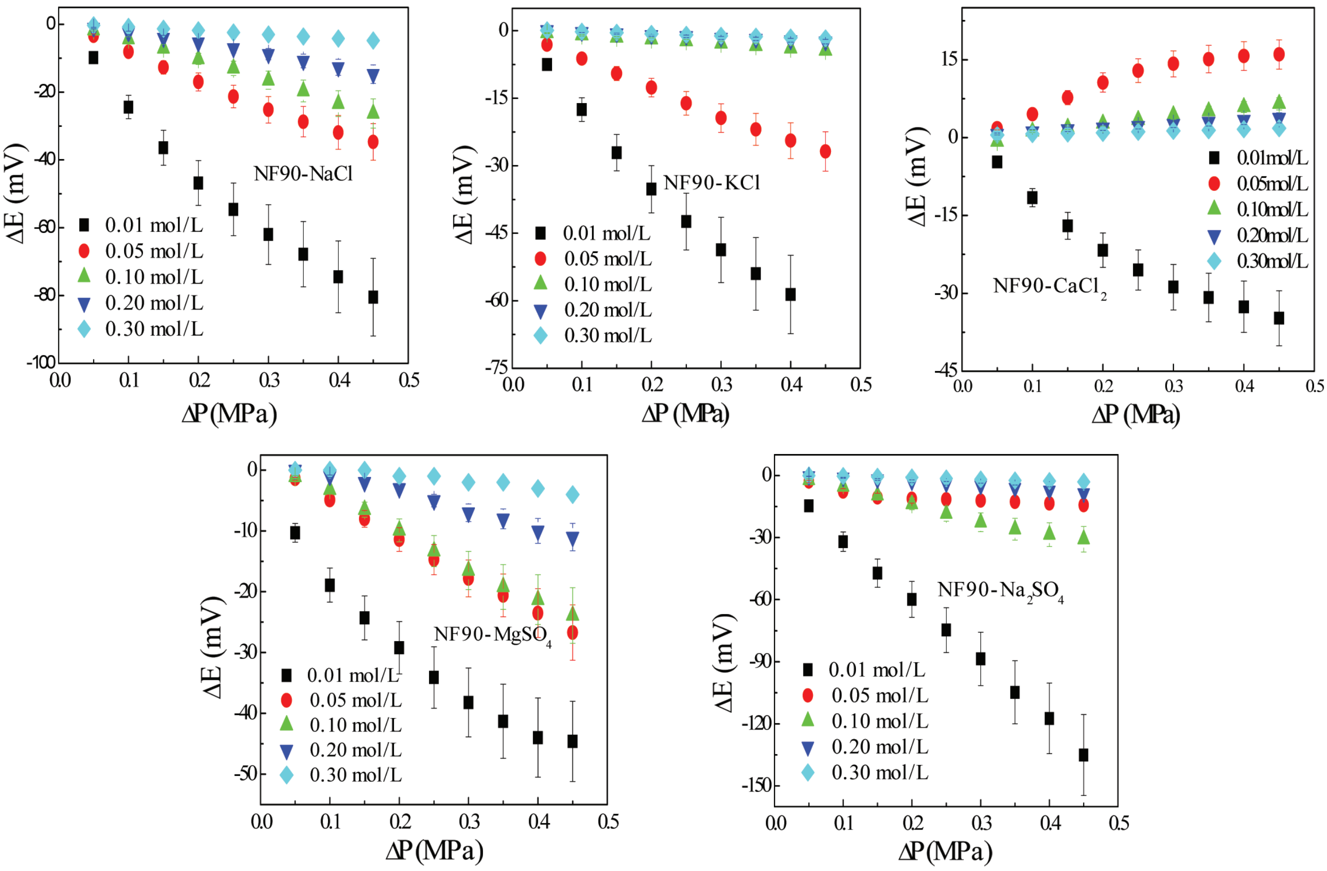

Fig. 2. Streaming potentials of NF-90 membrane as a function of the applied pressures measured in different electrolyte solutions.

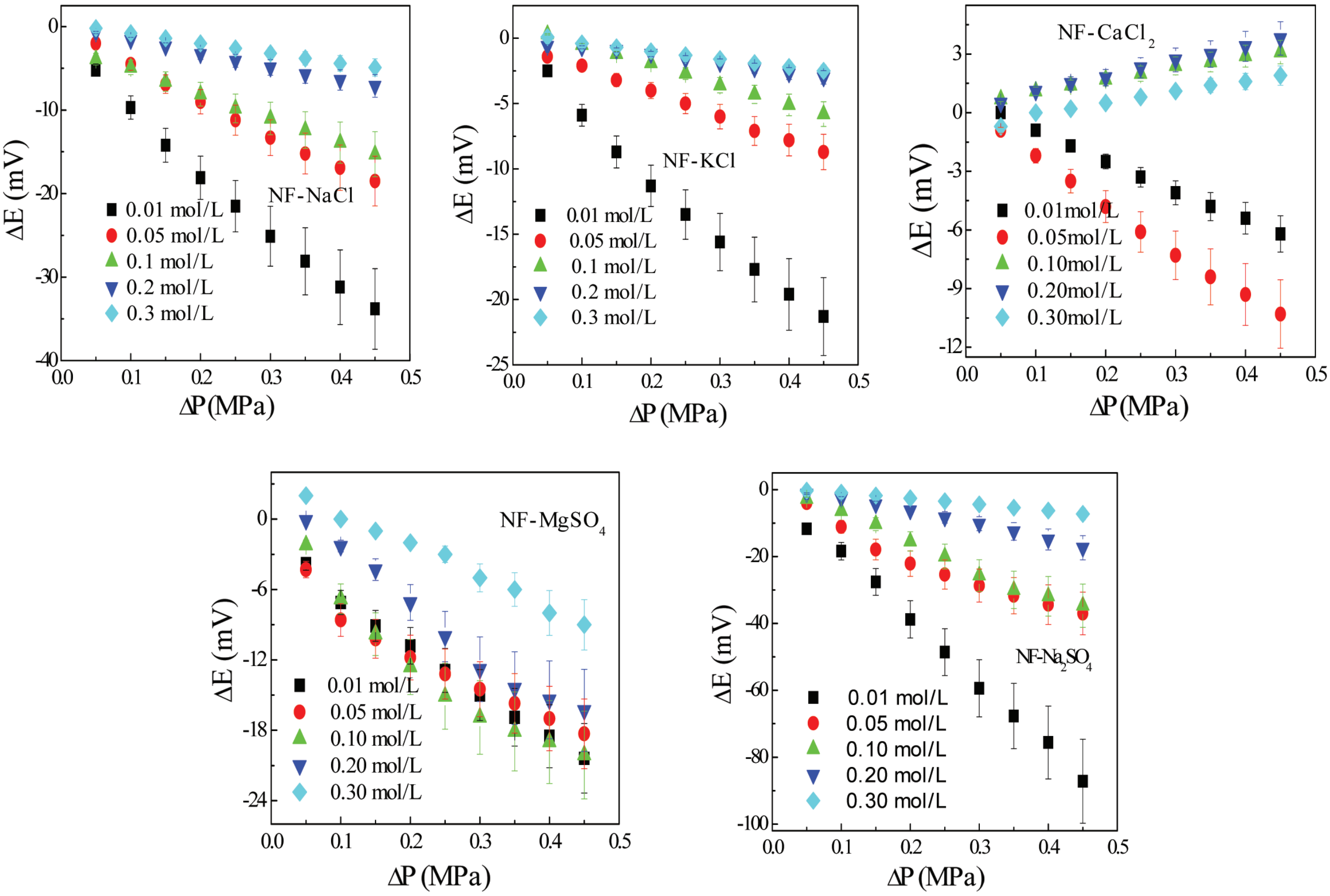

Fig. 3. Streaming potentials of NF membrane as a function of the applied pressures measured in different electrolyte solutions.

$CaCl_2$ solution, the streaming potentials were negative at a low concentration and switched to positive as the concentration increased. It was likely to be due to the specific adsorption of divalent cations, Ca^{2+}. At the low concentration, the adsorption of calcium ions was less than that of anions which resulted in the weak screening effect of counter-ions. With the concentration increased, the pore surface charge was neutralized and reversed sign due to the existence of more calcium ions in the diffuse layer. Therefore, the specific adsorption of divalent cations on the membrane had a remarkable influence on its charged behavior.

3.2. *Variation of zeta potential with concentration*

Figs. 4 and 5 show the zeta potentials of the membrane samples found in different electrolyte solutions which were calculated from the corresponding streaming potentials according to the Helmholtz–Smoluchowski equation [Eq. (1)].The relevant zeta potentials obtained in a given series of electrolyte solutions with the same anion (chloride ion) and different cations (potassium ion and calcium ion) are displayed in Fig. 4. In the case of KCl solution, the zeta potentials were always negative and took on a relative weak change as the increase of concentration in the studied concentration range. However, in the case of $CaCl_2$ solution, the zeta potentials were negative at a low concentration and switched to positive as the concentration increased. It was most probably due to the specific adsorption of divalent cations, Ca^{2+}. Calcium ions could penetrate into the compact layer to reach the internal Helmholtz plane by losing part of their hydration sphere and neutralized in part the negative charge because of its valence. This could even reverse the sign of the zeta potential [18]. Thus, it is obvious that the specific adsorption of cations on the membrane has a remarkable influence on its charged behavior.

As such, the relevant zeta potentials induced in a given series of electrolyte solutions were also obtained to explore the influence of anions on charged behavior of the membrane samples. It is seen clearly from Fig. 5 that the magnitude of the zeta potential increased first and then decreased with the increase of electrolyte concentration. That is to say, there existed a certain concentration in which the maximum magnitude of zeta potential was obtained. However, in general, the bulk solution is closer to the membrane surface as concentration increases. Accordingly, zeta potential determined at a fixed

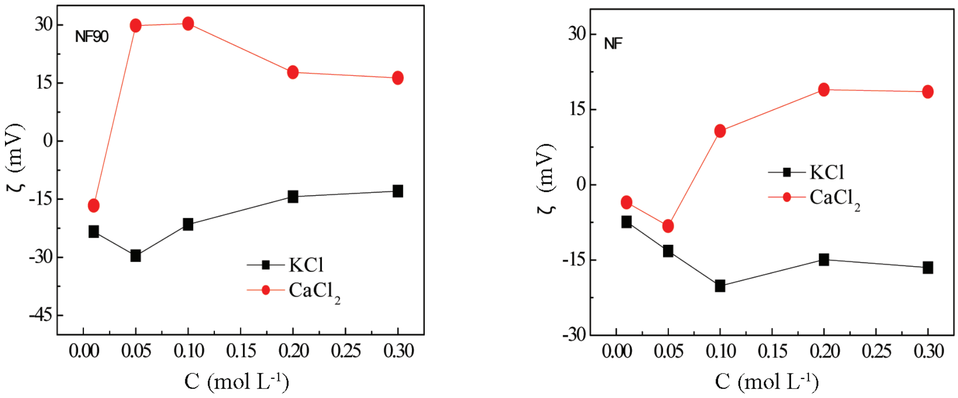

Fig. 4. Influence of KCl and $CaCl_2$ on zeta potential of NF90 and NF membranes.

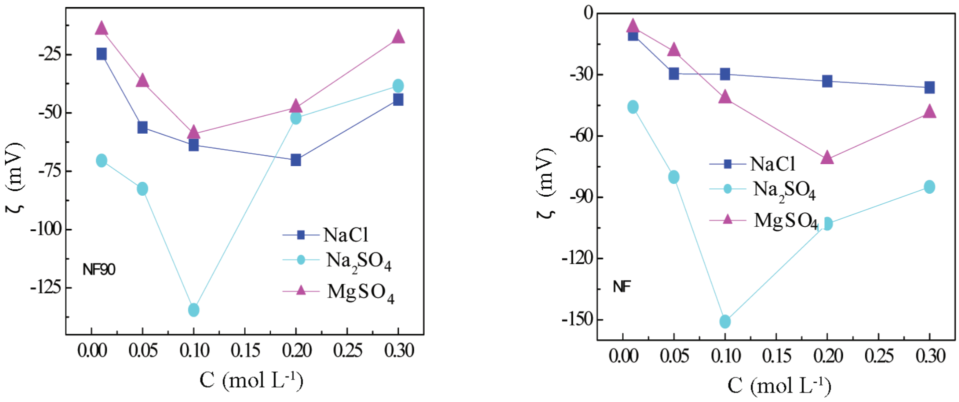

Fig. 5. Influence of NaCl, Na_2SO_4 and $MgSO_4$ on zeta potential of NF90 and NF membranes.

distance from the membrane surface will decrease. The "abnormal" phenomena observed in this work might be concerned with available adsorption sites of membrane pores and shield effect of counter-ions. At a low concentration, the proportion of available adsorption sites to a number of species in the bulk solution was high. In this concentration range, the membrane charged state would be strengthened along with the increase of bulk concentration. On the other hand, the amount of sites available for adsorption decreased as the bulk concentration increased. Moreover, the shield effect of counter-ions must also be attached importance with the increase of bulk concentration. The superfluous counter-ions in the pore surface vicinity partially screened the charge of the co-ions previously adsorbed on the membrane pore surface, which resulted in the decrease of zeta potential. In addition, it was also found that the zeta potential values obtained in sodium sulphate were always higher than those in sodium chloride and magnesium sulphate for every membrane sample. These might be resulted from the difference in the ability to adsorption (for SO_4^{2-} and Cl^-) and in the shield effect of counter-ions (for Mg^{2+} and Na^+). These results are in good agreement with the conclusion reported by Cavaco Morão et al. [19] in which the mechanism of charge formation on the membrane was elucidated based on the ion specific adsorption and displayed that the chemistry and concentration of the electrolyte solutions played an important role in the membrane electrokinetic properties.

3.3. Variation of volume charge density with concentration

The volume charge density of both membranes calculated from their corresponding zeta potentials according to the Gouy–Chapmann double-electric layers theory [Eq. (2)] are shown in Fig. 6. As can be seen from Fig. 6, the influence of the solution concentration (C_f) on the volume charge density (σ) was weaker for NaCl, KCl and $CaCl_2$ solution than that for $MgSO_4$ and Na_2SO_4 solutions. Moreover, for $MgSO_4$ and Na_2SO_4 solutions, the membrane samples embraced the maximum charge density at a certain solution concentration. This was due to the specific adsorption of the divalent anions (SO_4^{2-}) mentioned above. As for the effect of the salt nature, the magnitude of σ followed the order: $Na_2SO_4 > MgSO_4 > CaCl_2 > NaCl$

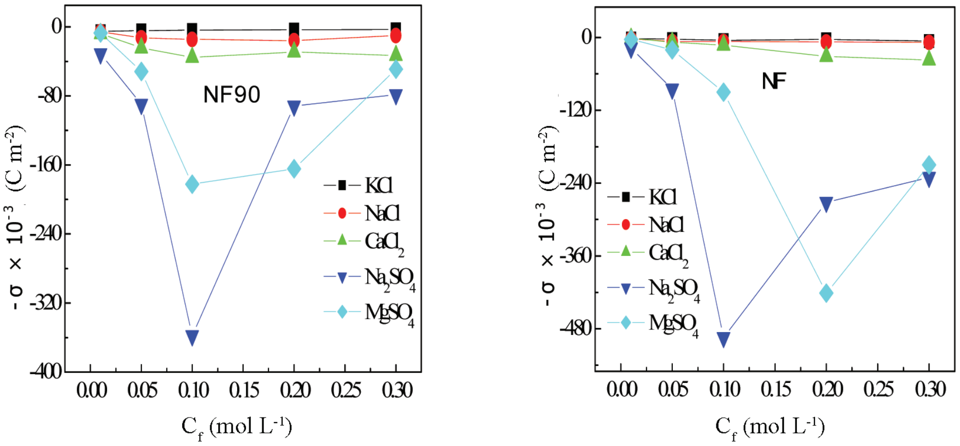

Fig. 6. Effect of salt concentration and nature on membrane charge density of NF90 and NF membranes.

> KCl. Obviously, the electrokinetic phenomenon of the studied membrane samples was dominated by the specific adsorption of ions, especially the bivalent anions.

It can be seen clearly from Fig. 6 that the magnitude of σ for NF was always higher than that of NF90. In addition, the plot of σ vs. C_f shows a curvilinear shape and the straight lines can be obtained by plotting these data in a ln–ln graphic with a correlation coefficient, *R*, approximate to unity (Tables 2 and 3). Thus, it appeared that the membrane pore surface charge could be correlated with the feed concentration in terms of a Freundlich isotherm:

$$\ln|\sigma| = a + b\ln C \quad (3)$$

where the parameters *a* and *b* depend on the electrolyte nature. Moreover, the slope of the straight line b is predicted by the equation found in: $b = (\theta_C Z_C)^{Z_C}/2$, where Z_c is the cation valence (eq/mol) and θ_C is the number of cation moles per mole of dissociated salt (mol/mol) [20].

Several researchers had reported the existence of a linear logarithmic correlation between σ calculated from the tangential streaming potential and C_f. For examples, Petropoulos et al. [21] found that the electrolyte concentration (NaCl) played a crucial role in the fixed charge density of weakly charged membranes prepared from regenerated cellulose. By plotting log σ vs. log C_f, the authors acquired straight lines with slopes ranging from 0.56 to 0.61. Bowen and Mukhtar [22,23] simulated the transport of single solutions of NaCl and Na_2SO_4 with different concentrations for six nanofiltration membranes. They also achieved straight lines for different single salt solutions (NaCl and Na_2SO_4) by plotting log σ vs. log C_f, whose slopes ranged from 0.499 to 0.875 for different experimental systems. Afonso et al. [24] surveyed the electrokinetic phenomenon of nanofiltration membranes in different electrolyte solutions and also observed the fact that the relation between the membrane surface charge vs. feed concentration could be depicted by Freundlich adsorption isotherms whose slope ranged from 0.475 to 0.527. In this work, a linear logarithmic correlation between the overall charge density calculated from the trans-membrane streaming potential and electrolyte solution concentration was also obtained, as shown in Fig. 7. That is to say, the membrane overall charge density of the two membranes could also be related to the feed concentration in terms of Freundlich adsorption isotherms. Therefore, it was confirmed that the charge formation of the studied membrane samples (NF and NF90) resulted from the specific adsorption of ions [3,25].

Table 2
Parameters of Freundlich adsorption isotherms in different electrolyte solutions for the NF90 membrane

Electrolyte solution	*a*	*b*	*R*
KCl	2.111	–0.173	0.985
NaCl	1.143	0.311	0.946
$CaCl_2$	1.268	0.427	0.906
Na_2SO_4	1.027	0.992	0.956
$MgSO_4$	–1.301	1.386	0.996

Table 3
Parameters of Freundlich adsorption isotherms in different electrolyte solutions for the NF membrane

Electrolyte solution	*a*	*b*	*R*
KCl	–0.178	0.324	0.905
NaCl	0.215	0.355	0.928
$CaCl_2$	–1.852	0.975	0.997
Na_2SO_4	–0.423	1.365	0.968
$MgSO_4$	–2.159	1.400	0.988

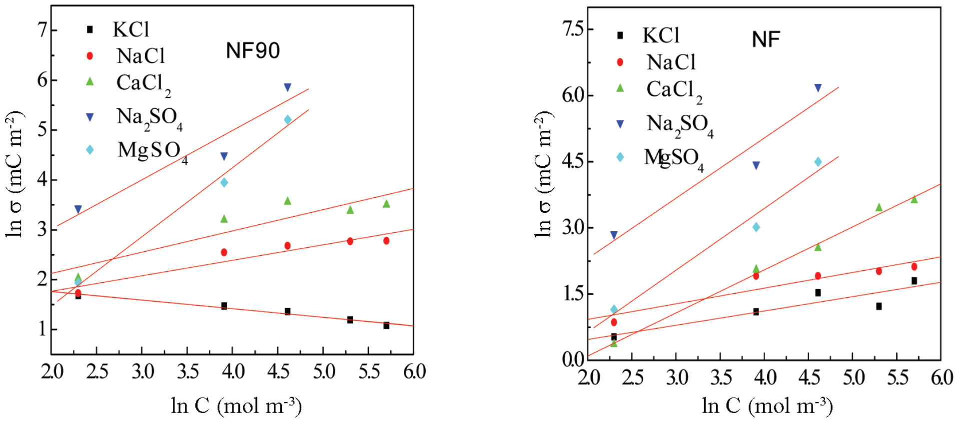

Fig. 7. ln–ln plot of the membrane charge density vs. electrolyte concentration for the NF90 and NF membranes.

4. Conclusions

In this work, an investigation of the overall charged behavior of the two polyamide nanofiltration membranes (NF90 and NF) by trans-membrane streaming potential measurements was carried out. The experimental results showed that the factors, such as concentrations of electrolyte solutions, the types and the valences of ions, had a important influence on the overall charged behavior of the nanofiltration membranes. Moreover, it was found that the relationship of the overall charge density of NF90 and NF membranes and the feed solution concentration can also be depicted by the Freundlich absorption isotherms:

$$\ln|\sigma| = a + b\ln C\,.$$

for KCl solution:

$$\ln|\sigma|\left(\mathrm{mc}\cdot\mathrm{m}^{-2}\right) = 2.111 - 0.173\ln C\left(\mathrm{mol}\cdot\mathrm{m}^{-3}\right),$$

$$\ln|\sigma|\left(\mathrm{mc}\cdot\mathrm{m}^{-2}\right) = -0.178 + 0.324\ln C\left(\mathrm{mol}\cdot\mathrm{m}^{-3}\right);$$

for NaCl solution:

$$\ln|\sigma|\left(\mathrm{mc}\cdot\mathrm{m}^{-2}\right) = 1.143 + 0.311\ln C\left(\mathrm{mol}\cdot\mathrm{m}^{-3}\right),$$

$$\ln|\sigma|\left(\mathrm{mc}\cdot\mathrm{m}^{-2}\right) = 0.215 + 0.355\ln C\left(\mathrm{mol}\cdot\mathrm{m}^{-3}\right);$$

for $CaCl_2$ solution:

$$\ln|\sigma|\left(\mathrm{mc}\cdot\mathrm{m}^{-2}\right) = 1.268 + 0.427\ln C\left(\mathrm{mol}\cdot\mathrm{m}^{-3}\right),$$

$$\ln|\sigma|\left(\mathrm{mc}\cdot\mathrm{m}^{-2}\right) = -1.852 + 0.975\ln C\left(\mathrm{mol}\cdot\mathrm{m}^{-3}\right);$$

for Na_2SO_4 solution:

$$\ln|\sigma|\left(\mathrm{mc}\cdot\mathrm{m}^{-2}\right) = 1.027 + 0.992\ln C\left(\mathrm{mol}\cdot\mathrm{m}^{-3}\right),$$

$$\ln|\sigma|\left(\mathrm{mc}\cdot\mathrm{m}^{-2}\right) = -0.423 + 1.365\ln C\left(\mathrm{mol}\cdot\mathrm{m}^{-3}\right);$$

for $MgSO_4$ solution:

$$\ln|\sigma|\left(\mathrm{mc}\cdot\mathrm{m}^{-2}\right) = -1.301 + 1.386\ln C\left(\mathrm{mol}\cdot\mathrm{m}^{-3}\right),$$
$$\ln|\sigma|\left(\mathrm{mc}\cdot\mathrm{m}^{-2}\right) = -2.159 + 1.400\ln C\left(\mathrm{mol}\cdot\mathrm{m}^{-3}\right).$$

Therefore, it was further confirmed that charge formation of polyamide nanofiltration membranes should be attributed to the specific adsorption of ions.

Acknowledgements

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