Chinese Journal of Chemical Engineering 24 (2016) 345–352

Contents lists available at ScienceDirect

Chinese Journal of Chemical Engineering

journal homepage: www.elsevier.com/locate/CJChE

Separation Science and Engineering

The effect of cation–π interactions in electrolyte/organic nanofiltration systems

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A R T I C L E I N F O

Article history:
Received 12 April 2015
Received in revised form 17 August 2015
Accepted 31 August 2015
Available online 10 November 2015

Keywords:
Nanofiltration
Cation–π interaction
Dehydration
Steric effect

A B S T R A C T

The rejection properties of a nanofiltration organic membrane were investigated using KCl solutions, NaCl solutions, NaCl/benzyl alcohol hybrid solutions and KCl/benzyl alcohol hybrid solutions. The presence of benzyl alcohol ($3.7\ \mathrm{mol\cdot m^{-3}}$) caused a decrease in electrolyte rejection within the range of 0 to 6%. The mechanism of the decrease was discussed. The cation–π bond was assumed to form in the hybrid solution and to further induce the partial dehydration of the cation. The steric and charge density inhibition of the salt activity was strengthened, and the salt rejection was thus decreased. A simulation was performed to evaluate the radius of the cation.

1. Introduction

Numerous works published in recent years have been pointed out nanofiltration (NF) technology as a downstream operation in organic acid production process is expected to be a large application field [1–4]. Organic acids are mainly produced by fermentation, which generates a broth containing the dissociated form of the acid and different impurities, such as mineral salts. However, the coexistence of salts and organic matter (OM) in NF usually causes the rejection of both of them to decrease in an obvious manner (especially in the system of π bonds contained organics and mineral salts [5]). The following proposals were suggested to explain these decreases, and the main points were summarized:

(1) The partial dehydration of the OM occurs in the presence of salts (*i.e.*, the Hofmeister effect) [5–8]. The smaller effective OM volume leads to increasing transfer through the pores of the membrane.
(2) More counterions converge in the membrane pores as the bulk salt concentration increases. The electrical double layer at the intrapore wall is thus compressed, resulting in stronger electrostatic repulsion (*i.e.*, the swelling effect) [5,6]. The expanded pores let the salt pass through easily.
(3) A membrane pore size distribution exists. When the solute concentration is high enough, the solute flux through the small pores decreases and can even become blocked (*i.e.*, the electroviscous effect) [9], which leads to an increase in the average pore size and a decrease in the steric effect.
(4) The viscosity at the membrane surface increases with the OM concentration. The back diffusion in the polarization layer is hindered [10], which results in a higher membrane surface concentration and a lower solute retention (for both the OM and the salt, if they coexist).
(5) If the functional group in the OM tends to polarize, the OM interacts with the charged membrane. The OM retention is then affected by the charge properties of both the membrane charge and the OM [11,12].

The above proposals can be categorized as follows:

(1) The effects of salting-out, pore swelling and electroviscosity reduce the OM rejection; these phenomena require a higher electrolyte concentration.
(2) The rejection change, which is caused by viscosity, is related mainly to the differences between forward diffusion and back diffusion. There seems to be a critical viscosity below which the retention is barely dependent on the organic concentration.
(3) The electrical effect, which is pronounced in the presence of OM, is weak on the membrane. Therefore, the negative rejection of the organics should be small enough that it can be ignored.

As indicated above, changes in solute rejection under conditions of low salt concentration and unaltered viscosity solutions are worth discussing. In addition, a previous report suggested that in sodium lactate (NaLac)/glucose solutions, the rejection of NaLac changed (2%–20%) [5]. However, in the previous study, the changes in OM rejection in the NF system were their primary target, so they did not take the changes in the NaLac rejection into consideration.

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http://dx.doi.org/10.1016/j.cjche.2015.11.004
1004-9541/

In this article, we suggest that the change in NaLac rejection cannot be ignored. This change in the NaLac rejection is the emphasis of the research into this phenomenon. Lactate is a type of carboxylate radical that contains the hydroxyl group; the three sp^2 hybrid orbitals combine with two oxygen atoms and one carbon atom, ultimately generating three σ bonds. The p orbital that does not participate in the orbital hybridization combines with another p orbital on the membrane to form a π bond, and the p orbital of the oxygen atom in the hydroxyl, which consists of the unshared electron pair, can p-π-conjugate with the π-bond on the carbonyl. Therefore, the phenomenon that occurred in report [5] might be the result of a cation–π interaction that occurred between Na^+ and Lac^-. Cation–π interactions are a type of electrostatic attraction between a cation and a large π bond. The six (four) $C^{\delta-}$–$H^{\delta+}$ bond dipoles of certain molecules such as benzene (ethylene) combine to produce a region of negative electrostatic potential on the surface of the π system. Simple electrostatics facilitates the natural attraction of cations to the surface [13–15]. Because the p-π-conjugate occurs in Lac^-, this effect enhances the interactions between the cation and the large π bond. Previous research showed that cation–π interactions in aqueous salt solutions can be characterized based on the ^{2}H nuclear magnetic resonance (NMR) spin-lattice relaxation time [16], so the existence of cation–pi interactions in solutions is unquestionable. In previous cases, when glucose was added, Na^+ would partially participate in the Hofmeister effect with glucose, which disrupts the original interaction balance of a single component system and leads to a large change in the rejection of NaLac.

In this study, experiments were used to demonstrate these assumptions. Therefore, we reasonably simplified the experiments: the NF systems consist of benzyl alcohol-KCl or benzyl alcohol-NaCl solutions. The rationale for the simplification consists of two parts: first, benzyl alcohol is soluble and forms a π bond in aqueous solution; second, in aqueous environments, due to the lower solvation energy of the alkali, the screening effect of the hydration shell is weaker than the screening effect of the other multivalent cations. As previously reported [13–15], K^+ and Na^+ can form a relatively strong cation–π interaction with OM.

In specific experiments, other factors have been added to analyze the influence of these factors, and the rejection differences of the electrolyte between these two systems should not be ignored. In this research, the velocity variation method (VVM) was used to extrapolate the rejection from observed rejection to intrinsic rejection. We also use the DSPM-DE model to program and fit the intrinsic rejection of KCl. Using these methods, the changes in the Stokes radius of an ion can be calculated and used for demonstration purposes. Finally, we concluded that both the steric effects and charge densities of the electrolytes (which are generated by the dehydration of the cation) are important.

2. Theory

2.1. Model description

The DSPM-DE model [17] was used here to model the rejection decrease of KCl. However, the variations in the steric and electrical effects, which are caused by the changes in the radius of the cation, are the main reasons for the change in KCl rejection in mixed solutions. Therefore, this model cannot be used accurately to fit multiple experimental points in mixed solutions because there is only one experimental point corresponding to one value for the steric and electrical effects. So the best way to fitting experimental points in this situation should coupling use DSPM-DE model and quadratic criterion, which required five steps:

1. The parameter r_p was determined from glucose real retention which would be discussed in Section 4.1; $r_{i,s}(0)$ in this step was fixed, which value is 0.125 nm.
2. DSPM-DE model was utilized to regression analysis the rejection data for KCl in pure KCl solutions to obtain $X_d(0)$.
3. Values of $X_d(0)$ were fixed in mixed solutions which were obtained from step 2, then the parameter $r_{i,s}(1)$ was adjusted to fulfill the minimum result of Eq. (1).
4. Fix $r_{i,s}(1)$ which was determined from step 3, then DSPM-DE model was repeatedly used in regression analysis the rejection data of KCl in mixed solutions to obtain $X_d(1)$. Eq. (1) was reused to fit a line and determine the minimum value.
5. Steps 2 and 3 were repeatedly used until $X_d(n\text{-}1) - X_d(n) \le 0.01$ and $r_{i,s}(n) - r_{i,s}(n\text{-}1) \le 0.001$.

$$Q = \frac{1}{m \times n} \sum_{1}^{m} \sum_{1}^{n} \left(R_{i,\exp} - R_{i,\mathrm{mod}}\right)^2 \tag{1}$$

where Q is the quadratic criterion, n is the number of experimental points and m is the number of ions. $R_{i,\mathrm{exp}}$ and $R_{i,\mathrm{mod}}$ are the experimentally obtained real rejections (*via* the VVM) and the values predicted by the model, respectively.

The variation in the average pore dielectric constant was estimated as proposed by Bowen and Welfoot [18]:

$$\varepsilon_p = 80 - 2(80 - \varepsilon^*)\left(\frac{d}{r_p}\right) + (80 - \varepsilon^*)\left(\frac{d}{r_p}\right)^2. \tag{2}$$

The use of the above equation implies that the pores consisted of one layer of oriented water molecules where the dielectric constant at the pore wall approached the high frequency limit of the dielectric constant.

The Stokes–Einstein equation follows:

$$D_i = \frac{RT}{6\pi\eta r_s N_A} \tag{3}$$

where D_i is the diffusion coefficient of the ion, r_s is the Stokes radius, η is the dynamic viscosity, and N_A is the Avogadro constant.

In low concentration solutions, because co-ion adsorption does not dominate the Donnan effect, the change in the Stokes radius of a cation also affects its concentration in the membrane [28], and the increased value of the membrane charge density (X_d) can be described as follows:

$$\sum_{i=1}^{n} z_i c_i = -X_d \tag{4}$$

2.2. Concentration polarization

Because we consider only the situation of single salts, the calculation of $c_{i,w}$ in both charged and uncharged nanofiltration systems utilizes the velocity variation method (VVM) [19,20], which extrapolates observed rejections to real rejections. It is expressed as follows:

$$R_{i,\mathrm{real}} = \frac{R_{i,\mathrm{obs}} \exp(J_v/k))}{1 - R_{i,\mathrm{obs}}(1 - \exp(J_v/k))} \tag{5}$$

$$R_{i,\mathrm{obs}} = 1 - \frac{c_{i,p}}{c_{i,f}} \tag{6}$$

$$c_{i,w} = \frac{c_{i,p}}{1 - R_{i,\mathrm{real}}}. \tag{7}$$

In Eq. (5), to calculate the real rejection, the method consists of determining the observed rejection $R_{i,\mathrm{obs}}$ for various increasing tangential velocities and extrapolating these values to infinity. The obtained limit value is the real rejection $R_{i,\mathrm{real}}$ that would correspond to a virtual situation where no polarization layer exists (that is, $c_{i,w}$