

The Production of Citric Acid Using Electrodialysis with Bipolar Membrane of Sodium Citrate Solutions

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Abstract

Investigations on sodium citrate conversion to citric acid by the pure electrodialysis process with bipolar membrane were carried out. The current efficiencies based on the number of moles of produced acid and on the concentration changes were determined. Both the mean and the instantaneous efficiencies were calculated. It was found that the mean efficiencies of acid and base are higher at the lowest current densities (52 mA/cm²), with the maximum being observed at 78 mA/cm² for the highest initial salt concentration (1.4 mol/dm³). Higher initial sodium citrate concentration in the salt circuit increases the process efficiency. In the case of low initial salt concentrations, as the process progresses, acid instantaneous efficiency, CE_a , decreases with time. For $c_s = 1$ mol/dm³ it is practically constant, and for higher salt concentrations they even grow. In the case of the highest investigated current density (104 mA/cm²), the opposite situation was observed; that is, the CE_a decreases with time for the higher salt concentration $c_s = 1.3$ mol/dm³.

Keywords: citric acid, electrodialysis, bipolar membrane, current efficiency

Introduction

Due to its buffering and complex-forming properties as well as its pleasant sour flavor and low toxicity, citric acid is widely used in the production of food, alcoholic and non-alcoholic beverages and in oil manufacture, pharmaceutical, metallurgical, chemical, cosmetics, textile, tobacco, plastics, plating industries and many others. The world demand for citric acid has shown a high rate of increase at 7%. At present, the total world production of citric acid and its calcium, sodium, potassium, and magnesium salts amounts to about 1 million tons per year [1, 2].

Citric acid is mainly obtained from saccharose or molasses by means of microbiological fermentation by the selected moulds *Aspergillus niger* [3-5]. In order to recover acid from the fermentation broth, calcium citrate is precipi-

tated with lime milk, and thus obtained precipitate is treated with sulfuric acid. Apart from the main product – citric acid – calcium sulfate is also produced. This waste, harmful to the natural environment, is produced at the ratio of 2.5 tons of gypsum per 1 ton of anhydrous citric acid [6].

In order to decrease the amount of wastes and sewage, attempts have been made to find environmentally-friendly technologies, that will not produce harmful wastes stored at waste dumps [7]. One such method is the electrodialysis with bipolar membrane - an alternative to the conventional method of obtaining citric acid [8, 9]. In that process the conversion of sodium citrate to citric acid and sodium base is conducted using energy and ion-exchange membranes [10-18].

The following membrane arrangements have been tested by other authors: A-C-BP-A-C, C-BP-C, BP-A-C-BP [13], BP-C-BP-C-BP [16], C-BP-A-C-BP-A-C, C-BP-C-BP-C [17], C-BP-A [18], where BP, A, C denote bipolar, anion-, cation-exchange membrane, respectively. In this work the

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BP-A-C membrane arrangement will be tested (Fig.1). The influence of the selected process parameters (current density, concentration of salt solution) on the efficiency of citric acid production will be investigated. Compared to other authors the process will be conducted to the higher values of $n_F/n_{s,0}$, where n_F is the number of moles of charge passed through the system, $n_{s,0}$ was the initial number of moles of sodium citrate to be converted. Both the mean and the instantaneous efficiencies of process will be determined. The influence of water transport on instantaneous efficiency will be shown.

Material and Methods

The investigations on sodium citrate conversion to citric acid and sodium hydroxide were carried out us-

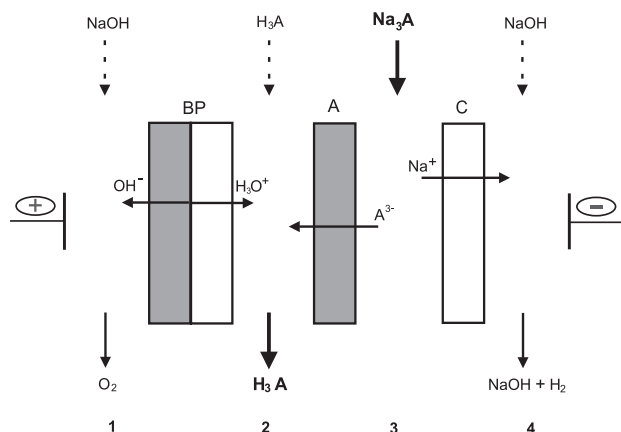
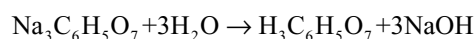


Fig. 1. Sodium citrate conversion (Na_3A) to citric acid (H_3A) – the BP-A-C arrangement of membranes; BP – bipolar membrane, A – anion-exchange membrane, C – cation-exchange membrane; 1, 2, 3, 4 – electrolysers compartments.

ing the laboratory electrolysers TS001 by FumaTech GmbH, Germany. The electrolysers consisted of four independent liquid circuits: acid (2), salt (3) and electrode solutions (1, 4) (Fig.1). In the electric field citrate anions migrate through an anion-exchange membrane from compartment 3 to compartment 2. Hydrogen ions, created in a bipolar membrane, are directed to the same compartment, which results in the citric acid production in compartment 2. The following equation presents the summary reaction:



Each circuit of electrolyte comprised a thermostated tank of solution, a pump, and a flowmeter. The stack was made of polypropylene and was equipped with platinized titanium electrodes. The process was carried out galvanostatically using a constant current power supply (Sorensen 9B2M2, AG Technology, USA). Neosepta membranes (Tokuyama Corp., Japan) were used. The effective area per membrane was 50 cm^2 . The inter-membrane space was 8 mm thick. The chemical reagents were purchased from POCh S.A. (Poland).

In all the experiments the initial values of citric acid (compartment 2) and sodium hydroxide (compartment 4) concentrations amounted to about 0.1 mol/dm^3 . The concentrations of sodium citrate amounted to 0.6; 1; 1.3 and 1.4 mol/dm^3 , while that of NaOH was 0.1 mol/dm^3 . The volumes of acid and base solutions were: 2 dm^3 in experiment No. 1, 1 dm^3 in other experiments (Table 1). All solutions were pumped at the speed of $100 \text{ dm}^3/\text{h}$. The experiments were conducted at the constant current densities: 52, 78, and 104 mA/cm^2 . The citric acid and sodium base concentrations were determined using potentiometric titration (Titrino 731GP, Metrohm).

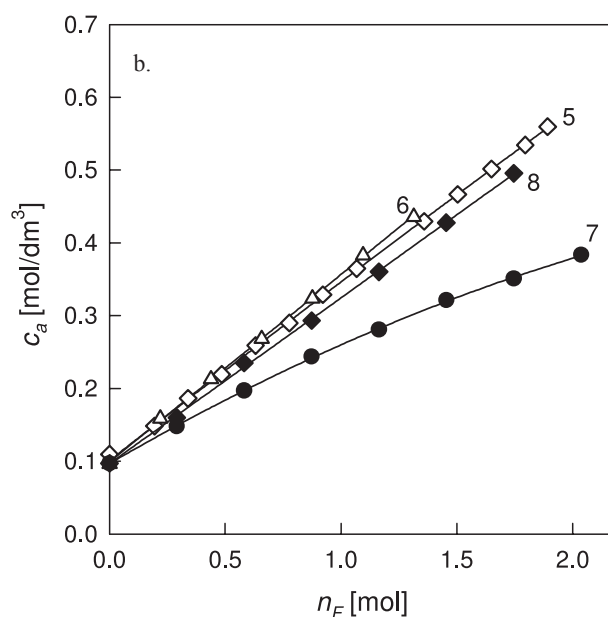
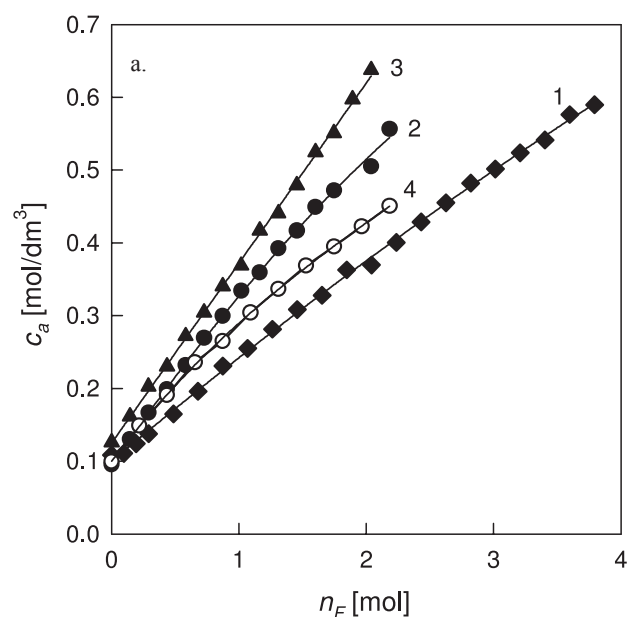


Fig. 2a,b. Acid concentration vs. n_F ; symbols – experimental points, lines – fitting polynomials; 1, 2, ... – number of ED run (Table 1).

Table 1. The basic parameters of the experiment run: c_s – initial salt concentration, $V_{a,0}$, $V_{b,0}$ – initial volumes of acid and base solutions, $n_{F,tot}$ – total transferred charge, $\overline{CE}_{a,c}$, $\overline{CE}_{a,n}$, $\overline{CE}_{b,c}$ – mean efficiencies of acid and base.

ED	I [A]	c_s [mol/dm ³]	$V_{a,0}$ [dm ³]	$V_{b,0}$ [dm ³]	$n_{F,tot}$ [mol]	$\overline{CE}_{a,c}$ eq.(1)	$\overline{CE}_{a,n}$ eq.(2)	$\overline{CE}_{b,c}$ eq.(1)
1	2.6	1.0	2	2	3.79	0.778	0.846	0.822
2	2.6	0.6	1	1	2.18	0.620	0.673	0.685
3	2.6	1.4	1	1	2.04	0.742	0.770	0.838
4	3.9	0.6	1	1	2.18	0.475	0.674	0.671
5	3.9	1.0	1	1	1.89	0.725	0.747	0.783
5a	3.9	1.0	1	1	2.18	0.715	0.773	0.790
6	3.9	1.4	1	1	1.31	0.773	0.821	0.840
7	5.2	0.6	1	1	2.04	0.421	0.679	0.632
8	5.2	1.0	1	1	1.75	0.684	0.716	0.763
9	5.2	1.3	1	1	1.75	0.707	0.741	0.764

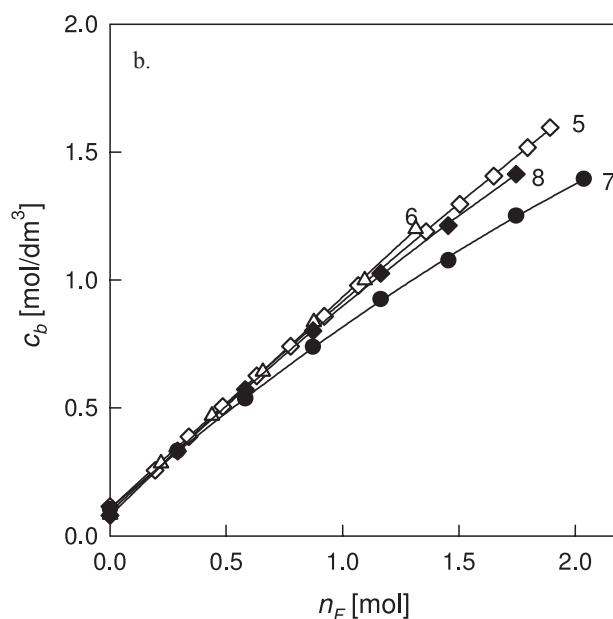
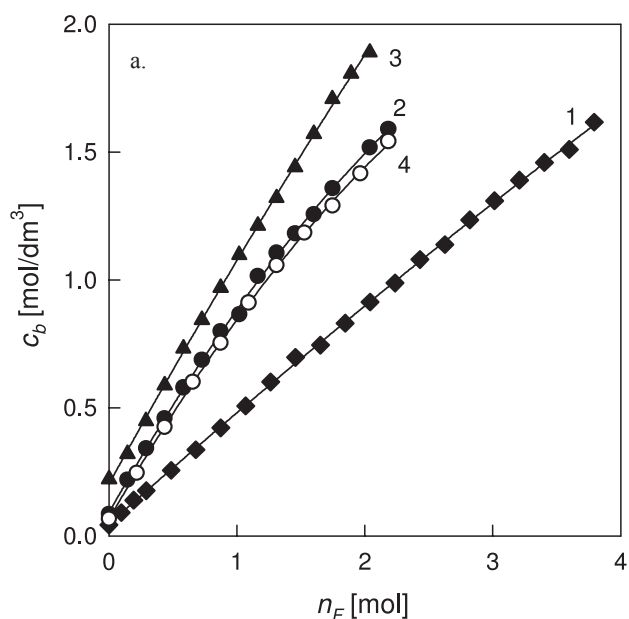


Fig. 3a,b. NaOH concentration (compartment 4 in Fig.1) vs. n_F ; symbols – experimental points, lines – fitting polynomials; 1, 2, ... – number of ED run (Table 1).

Because the volumes of solutions were changing during the process, the mean current efficiencies \overline{CE} were calculated in two ways:

1) from the change in concentration $\overline{CE}_{c,i}$:

$$\overline{CE}_{i,c} \equiv |z_i| V_{i,0} \Delta c_i / n_F = |z_i| V_{i,0} (c_{i,t} - c_{i,0}) / n_F \quad i = a, b \quad (1)$$

2) from the change in the number of moles of electrolyte $\overline{CE}_{a,c}$:

$$\overline{CE}_{i,n} \equiv |z_i| \Delta n_i / n_F = |z_i| (c_{i,t} V_{i,t} - c_{i,0} V_{i,0}) / n_F \quad i = a, b \quad (2)$$

where $c_{i,t}$, $V_{i,t}$ are concentration, volume of solution i (a

– acid, b – base) in time t , respectively, z_i is the charge number of anion: $z_a = -3$ (citrate), $z_b = -1$ (hydroxide), n_F is the transferred charge expressed in the number of moles of elementary charge:

$$n_F = It / F \quad (3)$$

In eq.(3) I is the electric current, t – time, F – Faraday constant ($F = 96485$ C/mol). In the formulae of current efficiency of acid there is $z_a = -3$, because in the Na_3A solutions practically only A^{3-} ions exist. In the concentration range 0.1-1 mol/dm³ Na_3A the mole fraction A^{3-} is greater than 0.999 (calculated according to the literature dissociation constants).

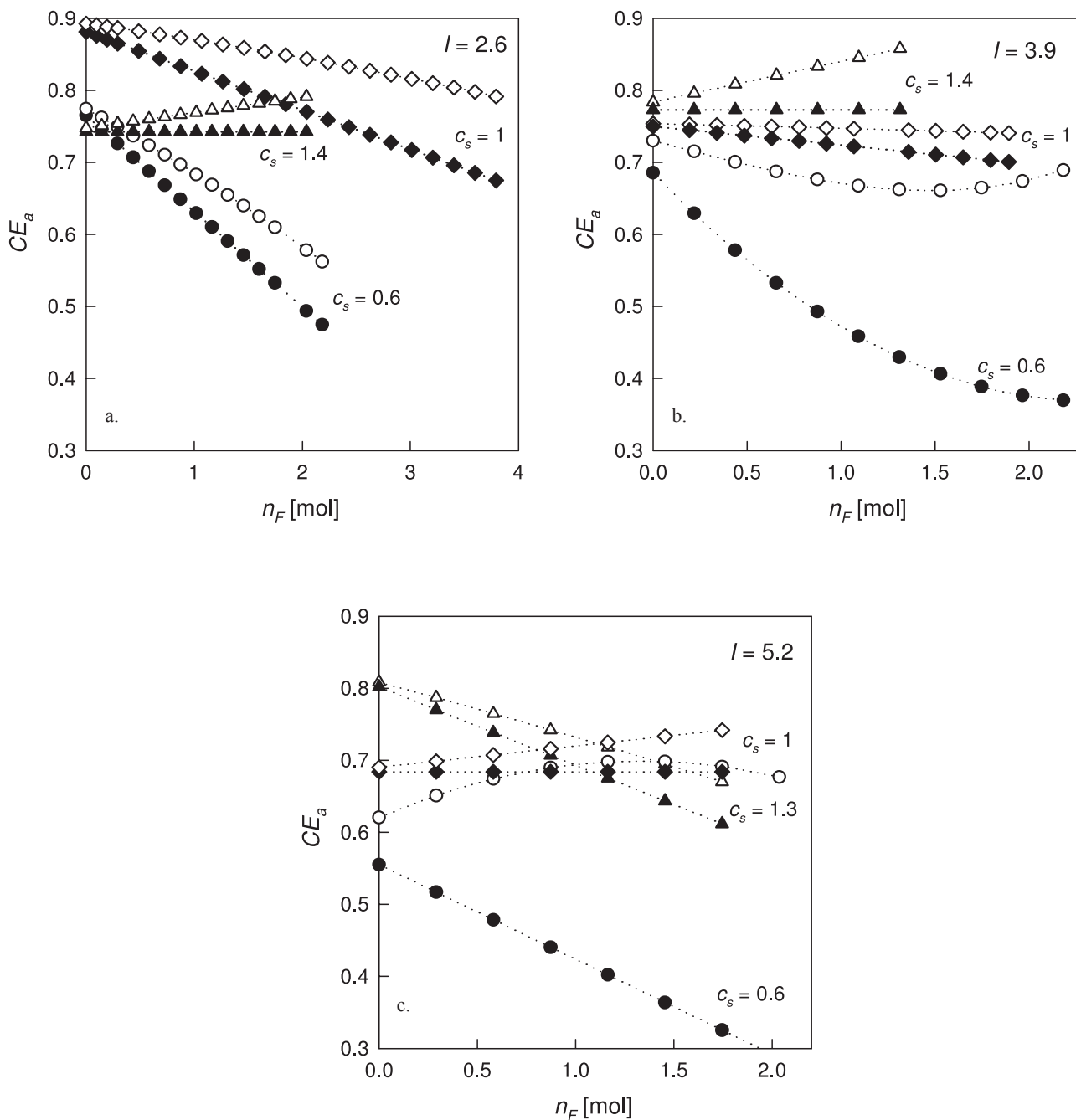


Fig. 4. Dependence of CE_a on n_F for the current density: a) 52, b) 78, c) 104 mA/cm²; concentrations of salt: o, ● – 0.6 mol/dm³, ◇, ◆ – 1 mol/dm³, △, ▲ – 1.3 or 1.4 mol/dm³; filled symbols – $CE_{a,c}$ eq.(4), hollow symbols – $CE_{a,n}$ eq.(5).

tion constants of citric acid $K_1 = 8.2 \cdot 10^{-4}$, $K_2 = 1.8 \cdot 10^{-5}$, $K_3 = 4 \cdot 10^{-7}$ [19]). Thus, from the salt solution only the anions A^{3-} enter the anion-exchange membrane.

The efficiency based on the concentration changes is essential in terms of determining the energy needed for the evaporation of solution to the solid form of acid.

Results and Discussion

The basic parameters of particular processes (I , c_s , n_{Ftot}) and the mean current efficiencies of acid (a) and

base (b) (eqs. (1), (2)) are presented in Table 1. Because of small changes of the base volume only $\overline{CE}_{b,c}$ is presented.

Analyzing the mean current efficiencies, it is found that both acid and base current efficiencies increase with the initial salt concentration at the same current density; however, above 1 mol/dm³ this increase is negligible. Moreover, when the current density increases, it has a negative influence on the efficiency of products; however, at high initial salt concentrations (1.4 mol/dm³) the maximum is observed for $I = 3.9$ A (78 mA/cm²). This results from the lower concentration polarization of membranes at lower current density. Because

of the increase in acid solution volume, caused by the osmotic water flow and migration of citrate anions, the current efficiency $CE_{a,n}$ (eq. (2)) is higher than $CE_{a,c}$ (eq. (1)).

Regarding the purity of acid, the content of Na^+ ions in the acid solution is scarce (determined by the F-AES method). It indicates that the migration of Na^+ from the compartment 1 to 2 (acid) through the bipolar membrane and the diffusion of these ions from salt to acid through the anion-exchange membrane are negligible.

In order to show the efficiency changes during the process, the instantaneous efficiencies were calculated from:

$$CE_{i,c} \equiv z_i \left| V_{i,0} \frac{dc_i}{dn_F} \right| \quad i = a, b \quad (4)$$

$$CE_{a,n} \equiv \left| z_a \left| \frac{d(V_a c_a)}{dn_F} \right| \right| \quad (5)$$

In eqs.(4) and (5) the concentrations of acid and base vs. n_F were fitted by a polynomial (1st to 3rd degree) (Fig. 2, Fig. 3). As the measurement of electrolyte volumes was inaccurate, the acid volume was approximated by the linear function taking the initial and final values of volume. This linear approximation is confirmed by the experimental data [16]. The volume of NaOH solution (compartments 1 and 4), V_b , was practically constant.

In Fig. 4 the instantaneous current efficiencies of acid – $CE_{a,c}$ (filled symbols) and $CE_{a,n}$ (hollow symbols) – are compared. It is seen that in the case of low initial salt concentrations ($c_s = 0.6 \text{ mol/dm}^3$) the acid efficiency decreases, for $c_s = 1 \text{ mol/dm}^3$ it is practically constant, and for higher salt concentrations it even increases. In the case of the highest investigated current density (104 mA/cm², 5.2 A), the opposite situation is observed, that is, CE_a decreases in time for a higher salt concentration $c_s = 1.3 \text{ mol/dm}^3$. Great differences between $CE_{a,c}$ and $CE_{a,n}$ are observed for the low initial salt concentration (1.4 mol/dm³) caused by significant changes in acid volume.

Qualitatively, the decrease of CE_a at low salt concentrations can be explained by the decrease of citrate concentration in the salt solution, which leads to the smaller selectivity of an anion-exchange membrane. The calculations based on the dissociation constants show that in citric acid solutions about 95% of acid occurs in the undissociated form H_3A , the remaining part in the form of H_2A^- , while the forms HA^{2-} and A^{3-} practically do not appear (Fig. 5). Consequently, another factor lowering CE_a is the diffusion of undissociated form H_3A . This diffusion is proportional to the difference in H_3A concentration across the anion-exchange membrane. As on the opposite side of that membrane (salt solution) practically there is no H_3A , the rate of diffusion of H_3A is proportional to its concentration in the acid solution.

Although many papers have been published on the sodium citrate conversion into citric acid by means of the

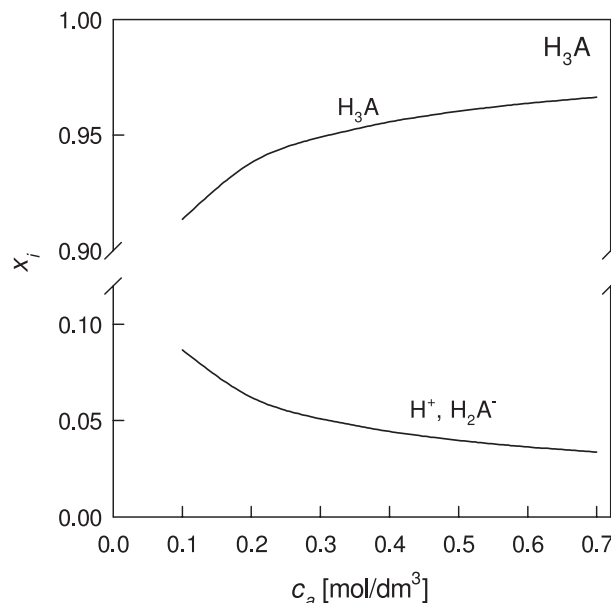


Fig. 5. Fraction of H^+ , H_2A^- and H_3A ($x_i = c_i/c_a$) vs. the concentration of citric acid c_a ; the concentrations of H^+ and H_2A^- are practically the same, the concentrations of HA^{2-} and A^{3-} are negligible (the calculations based on $K_1 = 8.2 \cdot 10^{-4}$, $K_2 = 1.8 \cdot 10^{-5}$, $K_3 = 4 \cdot 10^{-7}$ [19], neglecting the nonideality of the solutions).

EDB method, it is difficult to compare these findings due to various membrane arrangements and solutions used in the electrodialyser. For example, Novalic *et al.* [10] used 20% acid solution in the acid circuit and 10% acid in the salt circuit. Depending on the base concentration, the obtained acid efficiency ranged between 57% and 78%. However, the increase in acid concentration was not given.

In some papers [10, 12, 13, 15, 17], sodium sulphate was added to the produced acid in order to reduce electrical resistance. However, sodium sulphate is not added in our case (0.1 mol/dm³ of citric acid is used instead of Na_2SO_4). In [13] the arrangements: A-C-BP-A-C, C-BP-C, BP-A-C-BP were tested. The closest to ours is the last one. The obtained current efficiency, $\overline{CE}_{a,c}$, for that arrangement was about 0.6 for the ratio $n_F/n_{s,0} = 1$, where $n_{s,0}$ is the initial number of moles of sodium citrate. In our case, $\overline{CE}_{a,c}$ for the same $n_F/n_{s,0}$ equals about 0.5. The lower $\overline{CE}_{a,c}$ values can result from the fact that the initial concentration of H_3A solution introduced to the chamber was 0.1 mol/dm³, whereas Xu *et al.* [13] used the solution initially free of acid (0.5 mol/dm³ Na_2SO_4). The lower concentration of acid results in the higher selectivity of anion-exchange membrane and, consequently, in higher efficiency. The other reason of higher efficiency might be better quality of membranes used in [13].

Fig. 6 presents the dependence of NaOH current efficiency, CE_b , on n_F . Similarly to acid, a significant decrease of CE_b with n_F is noticed for the solutions of low initial salt concentration ($c_s = 0.6 \text{ mol/dm}^3$). Observed for $I = 2.6$ (78 mA/cm²), slightly higher CE_b for $c_s = 1 \text{ mol/dm}^3$ than for 1.4 mol/dm³ results from the two times larger volume of NaOH solution used in the experiment with $c_s = 1 \text{ mol/dm}^3$. For the

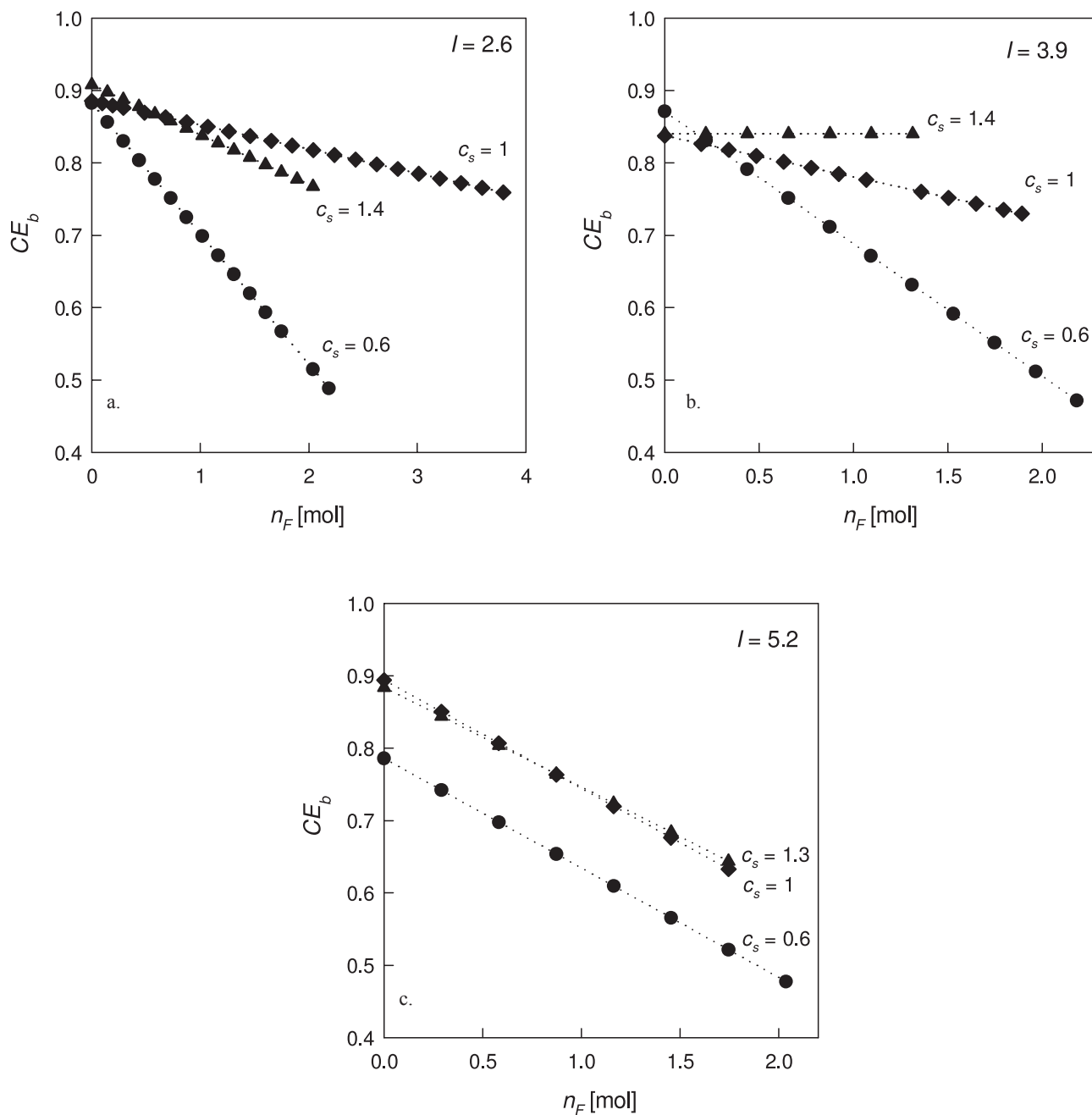


Fig. 6. Dependence of CE_b (eq.(4)) on n_F for the current density: a) 52, b) 78, c) 104 mA/cm²; the concentrations of salt: o – 0.6 mol/dm³, \diamond – 1 mol/dm³, Δ – 1.3 or 1.4 mol/dm³.

low salt concentration $c_s = 0.6$ mol/dm³ CE_b practically does not depend on the current density, while for higher c_s , CE_b increases with the increase of I from 2.6 to 3.9 A. A further augmentation of I to 5.2 A results in the CE_b decrease. For $I = 5.2$ A a strong efficiency decrease for all salt concentrations is noticed.

Conclusions

1. The mean efficiencies for reactants ($\overline{CE_{a,c}}$, $\overline{CE_{a,n}}$, $\overline{CE_{b,c}}$) are higher at the lower current densities (52 mA/cm²).
2. The difference between $\overline{CE_{a,n}}$ and $\overline{CE_{a,c}}$ increases with the amount of electrical charge passed through the system and the values of $\overline{CE_{a,n}}$ can be twice that of $\overline{CE_{a,c}}$ for low salt concentration.
3. The process efficiency increases with the initial sodium citrate concentration. This requirement is easily met due to the high solubility of sodium citrate.
4. The time changes of acid efficiency are represented by the instantaneous efficiencies. In the case of low initial salt concentrations, as the process progresses,

For the highest investigated salt concentration (1.4 mol/dm³), their maximum were noticed at 78 mA/cm².

the acid instantaneous efficiency CE_a decrease in time, for $c_s = 1 \text{ mol/dm}^3$ they are practically constant, and for higher salt concentration they even grow. In the case of the highest investigated current density (104 mA/cm^2), the opposite situation is observed, that is, CE_a decreases in time for $c_s = 1.3 \text{ mol/dm}^3$.

Acknowledgments

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