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The behaviour of ion exchange membranes in electrolysis and electrodialysis of sodium sulphate*

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There is an increasing interest in the electro-chemical splitting of sodium sulphate into caustic soda solution and sulphuric acid by means of ion exchange membranes. Adaptation of the product properties to the demands of recycling requires the use of cation exchange membranes, anion exchange membranes or a combination of both. Application of available membranes results in product concentrations which are below usual industrial standards. Extensive measurements prove that the current efficiency is either dependent on concentrations of the anode region (sulphuric acid, sodium sulphate) or on the concentrations of the cathode region (caustic soda, sodium sulphate) with regard to the range of concentrations. In order to explain these phenomena a model of an "acid" and an "alkaline" state of the membrane has been developed, which can be applied both for cation and anion exchange membranes. This model is a valuable help in optimizing the concentrations of sodium sulphate, sulphuric acid and caustic soda.

1. Introduction

Sodium sulphate occurs as a by-product in numerous chemical processes, if sulphuric acid solutions are neutralized by caustic soda or if alkaline solutions are neutralized by sulphuric acid [2]. While on the one hand the industrial demand for sodium sulphate is declining [3] on the other hand emission of sodium sulphate into sewage water leads to an increase of the salt content which often approaches the acceptable limit. Additional problems are frequently caused by the occurrence of process specific impurities. Such impurities prevent the production of pure sodium sulphate or waste disposal in the sewage water. Consequently the sodium sulphate has to be dumped at high costs.

Thus, there is an interest in splitting sodium sulphate into solutions of caustic soda and sulphuric acid both of which can be recycled into the production process [3, 4]. The value of caustic soda – mainly produced by electrolysis of common salt, coupled with the production of chlorine – will increase due to the fact that in the long term the demand for chlorine will decline. Moreover, there is no economic possibility of destroying or dumping chlorine. Recycling of sodium sulphate as caustic soda and sulphuric acid could reduce the consumption of caustic soda considerably in many processes.

2. Possibilities for the electro-chemical recycling of sodium sulphate as caustic soda and sulphuric acid

The electro-chemical conversion of sodium sulphate into caustic soda and sulphuric acid according to the overall reaction

$$Na_2SO_4 + 2H_2O \longrightarrow H_2SO_4 + 2NaOH \quad (1)$$

is separated into two steps:

(1A) splitting of water into H^+ ions and OH^- ions

(1B) separation of Na^+ ions and SO_4^{2-} ions.

Both steps can be realized in an electrolytic cell (type 2C, Fig. 1a), as is known for the membrane process of chlor-alkali electrolysis. Step 1A is accomplished by electrolysis of water at the anode:

$$H_2O \longrightarrow O_2 + 4H^+ + 4e^- \quad (2)$$

and at the cathode:

$$4H_2O + 4e^- \longrightarrow 2H_2 + 4OH^- \quad (3)$$

With regard to Step 1B the electrodialytic permselectivity of a cation exchange membrane (CEM) is used. Ideally, this membrane is permeable to hydrated cations only, in this particular case for Na^+ ions and H^+ ions. The sodium sulphate solution is fed to the anode compartment where it is partially converted into sulphuric acid. The migration of sulphate ions into the cathode compartment is largely suppressed, thus, pure caustic soda solution is obtained. However, the amount of sulphuric acid and caustic soda is smaller than the equivalent of the electrolytic current because OH^- ions and/or H^+ ions migrate through the membrane to some extent and reduce the current efficiency.

If special conditions (see §5) are observed, an anion exchange membrane (AEM) can be used (cell type 2A, Fig. 1b) to adjust the products to given process

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* This paper is dedicated to Professor Dr Fritz Beck on the occasion of his 60th birthday.

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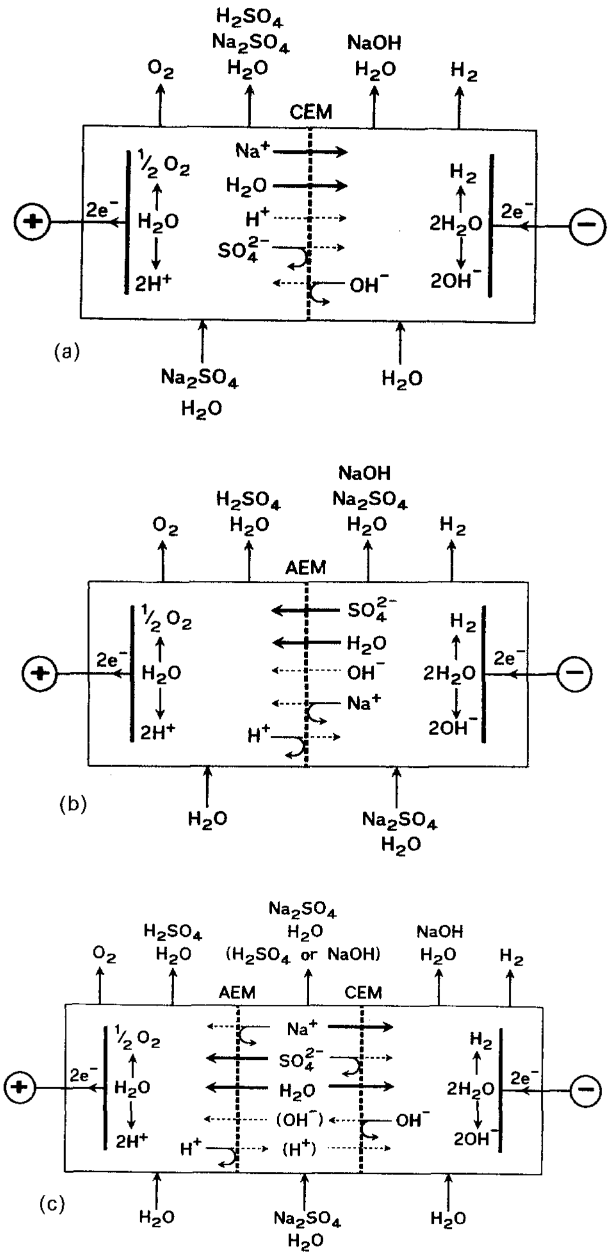

Fig. 1. (a) Two-chamber cell type 2C: cation exchange membrane (CEM). (b) Two-chamber cell type 2A: anion exchange membrane (AEM). (c) Three-chamber cell type 3CA: combination of cation exchange membrane (CEM) and anion exchange membrane (AEM).

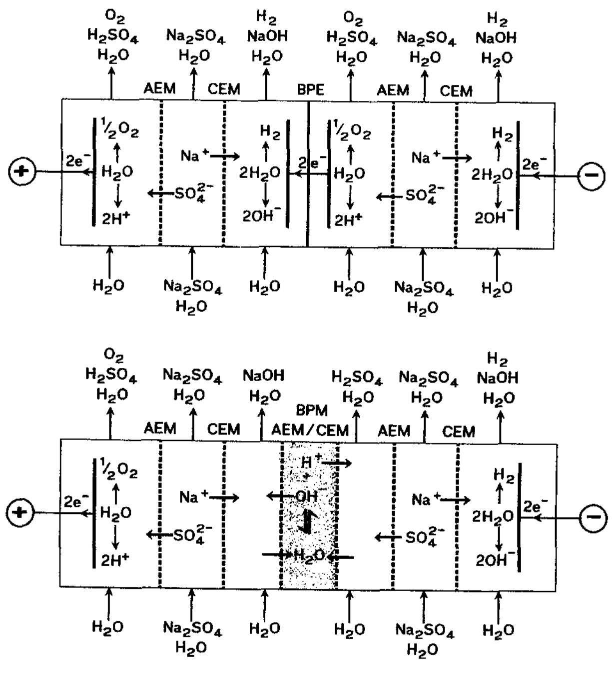

Fig. 2. Comparison of blocks of two cells type 3CA. Top: with bipolar electrode (BPE). Bottom: with bipolar membrane (BPM).

requirements. Under those circumstances sulphate ions migrate through the membrane and the products are pure dilute sulphuric acid and a mixture of caustic soda and sodium sulphate. Using a cation exchange membrane as well as an anion exchange membrane in a three-chamber cell (type 3CA, Fig. 1c) solutions of pure caustic soda and of pure sulphuric acid are produced.

Economic aspects of these processes have been discussed previously [3]. A disadvantage is the high energy consumption of step 1A during Reactions 2 and 3 due to the evolution of hydrogen and oxygen as undesired by-products. Experiments have proved that a large part of the required energy can be saved by use of gas diffusion electrodes. Either a hydrogen anode works with the hydrogen evolved at the cathode, i.e. Reaction 2 is replaced by 4:

$$2H_2 \longrightarrow 4H^+ + 4e^- \qquad (4)$$

or an oxygen cathode works with the oxygen evolved at the anode, i.e. Reaction 3 is replaced by 5:

$$O_2 + 2H_2O + 4e^- \longrightarrow 4OH^- \qquad (5)$$

Comparative measurements indicated that the first alternative is favourable in order to avoid the high overvoltage during oxygen evolution and undesirable oxidization at the anode (e.g. chloride to chlorine), which may reduce the lifetime of the anode and of the membrane.

Bipolar membranes offer a new, energetically favourable possibility of Step 1A without gas evolution. In the upper part of Fig. 2 the electrolytic cells of a cell block (only two cells according to Fig. 1c) are separated by a gas evolving bipolar electrode (BPE). In the lower part the bipolar electrode is replaced by a bipolar membrane (BPM), a combination of an anion exchange membrane and a cation exchange membrane in direct contact. Here, water is split by the electrical field between the membranes into H^+ ions and OH^- ions. The energy consumption of this step is, in theory, just about 40% of the energy requirements of electrolytic water splitting with gas evolution. The ions migrate in opposite directions through both membranes, supported by their different permselectivity, and form sulphuric acid and caustic soda. Bipolar membranes are available for use in pure sodium sulphate solutions [5, 6]. The operation of cation exchange membranes and anion exchange membranes for Step 1B does not in principle change with use of bipolar membranes instead of bipolar electrodes for Step 1A.

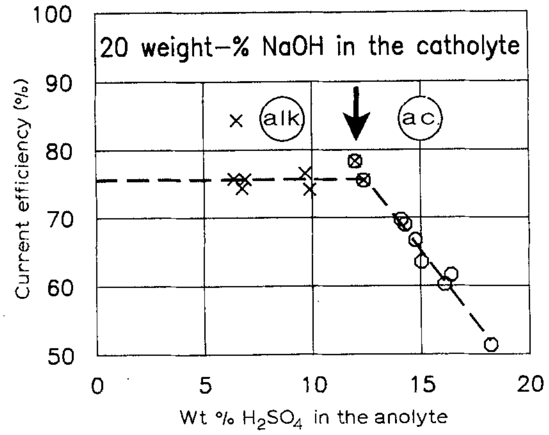

Fig. 3. Current efficiency as a function of sulphuric acid concentration for a cell type 2C [1], cation exchange membrane Nafion 390, 32 wt % Na_2SO_4 anolyte feed, current density 3 kA m^{-2}, temperature 80° C.

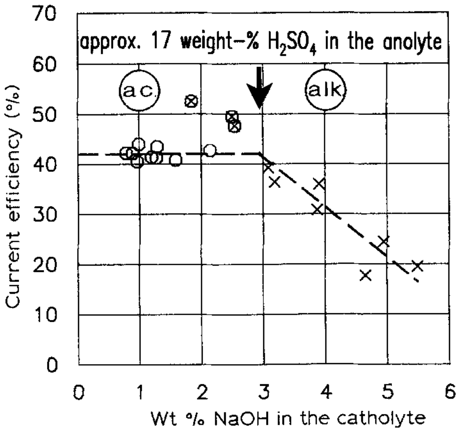

Fig. 5. Current efficiency as a function of caustic soda concentration for a cell type 2A, anion exchange membrane MA-3475, 10 wt % Na_2SO_4 catholyte feed, current density 3 kA m^{-2}, temperature 80° C.

3. Experiments with the cation exchange membrane Nafion 390

The Nafion 390 cation exchange membrane (Du Pont) was used in a two-chamber laboatory cell (type 2C, Fig. 1a) during continuous operation [1]. The relation between the current efficiency and the concentration of sulphuric acid in the anode compartment was measured at a constant concentration of 20 wt % caustic soda in the cathode compartment, as shown in Fig. 3.

As long as the sulphuric acid concentration did not exceed a threshold value, here 12 wt %, this concentration had no influence on the current efficiency (points marked with "x"). Increasing the acid content beyond this limit, the current efficiency dropped, as indicated by the points marked "o". Further experiments showed that the threshold value itself depended on the caustic soda concentration.

Similar behaviour was observed at a constant acid content in the anode compartment. As long as the caustic soda concentration in the cathode chamber was lower than a certain limit it did not influence the current efficiency. However, if this limit, which is a function of the acid content, was exceeded, the current efficiency decreased with an increase in the caustic soda concentration. The dependence is the same as for chlor-alkali electrolysis using a similar membrane [7] and is thus in agreement with comparable phenomena observed in preceding experiments [8].

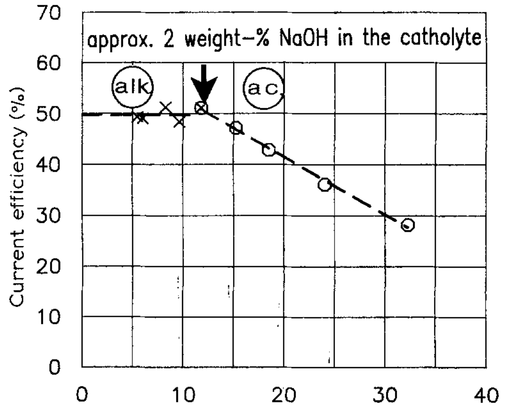

Fig. 4. Current efficiency as a function of sulphuric acid concentration for a cell type 2A, anion exchange membrane MA-3475, 10 wt % Na_2SO_4 catholyte feed, current density 3 kA m^{-2}, temperature 80° C.

4. Experiments with the anion exchange membrane MA-3475

For measurements with the MA-3475 anion exchange membrane (Sybron-Ionac) a cell of type 2A (Fig. 1b) was used. Current density and temperature corresponded to the above-stated experiments with the cation exchange membrane. The catholyte feed contained 10 wt % of Na_2SO_4. Approximately 2 wt % caustic soda was produced in the cathode compartment. Figure 3 and Fig. 4 are a similar shape. Up to a concentration of 12 wt % sulphuric acid did not affect the current efficiency. However, in the case of higher concentrations the current efficiency decreased considerably.

Similar experiments at constant sulphuric acid concentration of approximately 17 wt % and increasing caustic soda concentration (Fig. 5) resulted in a steady current efficiency up to a threshold value of 3 wt % NaOH and a strong drop at higher concentrations.

5. The model of the alkaline and the acid state of the membrane

The above-mentioned results can be explained by the model shown in Fig. 6 [1, 8]. It is known that at high caustic soda concentration in the catholyte and low concentration of acid in the anolyte (the working conditions of chlor-alkali electrolysis) losses in current efficiency are caused by migration of OH^- ions. Thus, the current efficiency of cation exchange membranes for chlor-alkali electrolysis is improved by suppression of OH^- ion migration (also see §6). In that case the membrane is in an alkaline state through its entire thickness (as indicated in Fig. 6a) and an alkaline boundary layer is developed on the anode side

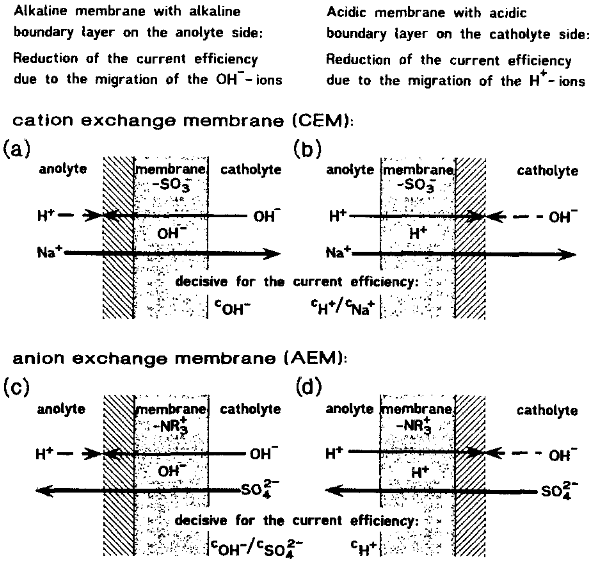

Fig. 6. Model of the alkaline and the acid state of the membrane.

towards the acid anolyte. This assumption has been confirmed by measurements [9] and is supported by the result that in the case of an insufficiently pure anolyte acid soluble earth alkaline hydroxides precipitate on the membrane surface on the anode side [9, 10].

Under these circumstances, we define as the "alkaline membrane state", the acid concentration in the anolyte having no influence on the current efficiency because the H^+ ions have already been neutralized in the alkaline boundary layer (shaded in Fig. 6a) and cannot reach the membrane itself. If membrane type, current density and temperature are fixed, the current efficiency depends on the caustic soda concentration in the cathode compartment (region marked "alk." in Fig. 3) only. This model is also valid for anion exchange membranes (Fig. 6c and 4).

The situation changes, if, owing to an increase of the acid concentration of the anolyte and/or due to a decrease in the caustic soda concentration of the catholyte, more H^+ ions migrate from the anolyte to the boundary layer of the membrane than OH^- ions arrive through the membrane from the catholyte. Under these circumstances the alkaline boundary layer disappears. Now, the H^+ ions migrate through the membrane to the catholyte and form an acid boundary layer as shown shaded in Fig. 6b and d.

For that situation, which we define as the "acid membrane state", the catholyte concentration has no influence on the current efficiency because the OH^- ions have been neutralized in the acid boundary layer on the cathode side and do not effect the behaviour of the membrane itself (region marked "ac." in Fig. 5).

According to this model, there exists a definite acid concentration in the anolyte for each caustic soda content in the catholyte, at which the membrane shifts from the alkaline state into the acid state or vice versa. The intermediate state, i.e. OH^- ions as well as H^+ ions penetrate into the membrane and react to water, could be constant only if the quantities of OH^- ions and of H^+ ions are equal. Since this situation appears to be improbable only the alkaline state or the acid state of the membrane exists in steady state operation.

This model explains the obvious change in gradient of the current efficiency function with increasing acid concentration (marked in Fig. 3 and 4 with an arrow) as a change from the alkaline state to the acid state of the membrane. Figure 5 similarly shows the change from the acid state into the alkaline state with increasing concentration of caustic soda.

The validity of this model is supported by extensive experiments; only some can be presented in this paper. Experiments with various concentrations of sodium sulphate, caustic soda and sulphuric acid have been carried out in a cell type 2C (Fig. 1a) [1] and a cell type 3CA (Fig. 1c). Further measurements have been performed in a cell type 2C (Fig. 1a) at very low anolyte and catholyte concentrations (combinations of 0.2 M and 0.1 M sulphuric acid, of 0.2 M and 0.1 M caustic soda and of solutions, buffered with NaH_2PO_4/Na_2HPO_4 to pH 7). The model was also verified for these conditions. With both cell compartments buffered up to pH 7, i.e. neither a considerable concentration of H^+ ions nor of OH^- ions was available for the migration through the membrane instead of Na^+ ions, a current efficiency of almost 100% could be achieved.

As shown in Fig. 4 and 5 the transition from the acid state to the alkaline state of the anion exchange membrane MA-3475 causes a change in the gradient of the current efficiency curve (marked by the arrow). Additionally the transition point could be visually identified. Approaching that value (at decreasing acid concentration in Fig. 4 or increasing caustic soda concentration in Fig. 5), a brown discolouring indicated the onset of the membrane decomposition in strongly alkaline media ($pH > 12$–13), which is typical for available anion exchange membranes. The membrane stability in the acid state, as confirmed in previous measurements, can be explained by the existence of an acid boundary layer on the cathode side of the membrane (Fig. 6d), which avoids reaction of the caustic soda with the membrane.

6. Migration of counter-ions and Co-ions through the membrane

The function of an ion exchange membrane depends on ions immobilized at a polymer matrix. Cation exchange membranes (CEM) are based on negatively charged ions, e.g. sulphonic acid groups, and anion exchange membranes are based on positively charged ions, e.g. quaternary ammonium groups. Ideally, the charge transport in the membrane is only effected by the mobile counter-ions. In the case of sodium sulphate electrolysis these counter-ions are Na^+ ions in the cation exchange membrane (CEM) and SO_4^{2-} ions in the anion exchange membrane (AEM). The undesirable transport of co-ions, i.e. ions with the same charge as the fixed ions, is repressed because the fixed ions build-up a potential barrier which causes the permselectivity (Donnan potential, [11, 12]).

The permeation of co-ions countercurrent to the electrical field inside the cell, i.e. of SO_4^{2-} ions in the CEM (Fig. 1a) or of Na^+ ions in the AEM (Fig. 1b), is almost suppressed because the electrical field supports the permselectivity. Due to that fact the products scarcely contain sodium sulphate: in the cathode compartment of the cell type 2C (Fig. 1a) about 1 wt % of Na_2SO_4 (based on 100% NaOH) and in the anode compartment of the cell type 2A (Fig. 1b) about 0.1 wt % of Na_2SO_4 (based on 100% H_2SO_4) were determined.

The exclusion of co-ions, the transport of which is accelerated by the electrical field (OH^- ions in the CEM or H^+ ions in the AEM), is incomplete. A similar case is known for OH^- ions in a CEM used in chlor-alkali electrolysis. The decline of current efficiency, caused by migration of OH^- ions through a CEM with increasing OH^- ion concentration is illustrated in the right hand part of Fig. 8. Figure 4 shows in the region marked with "ac." the corresponding behaviour of an AEM with increasing concentration of H^+ ions.

The presence of co-ions transfers the CEM into the alkaline state (OH^- ions) and the AEM into the acid state (H^+ ions). As explained (Fig. 6a and d), the transport of co-ions through the membranes is influenced only by the concentration of the co-ions in that adjacent electrolyte from where the co-ions enter the membrane. As long as the membrane state does not change, the concentrations in the solution on the opposite side of the membrane have no influence.

If, however, the CEM turns over into the acid state, or the AEM changes into the alkaline state, the ion transport, which decreases the current efficiency, is not caused by co-ions. Migration of co-ions is repressed by the permselectivity of the membrane, but additional counter-ions, i.e. H^+ ions in the CEM (Fig. 6b) or OH^- ions in the AEM (Fig. 6c) are mobile with respect to the required function of the membrane. The transport of these ions cannot be prevented by increasing the permselectivity. Thus, the transition from the alkaline state into the acid state or vice versa implies a fundamental change of the transport mechanism within the membrane.

The current efficiency in the acid state of the CEM (Fig. 6b) and in the alkaline state of the AEM (Fig. 6c) is determined by the concentration ratio of the competitive counter-ions, given in that electrolyte from where they penetrate into the membrane.

Figure 7 shows that the current efficiency of the CEM Nafion 390 in the acid state is a definite function of the concentration ratio of H^+ ions and Na^+ ions in the anolyte, independent of individual concentrations of sulphuric acid and sodium sulphate. In Fig. 7 the total amount of H^+ ions, analytically determined by titration with caustic soda solution, is used. The same value for the ratio C_{H^+}/C_{Na^+} results from the conversion of the sodium sulphate feed (scale on top of the diagram, Fig. 7).

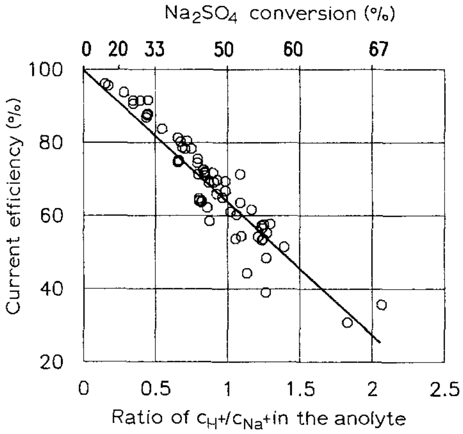

Fig. 7. Current efficiency as a function of the concentration ratio C_{H^+}/C_{Na^+} in the anolyte of a cell type 2C [1], cation exchange membrane Nafion 390, acid membrane state, current density $3\,kA\,m^{-2}$, temperature 80°C. Na_2SO_4 in the anolyte feed: 10.1–33.6 wt %; Na_2SO_4 in the anolyte: 5.3–28.3 wt %; H_2SO_4 in the anolyte: 2.9–18.2 wt %; and NaOH in the catholyte: 1.1–32.5 wt %.

Obviously, Na^+ ions are preferred for the current transport through the membrane although their transport number in aqueous solution is four times lower compared to the H^+ ions. For the ratio C_{H^+}/C_{Na^+} 1 : 1 (in accordance with a $NaHSO_4$ solution) the current efficiency is about 65%, i.e. the ratio of the effective transport numbers of Na^+ ions and H^+ ions in the membrane is 2 : 1. That behaviour, an advantage concerning sodium sulphate electrolysis, can be partially explained as follows: the effective concentration of H^+ ions in the anolyte is only as half as large as the concentration analytically determined since, in the case of the investigated high acid concentrations, the equilibrium

$$H^+ + SO_4^{2-} \rightleftharpoons HSO_4^- \qquad (6)$$

mainly tends to the right. The HSO_4^- ions are scarcely dissociated although they are analytically found as H^+ ions.

Similarly the measurements with the anion exchange membrane MA-3475 in the alkaline state (Fig. 4 and 5, section marked with "alk.") prove the expected, definite relation between the current efficiency and the concentration ratio $C_{OH^-}/C_{SO_4^{2-}}$ in the catholyte (see Fig. 6c). However, this membrane possesses no long-term stability in the alkaline state.

7. Selection of the optimal concentrations

The model of either an acid or alkaline state of the membrane is not only of theoretical interest for explanation of the phenomena mentioned above, but also results in practical consequences for the selection of optimal working conditions for sodium sulphate electrolysis.

As described in §5, using the CEM as an example, a membrane, CEM as well as AEM, changes from the alkaline state into the acid state if the H^+ ion transport from the anode side is higher than the OH^- ion migration from the cathode side. In the reverse case the change is effected correspondingly. Due to the fact that the undesired currents of OH^- ions and of H^+ ions cannot exist together in the membrane the larger

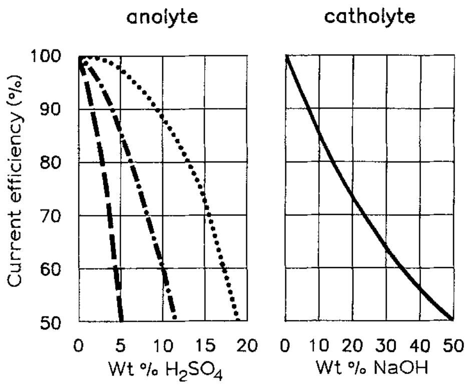

Fig. 8. Characteristic current efficiency curves. Cation exchange membrane Nafion 390 (fitted curves of all measurements in [1]), current density 3 kA m^{-2}, temperature 80° C. Left: acid state; right: alkaline state. (– – –) 10, (-·-·-) 22 and (····) 32 wt % Na_2SO_4 in the anolyte feed.

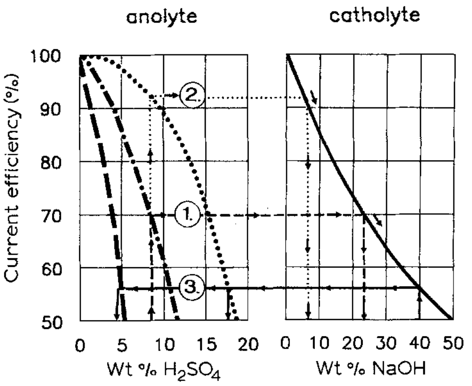

Fig. 9. Method of estimation of the concentration ranges of Na_2SO_4 in the anolyte feed, H_2SO_4 and NaOH in the effluents. (– – –) 10, (-·-·-) 22 and (····) 32 wt % Na_2SO_4 in the anolyte feed.

one, i.e. the ion current causing the lower current efficiency, appears alone.

Therefore, this current determines: (i) the state of the membrane; (ii) the transport mechanism in the membrane; and (iii) whether the current efficiency is dependent on the concentrations on the cathode side or on the anode side.

In Fig. 8 characteristic curves of current efficiency for the CEM Nafion 390 are given as an example. The right hand part of Fig. 8, showing the alkaline state, corresponds to the known function of chlor-alkali electrolysis [7, 8]. The curves in the left hand part are valid for the acid state and correspond to Fig. 7, however, they use the immediately evident concentrations of sulphuric acid in the anolyte and of sodium sulphate in the anolyte feed (the different concentration values shown in Figs 7 and 8 were experimentally determined, their relation also considers the transport of water through the membrane).

The curves demonstrate a strong dependence of the current efficiency in the acid state on the concentration of Na_2SO_4 in the anolyte feed. This concentration should therefore be as high as possible in order to attain an advantageous ratio of C_{H^+}/C_{Na^+} in the anolyte, even at higher sulphuric acid concentrations.

The characteristic curves indicate the maximum current efficiency which can be attained according to the given conditions either in the acid state (left part of Fig. 8) or in the alkaline state (right part). Current efficiencies can be estimated for a given membrane type, current density and temperature on the basis of a few measurements. For the acid state the required experiments include different H_2SO_4 concentrations in the anolyte and a sufficiently low concentration of NaOH in the catholyte so that the acid state can be maintained. If the Na_2SO_4 concentration in the anolyte feed is not fixed as a process parameter several measurements have to be carried out. However, the linear relation between current efficiency and the ratio C_{H^+}/C_{Na^+} in the anolyte (Fig. 7) can be used for interpolation and to reduce the number of necessary experiments. The characteristic curve for the alkaline state is obtained from measurements varying the NaOH content in the catholyte while the ratio C_{H^+}/C_{Na^+} in the anolyte is kept sufficiently low (by small concentration of H_2SO_4 and/or high concentration of Na_2SO_4) in order to maintain the membrane in the alkaline state.

The characteristic curves allow the determination of the most favourable combination of the concentrations in anolyte and catholyte. This is demonstrated in Fig. 9 (which corresponds to Fig. 8) for three examples. The first refers to a solution containing 22 wt % sodium sulphate, as anolyte feed. This solution is converted into sulphuric acid up to a concentration of 8 wt %. The current efficiency in the acid membrane state is 70% as indicated by the broken, thin line (example 1) in the left part of Fig. 9. Observing the right part (following the broken, thin line) a current efficiency of 70% can also be obtained in the alkaline state, with a concentration of 24 wt % NaOH in the catholyte.

If an anolyte feed of 32 wt % Na_2SO_4 is used to produce a solution with the same concentration of 8 wt % H_2SO_4 the current efficiency becomes approximately 92%. The same efficiency is achieved for 8 wt % NaOH in the catholyte (example 2, dotted, thin line).

According to the above anolyte concentrations the membrane is in the acid state if the NaOH content of the catholyte does not exceed 24 wt % (example 1) and 8 wt % (example 2). In this case the current efficiency is determined by the concentrations of the anolyte (see left side). It would be of no advantage to lower the NaOH concentration, since this is of no influence on current efficiency.

However, if the caustic soda concentration exceeds 24 wt % and 8 wt % the membrane changes to the alkaline state. The current efficiency decreases according to the arrow direction (right side), e.g. down to 56% for a NaOH concentration of 40 wt % (example 3). In this case, i.e. if a high concentration of NaOH is required, the current efficiency is less than that corresponding to the given anolyte concentrations. Therefore, it is possible to increase the concentration of sulphuric acid in the anolyte and/or to reduce the concentration of sodium sulphate in the anolyte feed without an additional loss in current efficiency.

Following the thin line (example 3), the current efficiency remains at 56% (for 40 wt % NaOH) up to 18 wt % H_2SO_4 in the anolyte at 32 wt % Na_2SO_4 in the anolyte feed, or up to 4.5 wt % H_2SO_4 in the anolyte at 10 wt % Na_2SO_4 in the anolyte feed. This conclusion is also valid for the reverse direction: if the low current efficiency of 56% is accepted due to the given concentrations on the anode side (example 3), the content of NaOH in the catholyte can be increased up to 40 wt % without a further loss in current efficiency.

Consequently, according to the model, the optimal combination of concentrations is given at the transition point of the acid/alkaline membrane state. This point is achieved for concentrations with the same current efficiency for the acid, as well as for the alkaline state of the membrane, i.e. taken from both characteristic curves in Fig. 8 (left and right side). Similar, as explained in Figs 8 and 9 for a CEM, the optimal combination of concentrations can be determined by means of characteristic curves for an AEM.

8. Practical consequences of the alkaline and acid membrane state model

For an economic, industrial use of sodium sulphate electrolysis or electrodialysis the currently available ion exchange membranes, especially the anion exchange membranes, should be improved with regard to current efficiency and attainable concentrations, which are below usual industrial standards at present.

The cation exchange membranes, which work with high current efficiency in chlor-alkali electrolysis (e.g. Nafion 900 series), cannot be used in sodium sulphate electrolysis. Due to their small permeability for OH^- ions a low acid concentration in the anolyte is sufficient to change the membrane into the acid state (see §6). However, their carboxylic ion exchange groups are weak acids and dissociate only in the alkaline state of the membrane. In the acid state there are insufficient freely mobile counter-ions and the voltage drop in the membrane increases until its destruction. Thus, for use with high acid concentrations in the anolyte only membranes with strong acid exchange groups (sulphonic acid) are applicable, although their current efficiency is lower.

Aiming at the production of sulphuric acid and caustic soda, free of sodium sulphate, a combination of cation exchange membranes and anion exchange membranes is used. The current efficiency of the entire plant is determined by the lowest value, which is at present limited by the anion exchange membranes. According to our model (see §7) it should be possible, without additional losses in current efficiency, to increase the concentration of caustic soda until the cation exchange membrane works with the same low current efficiency. The attained savings in the evaporation of the caustic soda solution can be offset against the energy loss due to the low current efficiency.

Due to the strong dependence of the current efficiency on concentration considerable energy savings can be obtained on using a cascade connection of cells or cell blocks. For this case the anolyte or the catholyte, or both, flow from stage to stage [1, 7, 8]. Figure 10 schematically compares, for the case of three cells of type 2C (Fig. 1a), the conventional parallel connection (top) with the co-current connection in series (bottom). With use of parallel connections all cells work with the same, high concentrations of sulphuric acid in the anolyte A_{end} and of caustic soda in the catholyte C_{end} and, thus, with the low current efficiency β_{par}. In the case of a cascade connection the concentrations of sulphuric acid ($A_1 - A_3$) and of caustic soda ($C_1 - C_3$) increase from cell to cell and achieve the high final concentrations ($A_3 = A_{end}$ and $C_3 = C_{end}$) in the last stage. The current efficiency, β_i, in all stages is larger than in the last one ($\beta_1 > \beta_2 > \beta_3 = \beta_{end} = \beta_{par}$). Consequently, a favourable average current efficiency, compared with that of the parallel connection, is obtained.

An interesting possibility results from the small sensitivity of the membrane in the acid state (not suitable for membranes with carboxyl groups) regarding deposits of earth alkali hydroxides. During operation

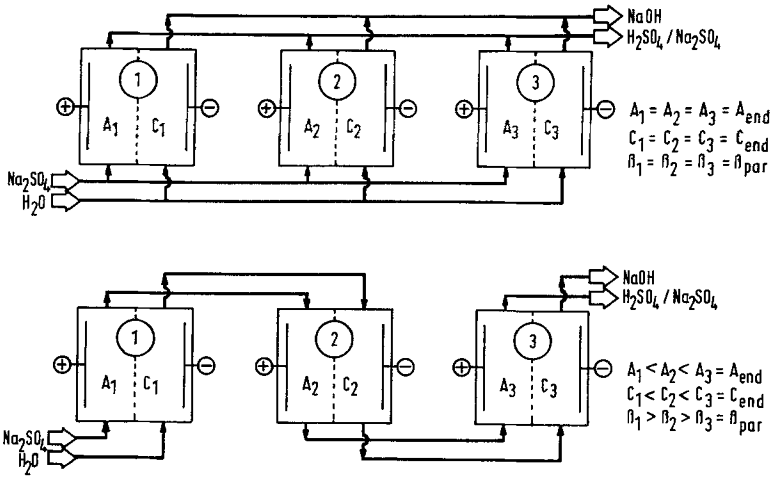

Fig. 10. Variants of cell connections (or of cell blocks). Top: conventional parallel connection; bottom: cascade connection in series (co-current of anolyte and catholyte). A_i = anolyte concentration of sulphuric acid; C_i = catholyte concentration of caustic soda; and β_i = current efficiency.

in the alkaline state extremely high purity of the feed solution is required, as shown from chlor-alkali electrolysis [13]. These requirements can be achieved only by means of expensive treatments with specific ion exchange resins. However, in experiments with a solution of sodium chloride and hydrochloric acid as anolyte, a steady operation may be accomplished in the acid state at relatively high alkali earth concentrations ($4\,\mathrm{mg\,dm^{-3}}$ Ca^{2+}, $2\,\mathrm{mg\,dm^{-3}}$ Mg^{2+}). Thus the purification by precipitation, usual in chlor-alkali electrolysis at concentrations of Ca^{2+} $2\text{–}3\,\mathrm{mg\,dm^{-3}}$ and Mg^{2+} $0.5\text{–}1\,\mathrm{mg\,dm^{-3}}$ [14], is sufficient. In order to maintain the acid state of the membrane the concentrations are shifted slightly compared with the results in the previous part concerning the selection of the optimal concentrations. The loss in current efficiency by this shift is small.

Today anion exchange membranes are suitable for operation in the acid state only. This situation is maintained safely in a three-chamber cell (Fig. 1c). However, the anion exchange region of the bipolar membrane (Fig. 2, bottom) is generally in the alkaline state. Obviously, an anion exchange membrane, sufficiently resistant against OH^- ions, has been developed [5, 6]. It is not known whether the concentration of caustic soda can exceed the mentioned value of 12–16 wt% [5] or whether the material exhibits the usual sensitivity towards alkali earth ions in the alkaline state. In contrast to this situation, the electrolysis variant (Fig. 1c) permits, according to the present status of knowledge, higher concentrations of the products as well as of impurities. Thus, it is still a reasonable alternative to the use of bipolar membranes, especially, if it becomes possible to lower the energy consumption by means of gas diffusion electrodes down to the same level as required for use of the bipolar membranes.

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