

Two-compartment bipolar membrane electro dialysis for splitting of sodium formate into formic acid and sodium hydroxide: Modelling

Jesus Salvador Jaime-Ferrer, Estelle Couallier, Philippe Viers, Mohammed Rakib

► To cite this version:

Jesus Salvador Jaime-Ferrer, Estelle Couallier, Philippe Viers, Mohammed Rakib. Two-compartment bipolar membrane electro dialysis for splitting of sodium formate into formic acid and sodium hydroxide: Modelling. *Journal of Membrane Science*, Elsevier, 2009, 328, pp.75-80. <10.1016/j.memsci.2008.10.058>. <hal-00789483>

HAL Id: hal-00789483

<https://hal-ecp.archives-ouvertes.fr/hal-00789483>

Submitted on 18 Feb 2013

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Elsevier Editorial System(tm) for Membrane Science
Manuscript Draft

Manuscript Number:

Title: Two-compartment bipolar membrane electro dialysis for splitting of sodium formate into formic acid and sodium hydroxide: modelling

Article Type: Full Length Article

Keywords: Bipolar membrane electro dialysis, two-compartment electro dialysis, salt splitting, formic acid, modelling.

Corresponding Author: Prof Mohammed RAKIB, PhD

Corresponding Author's Institution: Ecole Centrale Paris

First Author: Jesus Salvador. Jaime-Ferrer, Dr

Order of Authors: Jesus Salvador. Jaime-Ferrer, Dr; Estelle Couallier, Dr; Philippe Viers, DR; Mohammed RAKIB, PhD

Abstract: The aim of this work is to model the two-compartment bipolar membrane electro dialysis for organic salts acidification. The salt studied is sodium formate which splits into formic acid and sodium hydroxide thanks to water splitting by bipolar membrane. The contamination of sodium hydroxide by formate ion is due to diffusion of molecular formic acid through the bipolar membrane and to leakage of formate ion through the same membrane under the applied current. The cation-exchange membrane does not participate to contamination of sodium hydroxide. But the leakage of hydroxide ion through the cation-exchange membrane is the major factor that influences the current efficiency of electro dialysis. The average current efficiency decreases with time principally because the sodium hydroxide concentration increases. The development of a membrane with limited hydroxide leakage is desirable.

Suggested Reviewers: Gerald Pourcelly
gerald.pourcelly@iemm.univ-montp2.fr

Tongwen Xu

twxu@ustc.edu.cn

Lasaad Dammak

dammak@univ-paris12.fr

M. Rakib
Professor
ECP/LGPM

Dear editor

This article deals with two-compartment bipolar membrane electro dialysis and modelling. The flux rates of leakage of formate ion and sodium ion through the bipolar membrane are determined. The model gives minor and major species concentration.

Best regards

1
2
3
4 **Two-compartment bipolar membrane electro dialysis for splitting of sodium formate**
5 **into formic acid and sodium hydroxide: modelling**

6
7 **J. S. Jaime-Ferrer, E. Couallier, Ph. Viers, M. Rakib***

8
9 Laboratoire de Génie des Procédés et Matériaux

10
11 Ecole Centrale Paris

12
13 Grande Voie des Vignes, 92295 Châtenay-Malabry Cedex

14
15
16 *Author for correspondence. Tel: +33 1 41 13 15 56; fax: +33 1 41 13 11 33; E-mail
17 address: mohammed.rakib@ecp.fr (M. Rakib)

18
19
20
21
22
23
24
25
26 Abstract:

27
28 The aim of this work is to model the two-compartment bipolar membrane electro dialysis for
29 organic salts acidification. The salt studied is sodium formate which splits into formic acid
30 and sodium hydroxide thanks to water splitting by bipolar membrane. The contamination of
31 sodium hydroxide by formate ion is due to diffusion of molecular formic acid through the
32 bipolar membrane and to leakage of formate ion through the same membrane under the
33 applied current. The cation-exchange membrane does not participate to contamination of
34 sodium hydroxide. But the leakage of hydroxide ion through the cation-exchange membrane
35 is the major factor that influences the current efficiency of electro dialysis. The average
36 current efficiency decreases with time principally because the sodium hydroxide
37 concentration increases. The development of a membrane with limited hydroxide leakage is
38 desirable.

39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
66
67
68
69
70
71
72
73
74
75
76
77
78
79
80
81
82
83
84
85
86
87
88
89
90
91
92
93
94
95
96
97
98
99
100
101
102
103
104
105
106
107
108
109
110
111
112
113
114
115
116
117
118
119
120
121
122
123
124
125
126
127
128
129
130
131
132
133
134
135
136
137
138
139
140
141
142
143
144
145
146
147
148
149
150
151
152
153
154
155
156
157
158
159
160
161
162
163
164
165
166
167
168
169
170
171
172
173
174
175
176
177
178
179
180
181
182
183
184
185
186
187
188
189
190
191
192
193
194
195
196
197
198
199
200
201
202
203
204
205
206
207
208
209
210
211
212
213
214
215
216
217
218
219
220
221
222
223
224
225
226
227
228
229
230
231
232
233
234
235
236
237
238
239
240
241
242
243
244
245
246
247
248
249
250
251
252
253
254
255
256
257
258
259
260
261
262
263
264
265
266
267
268
269
270
271
272
273
274
275
276
277
278
279
280
281
282
283
284
285
286
287
288
289
290
291
292
293
294
295
296
297
298
299
300
301
302
303
304
305
306
307
308
309
310
311
312
313
314
315
316
317
318
319
320
321
322
323
324
325
326
327
328
329
330
331
332
333
334
335
336
337
338
339
340
341
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
358
359
360
361
362
363
364
365
366
367
368
369
370
371
372
373
374
375
376
377
378
379
380
381
382
383
384
385
386
387
388
389
390
391
392
393
394
395
396
397
398
399
400
401
402
403
404
405
406
407
408
409
410
411
412
413
414
415
416
417
418
419
420
421
422
423
424
425
426
427
428
429
430
431
432
433
434
435
436
437
438
439
440
441
442
443
444
445
446
447
448
449
450
451
452
453
454
455
456
457
458
459
460
461
462
463
464
465
466
467
468
469
470
471
472
473
474
475
476
477
478
479
480
481
482
483
484
485
486
487
488
489
490
491
492
493
494
495
496
497
498
499
500
501
502
503
504
505
506
507
508
509
510
511
512
513
514
515
516
517
518
519
520
521
522
523
524
525
526
527
528
529
530
531
532
533
534
535
536
537
538
539
540
541
542
543
544
545
546
547
548
549
550
551
552
553
554
555
556
557
558
559
560
561
562
563
564
565
566
567
568
569
570
571
572
573
574
575
576
577
578
579
580
581
582
583
584
585
586
587
588
589
590
591
592
593
594
595
596
597
598
599
600
601
602
603
604
605
606
607
608
609
610
611
612
613
614
615
616
617
618
619
620
621
622
623
624
625
626
627
628
629
630
631
632
633
634
635
636
637
638
639
640
641
642
643
644
645
646
647
648
649
650
651
652
653
654
655
656
657
658
659
660
661
662
663
664
665
666
667
668
669
670
671
672
673
674
675
676
677
678
679
680
681
682
683
684
685
686
687
688
689
690
691
692
693
694
695
696
697
698
699
700
701
702
703
704
705
706
707
708
709
710
711
712
713
714
715
716
717
718
719
720
721
722
723
724
725
726
727
728
729
730
731
732
733
734
735
736
737
738
739
740
741
742
743
744
745
746
747
748
749
750
751
752
753
754
755
756
757
758
759
760
761
762
763
764
765
766
767
768
769
770
771
772
773
774
775
776
777
778
779
780
781
782
783
784
785
786
787
788
789
790
791
792
793
794
795
796
797
798
799
800
801
802
803
804
805
806
807
808
809
810
811
812
813
814
815
816
817
818
819
820
821
822
823
824
825
826
827
828
829
830
831
832
833
834
835
836
837
838
839
840
841
842
843
844
845
846
847
848
849
850
851
852
853
854
855
856
857
858
859
860
861
862
863
864
865
866
867
868
869
870
871
872
873
874
875
876
877
878
879
880
881
882
883
884
885
886
887
888
889
890
891
892
893
894
895
896
897
898
899
900
901
902
903
904
905
906
907
908
909
910
911
912
913
914
915
916
917
918
919
920
921
922
923
924
925
926
927
928
929
930
931
932
933
934
935
936
937
938
939
940
941
942
943
944
945
946
947
948
949
950
951
952
953
954
955
956
957
958
959
960
961
962
963
964
965
966
967
968
969
970
971
972
973
974
975
976
977
978
979
980
981
982
983
984
985
986
987
988
989
990
991
992
993
994
995
996
997
998
999
1000

1. Introduction

Bipolar membrane electro dialysis (BMED) is used to regenerate organic acids and sodium hydroxide from sodium organic salts [1-4]. It is based on the ability of a bipolar membrane to split water into H^+ and OH^- at membrane bilayer interface. The two-compartment configuration with a cation-exchange membrane is the most widely used configuration

1
2
3
4 because it is simpler and more favourable in terms of energy than the three-compartment
5 configuration. In the two-compartment configuration represented in Fig. 1, This Fig refers to
6 regeneration of formic acid and sodium hydroxide from sodium formate. H^+ produced by the
7 bipolar membrane forms formic acid with formate (almost quantitatively due to the weak acid
8 character of formic acid $pK = 3.75$) while OH^- produced by the other face of the bipolar
9 membrane and Na^+ which crosses the cation-exchange membrane forms sodium hydroxide.
10 The acid is obtained in a mixture with its salt.

11
12
13
14
15
16 The three-compartment electro dialysis was studied and modelled [5]. The mass balance of the
17 three-compartment electro dialysis may be predicted knowing volume variations with current
18 quantity for acid, base and salt solutions. Diffusion rates of molecular formic acid through
19 bipolar and anion-exchange membrane and the leakage rate of hydroxide ion through the
20 cation-exchange membrane are the model parameters. The current efficiency of formic acid
21 production is a function of diffusion of molecular acid through the anion-exchange membrane
22 and the bipolar membrane. Among carboxylic acids, formic acid is less studied than others
23 like acetic or lactic acids [6,7].

24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65
Wilhem et al. [8] studied the salt ion fluxes across bipolar membranes and estimated the
proportion of contaminant to 1% molar when the concentrations reach 4 mol dm^{-3} . To our
knowledge, no predictive model has been developed giving current efficiency for the two-
compartment configuration.

Ideally, sodium hydroxide solutions obtained by two-compartment bipolar membrane
electro dialysis with cation-exchange membrane is recovered pure in solution and no formate
is present. However, this is not the case. Some formate pollutes the sodium hydroxide solution
and this may be undesired.

Carboxylic acids diffusion was mentioned as one factor reducing the current efficiency. Koter
S. [9] studied the weak acids production. The modelling given is very complex. Except [5,
10], literature is poor concerning the conversion of sodium formate into formic acid and
sodium hydroxide by bipolar membrane electro dialysis.

The performance of an electromembrane process is given in term of current efficiency which
represents the ratio of the mole number produced or transferred and the number of faradays
passed through the system. The integral or average current efficiency (ICE) between time 0
and time t is defined by the relation:

$$ICE_{0,t} = \frac{\Delta N}{iAt / F} \quad (1)$$

1
2
3
4 where ΔN is the variation of mole number of the component between time 0 and time t , i the
5 current density constant during time t , A is the membrane area, F is the faraday constant
6 (96485 A s mol⁻¹ = 26.8 Ah mol⁻¹)
7

8
9 The differential current efficiency (DCE) is defined as:

$$10 \quad DCE_t = \frac{dN}{iAdt/F} \quad (2)$$

11
12 The aim of this study is to model the functioning of the two-compartment bipolar membrane
13 electro dialysis configuration. It is also to identify the contamination of sodium hydroxide by
14 formate ion and the factors limiting the current efficiency of formic acid production.
15
16
17
18
19
20

21 **2. Experimental details**

22 **2.1. Experimental set-up**

23
24 CMB cation exchange membrane and BP-1 bipolar membrane were used. These membranes
25 were supplied by Eurodia Industries. Electrodialysis was performed with a cell stack EUR
26 2B-BIP supplied by the same company. It was composed of 6 cells with two-compartments
27 (Fig. 1). The active area of each cell was 2 dm². Two nickel electrodes with NaOH 2 mol dm⁻³
28 rinsing solution terminated the stack. They did not interfere with the electro dialysis.
29 Temperature was measured but not controlled (average temperature has been taken). A
30 constant current was applied. The circulation of solutions in the cell was started 5 to 10 min
31 before the current was switched on.
32
33
34
35
36
37
38
39

40 The experiments of diffusion of formic acid from a mixture of formic acid sodium formate
41 were done as described in a previous paper [5].
42
43
44

45 **2.2. Reagents and solutions:**

46 Sodium formate 98% and sodium hydroxide 37% were supplied by VWR.

47 Initial concentration of sodium formate solution was about 2 mol dm⁻³ and initial
48 concentration of sodium hydroxide was about 0.5 to 1 mol dm⁻³. The volume of both solutions
49 was 1 to 2 dm³ for 6 cells
50
51
52

53 These solutions were titrated for acid and base contents. Formate (as formic acid or sodium
54 formate) and sodium ion in low concentration were determined using ionic chromatography
55 (Dionex).
56
57
58
59
60
61
62
63
64
65

3. Results and discussion

The model proposed describes the functioning of a two-compartment bipolar membrane electro dialysis with a cation-exchange membrane in alternation with bipolar membrane. The model is able to describe the contamination of sodium hydroxide solution by formate and to give the mass-balance of the electro dialyser.

3.1. Modelling

The subscripts a and b refer to acid/salt and sodium hydroxide solutions respectively. According to Fig. 1, formic acid may diffuse through bipolar membrane into sodium hydroxide solutions. Also, leakage of formiate ion through the bipolar membrane participates to contamination of sodium hydroxide solution. The transfer of formate ion through the cation-exchange membrane is unlikely due to migration. Fig. 1 summarises the exchange of species in the electro dialysis device. Some fluxes are desired (sodium from salt compartment to base compartment, H^+ and OH^- from the bipolar membrane to acid/salt and base compartment respectively). The others are undesired.

3.1.1. Model assumptions

To model the two-compartment bipolar membrane electro dialysis the following assumptions are made:

Assumption 1: Hydroxide ion migration (leakage) through the cation-exchange membrane is observed. It is the same than for the three-compartment configuration. It depends only on sodium hydroxide solution concentration, on temperature and on the membrane. The hydroxide leakage flux rate is noted h. The number of moles of hydroxide ion N_{OH} crossing the unit area of cation-exchange membrane during an unit of time is $N_{OH} = hi[NaOH]_b$ where $[NaOH]_b$ is the concentration of sodium hydroxide in base compartment.

Assumption 2: diffusion of formate ion through the cation-exchange membrane is negligible because migration is the major effect. Without current diffusion of formate ion through the cation-exchange membrane occurs. The diffusion of molecular acid through the cation-exchange membrane is counteracted by sodium hydroxide ion leakage. Due to the passage of hydroxide ion through this membrane, reaction of formic acid with sodium hydroxide occurs in the membrane or in the boundary layers. This leads to formate ion which migrates towards the anode making an U-turn. So, diffusion of formate ion through the cation exchange membrane does not occur during electro dialysis.

1
2
3
4 **Assumption 3:** The formic acid diffusion through the bipolar membrane is proportional to
5 acid concentration. This will be checked.
6
7

8 **3.1.2. Diffusion and migration**

9
10 For diffusion of neutral species through surface A of solution-membrane the number of moles
11 crossing A during a time dt, is written:
12

$$13 \quad dN = -D_m A \frac{d[X]}{dx} dt \quad (3)$$

14 x is the direction perpendicular to the membrane and D_m is the diffusion coefficient of X in
15 the solution or in the membrane.
16

17 The concentration of X in solution and the boundary layers is constant since an increase of
18 mixing had no effect. The concentration in the receiving solution is very low and could be
19 taken equal to zero. Thus the concentration difference in the membrane is nearly [X]. The
20 diffusion number of moles may be written:
21

$$22 \quad dN = -\frac{D}{e} A [X] dt \quad (4)$$

23 Where D is the diffusion coefficient in the membrane and e is the thickness of the membrane.
24 For diffusion and migration the number of moles crossing A during a time dt is given by
25 Nernst-Planck equation:
26

$$27 \quad dN = -DA \left(\frac{d[X]}{dx} + [X] z_X \frac{d\phi}{dx} \right) dt \quad (5)$$

28 where z_X is the charge of X and ϕ is the electrical potential. If the migration takes place alone
29 the flux is proportional to the concentration [X] and proportional to the current.
30

31 Diffusion or migration of a species X is proportional to X concentration in the solution from
32 which it diffuses or migrates, to surface area of membrane and duration of diffusion or
33 migration considered. The mole number dN of species X (diffusion: dN_{dif} , migration: dN_{mig} ,)
34 is written:
35

$$36 \quad dN_{dif} = k_{dif} A [X] dt \quad (6)$$

$$37 \quad dN_{mig} = k_{mig} i A [X] dt \quad (7)$$

38 k_{dif} and k_{mig} are the flux rates with: $k_{dif} = k_{mig} = .D/e$
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

3.1.3. Mass balance of the cell stack

The mass-balance is written taking into account:

- The migration of formate ion through the bipolar membrane (leakage)
- The migration of sodium ion through the bipolar membrane (leakage)

Thus the number of moles of H^+ and OH^- produced by the bipolar membrane (surface A) during time dt is given by:

$$dn_{H^+} = dn_{OH^-} = \frac{iA}{F} dt - dn_{formate} - dn_{Na^+} \quad (8)$$

This is because the current is transported by all ions (the total current density being i)

If f and g are the flux rates for leakage of formate ion and sodium ion respectively, then:

$$dn_{formate} = fiA[HCOO^-]_a dt \quad (9)$$

and

$$dn_{Na^+} = giA[Na^+]_b dt \quad (10)$$

The acid balance is the following:

$$d(V_a[HCOOH]_a) = \left(\frac{iA}{F} - fiA[HCOO^-]_a - giA[Na^+]_b - k_{bip} A[HCOOH]_a - hiA[OH^-]_b \right) dt \quad (11)$$

The flux rate of diffusion of formic acid through the bipolar membrane has been determined [5]: $k_{bip} = 0.0045$ to 0.005 dm h^{-1} at 298 K with an activation energy of 18 kJ mol^{-1} .

The value of flux rate of leakage of hydroxide anion through the cation exchange membrane is $h = 0.0032 \text{ dm}^3 \text{ Ah}^{-1}$ at 298K. The activation energy is estimated to 23 kJ mol^{-1} .

This equation expresses that the acid accumulation is equal to the number of moles of H^+ produced minus the acid lost by diffusion from compartment a to compartment b and the acid which reacts with the leaked hydroxide ions.

The salt balance is given by the equation:

$$d(V_a[HCOO^-]_a) = -dn_{H^+} - fiA[HCOO^-]_a dt + hiA[OH^-]_b dt = \left(-\frac{iA}{F} + giA[Na^+]_b + hiA[OH^-]_b \right) dt \quad (12)$$

Leakage of formate ion through the bipolar membrane does not appear formally in this equation because its transport takes part in total current passage $iAdt/F$.

The hydroxide ion balance gives:

$$d(V_b[OH^-]_b) = dn_{OH^-} - (hiA[OH^-]_b + k_{bip}A[HCOOH]_a)dt = \left(\frac{iA}{F} - fiA[HCOO^-]_a - giA[Na^+]_b - hiA[OH^-]_b - k_{bip}A[HCOOH]_a\right)dt \quad (13)$$

Formate ion (contaminant) in sodium hydroxide solution is given by the following equation:

$$d(V_b[HCOO^-]_b) = (k_{bip}A[HCOOH]_a + fiA[HCOO^-]_a)dt \quad (14)$$

The first member of equations 11 to 14 is the differentiation of the product of a volume and a concentration both function of time. Hence:

$$d(V[X]) = Vd[X] + [X]dV \quad (15)$$

The volume variations are linear versus time and versus the current [11].

$$dV_a = aiAdt \text{ et } dV_b = biAdt \quad (16)$$

a and b are determined experimentally.

3.2. Application of the model

In order to test this model, the experimental data obtained during electro dialysis experiments were fitted to equations 11 to 16. The calculation is done as follows: the initial conditions are stated. Then the calculation is undertaken for dt increment: The elemental variations $d[HCOOH]_a$, $d[HCOO^-]_a$, $d[OH^-]_b$ are calculated using equations 11 – 15 and using the previous values for the concentrations $[HCOOH]_a$, $[HCOO^-]_a$ and $[OH^-]_b$. Then the actual values for $[HCOOH]_a$, $[HCOO^-]_a$ and $[OH^-]_b$ are obtained. The concentration of formate ion in sodium hydroxide $[HCOO^-]_b$ is computed also (equation 15)

3.2.1 Volume variations

Fig. 2 reports variations of specific volumes of the two solutions versus specific current quantity (quantity of electricity per an unit of area surface). Different experiments are considered in Fig. 2 included different current densities. The variations are linear

Acid/salt solution: $\Delta V_a = aiAt$ with $a = -3.1 \cdot 10^{-3} \text{ dm}^3 \text{ Ah}^{-1}$

Base solution: $\Delta V_b = biAt$ with $b = 2.1 \cdot 10^{-3} \text{ dm}^3 \text{ Ah}^{-1}$

These volume variations are essentially due to water transfer by electroosmosis.

3.2.2 Sodium transfer through the bipolar membrane

The sodium ion transfer from base solution to acid/salt solution through the bipolar membrane can not be measured in the two compartment configuration because of the presence of sodium

ion in the receiving solution. This study was done with the three-compartment configuration. The leakage of sodium is quite the same in the two configurations. Sodium ion was determined in acid compartment. Fig. 3 shows the variations of mole number of sodium in the acid compartment versus time for an experiment where sodium hydroxide solution and sodium formate solution are renewed. For sodium hydroxide concentration between 1 and 3 mol dm⁻³ (average value 2 mol dm⁻³) and a current density of 5 A dm⁻² it is found that:

$$\frac{dN_{Na^+}}{A dt} = 210^{-4} \text{ mol.dm}^{-2}.h^{-1} \quad (17)$$

$$dN_{Na^+} = giA[\overline{NaOH}]_b dt \quad (18)$$

Where $[\overline{NaOH}]_b$ is the average concentration of sodium hydroxide solution.

This permits the calculation of the sodium ion flux rate of leakage through the bipolar membrane. The magnitude of the value of the flux rate g may be calculated $g \approx 2 \cdot 10^{-5} \text{ dm}^3 \text{ Ah}^{-1}$.

3.2.3 Fitting of formate in sodium hydroxide

Before starting, a non-negligible concentration of formate is detected in sodium hydroxide solution. This is probably due to diffusion of sodium formate when no current is applied. It is better to limit the contact between solutions when the current is switched off.

The mole number of formate crossing the membranes between time 0 and time t , N_F , is calculated from the concentrations and the volumes at these moments.

$$N_F = \frac{V_b(t)}{A} [HCOO]_b - N_{F0} = \frac{V_b(t)}{A} [HCOO]_b - \frac{V_b(0)}{A} [HCOO]_{b0} \quad (18)$$

where $[HCOO]_{b0}$ and $V_b(0)$ are respectively the concentration of formate in sodium hydroxide solution and the volume of this solution at $t = 0$.

Fig. 4 reports the variations of the mole number of formate crossing the unit area of bipolar membrane versus time. The experimental points are drawn (calculated by equation.18 with an interval of error estimated to 10%). The average temperature is near 300 K. Several experiments were made. Not all are reported here. The experiments show that the current density has an effect on the passage of formate: the higher the current density the higher the flux through membranes. The curve fitting is done by the method of least squares. It leads to the following value of the flux rate $f = (2.2 \pm 0.2) \cdot 10^{-4} \text{ dm}^3 \text{ Ah}^{-1}$. The value of the flux rate of leakage of sodium ion through the bipolar membrane, g , is about $2 \cdot 10^{-5} \text{ dm}^3 \text{ Ah}^{-1}$ but this small value has no effect on the passage of formate through the membrane. The low

1
2
3
4 dispersion of f values shows that the model describes well the contamination of sodium
5 hydroxide solution by formate ion. Thus, the assumptions made are validated. The bipolar
6 membrane is the only responsible of contamination of sodium hydroxide solution
7
8 The contribution of formate migration through the bipolar membrane is obtained by
9 comparing the flux of formate during time dt i.e. $fi[HCOO^-]_a$ to the total flux through the
10 membrane (i/F). The value θ of the transport number of formate ion is equal to:

$$\theta = fF[HCOO^-]_a = 0.006[HCOO^-]_a \quad (19)$$

16 The highest value corresponds to the beginning of the operation generally at 2 mol dm^{-3} . Thus
17 the maximum value for transport number of formate ion through the bipolar membrane is near
18 1 %. This is in agreement with the known results [8].
19
20
21
22

23 **3.2.4 Diffusion of formic acid from acid/salt solutions through bipolar membrane**

24 Diffusion through the bipolar membrane for mixtures of formic acid and sodium formate was
25 measured. The total concentration of formate (formic acid or formate ion forms) was fixed to
26 2 mol dm^{-3} . The receiving phase was sodium hydroxide solution 1 mol dm^{-3} . Fig. 5 reports the
27 variations of formate flux through the bipolar membrane vs. the concentration of formic acid.
28 At concentration of acid equal to 0 diffusion of 2 mol dm^{-3} formate ion solution is observed.
29 The flux of diffusion increases as the acid concentration increases. Deviation from linearity is
30 observed. Diffusion of formate ion is decreasing from its initial value to zero for the 2 mol
31 dm^{-3} formic acid solution. This means that the mixture does not behave ideally. But the
32 deviation is small and may be neglected in a first step.
33
34

35 The diffusion flux of formic acid is then nearly proportional to the acid concentration. The
36 diffusion of formate ion does not occur when the current is switched on as seen before.
37
38
39
40
41

42 **3.2.5. Fitting of variations of acid, base and salt**

43 The experimental variations of concentrations of formic acid, sodium formate and sodium
44 hydroxide are confronted to the curves determined by the model. Fig. 6 reports an example of
45 results. The agreement is remarkable. The current efficiencies for production of acid and base
46 and for consumption of sodium formate may be predicted by the model. The average current
47 efficiency between time 0 and time t (as defined by equation 1) decreases with time. This is
48 due in part to diffusion of molecular acid through the bipolar membrane which increases
49 when the acid concentration increases. The major factor that decreases the current efficiency
50 is the leakage of hydroxide ion. During the experiment, the base concentration increases and
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4 consequently the leakage. This explains the variations of current efficiency during the
5 experiment. Fig. 7 reports the variations of current efficiency during an experiment of
6 electro dialysis. The error on current efficiency is estimated to 3%. Experimental points are in
7 accordance with calculated values. This is in favour of the assumption of proportionality of
8 leakage flux of hydroxide ion to the concentration of sodium hydroxide. The current density
9 has only a little effect on variations of current efficiency. To obtain high current efficiency,
10 one has to limit the concentration of sodium hydroxide. Only a slight decrease should be
11 obtained if this concentration is maintained constant. An increase of the volume of sodium
12 hydroxide solution is favourable as could be seen in Table 1 which gives calculated current
13 efficiencies versus the specific initial volume of sodium hydroxide solution.
14
15
16
17
18
19
20
21
22

23 **4. Conclusion**

24 The two-compartment configuration with a cation-exchange membrane is widely used in the
25 acidification of organic salts. This is because it is simpler and more favourable in term of
26 energy consumption than the three-compartment configuration.
27

28 The contamination of sodium hydroxide solution by formate is due to:

- 29 - diffusion of molecular formic acid through the bipolar membrane
- 30 - leakage (migration) of formate ion through the bipolar membrane

31 The cation-exchange membrane is not concerned as far as contamination is considered.

32 The contribution of diffusion of formic acid and leakage of formate ion through the bipolar
33 membrane to current efficiency is small. The current efficiency is principally defined by the
34 leakage of hydroxide ion through cation-exchange membrane. During the electro dialysis, the
35 current efficiency decreases as time increases. This may be explained by the increase of
36 sodium hydroxide concentration, which means an increase of leakage of hydroxide ion.
37
38
39
40
41
42
43
44

45 The leakage of formate ion through the bipolar membrane is proportional to current density
46 and to sodium hydroxide concentration. The values of flux rate of leakage of formate ion are
47 given in Table 2, which recapitulates all the flux rates of interest in modelling of a two-
48 compartment bipolar membrane electro dialysis of sodium formate. Note that the flux of
49 leakage of formate is not to consider for the three-compartment configuration because the
50 formate in the acid compartment is under acid form and the formate ion concentration is very
51 small [12].
52
53
54
55
56

57 To maintain a high current efficiency, the sodium hydroxide concentration should be low but
58 an optimal value must be used since too low concentration of sodium hydroxide will be
59 energetically unfavourable.
60
61
62
63
64
65

References

1. H. Strathmann, Ion-exchange membrane separation processes, Elsevier, Amsterdam (2004)
2. S. Thate, G. Eigenberger, H.J. Rapp, Handbook on bipolar membrane technology, A.J.B. Kemperman, Twente University Press, Enschede, The Netherlands (2000)
3. C. Huang, T. Xu, Y. Zhang, Y. Xue, G. Chen, Application of electrodialysis to the production of organic acids: State-of-the-art and recent developments, *J. Membrane Sc.e* 288 (2007) 1–12
4. X. Tongwen, Electrodialysis processes with bipolar membranes (EDBM) in environmental protection—a review, *Resources, Conservation and Recycling*, 37, (2002) 1-22
5. J.S. Jaime Ferrer, E. Couallier, Ph. Viers, G. Durand, M. Rakib, Three-compartment bipolar membrane electrodialysis for splitting of sodium formate into formic acid and sodium hydroxide: role of diffusion of molecular acid, *J. Membrane Sc.*(2008), doi:10.1016/j.memsci.2008.07.059
6. Y.H. Kim, S.H. Moon, Lactic acid recovery from fermentation broth using one stage electrodialysis, *J. Chem. Tech. Biotech.* 76 (2001) 169-178
7. G.S. Trivedi, B.G Shah, S.K. Adhikary, V.K. Indusekhar, R. Rangarajan, Studies on bipolar membranes. Part II – Conversion of sodium acetate to acetic acid and sodium hydroxide, *Reactive Func. Polymers* 32 (1997) 209-215
8. F. G. Wilhelm, I. Pünt, N.F.A. van der Vegt, M. Wessling, H. Strathmann, Optimisation strategies for the preparation of bipolar membranes with reduced salt ion leakage in acid-base electrodialysis, *J. Membrane Sc.* 182 (2001) 13-28
9. S. Koter, Modeling of weak acid production by the EDB method, *Sep.Purif. Tech.* 57 (2007) 406–412
10. J.S. Jaime Ferrer, S. Laborie, G. Durand, M. Rakib, Formic acid regeneration by electromembrane processes, *J. Membrane. Sc.*, 280 (2006) 509-516
11. J.L. Gineste, G. Pourcelly, Y. Lorrain, F. Persin, C. Gavach, Analysis of factors limiting the use of bipolar membranes: a simplified model to determine trends, *J. Membrane. Sc.* 112 (1996) 199-208

- 1
2
3
4 12. J.S. Jaime Ferrer, E. Couallier, M. Rakib, G. Durand, Electrochemical determination
5 of acidity level and dissociation of formic acid/water mixtures as solvent, *Electrochim.*
6 *Acta*, 52 (2007) 5773-5780
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4 Fig. 1: Two-compartment BMED principle and the fluxes through the membranes (dashed
5 arrows: undesirable flux, continuous arrows: desirable flux)
6
7
8

9 Fig. 2: Volume variations for the acid circuit (negative values) and for the base circuit
10 (positive values) vs. current quantity for current densities 2.5-5-7.5-10 A dm⁻²
11
12
13

14 Fig. 3: Formic acid contamination by sodium ion in the three-compartment experiment, base
15 and salt solutions renewed (average concentration of base 2 mol dm⁻³, $i = 5.00 \text{ A dm}^{-2}$, $T =$
16 303 K)
17
18
19
20

21 Fig. 4: Specific formate mol number crossing the membrane vs. time, $T = 300 \text{ K}$
22

23 initial specific volume of salt (base) 0.14 dm (0.08 dm), concentration of salt (base) 1.84
24 mol dm⁻³ (0.90 mol dm⁻³), $i = 9.95 \text{ A dm}^{-2}$; \diamond initial volume of salt (base) 0.14 dm (0.09 dm);
25 concentration of salt (base) 1.87 mol dm⁻³ (0.85 mol dm⁻³), $i = 7.50 \text{ A dm}^{-2}$; Δ initial volume
26 of salt (base) 0.16 dm (0.12 dm); concentration of salt (base) 1.81 mol dm⁻³ (0.97 mol dm⁻³), i
27 = 5.00 A dm⁻²; \blacksquare initial volume of salt (base) 0.16 dm (0.09 dm); concentration of salt (base)
28 1.84 mol dm⁻³ (0.86 mol dm⁻³), $i = 2.50 \text{ A dm}^{-2}$
29
30
31
32
33
34

35 Fig. 5: Diffusion from acid/salt mixtures through BP1 membrane ($[\text{HCOOH}] + [\text{NaHCOO}] =$
36 2 mol dm⁻³, $T = 298 \text{ K}$)
37
38
39
40
41

42 Fig. 6: Mass balance of major products in BMED vs. time, \blacksquare formic acid, \diamond sodium formate,
43 Δ sodium hydroxide
44
45
46

47 Fig. 7: Average current efficiency vs. time, experimental points and fitted curve. Initial
48 specific volume of salt (base) 0.14 dm (0.08 dm), concentration of salt (base) 1.84 mol dm⁻³
49 (0.90 mol dm⁻³), $T = 300\text{K}$, $i = 9.95 \text{ A dm}^{-2}$
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

1
2
3
4 Lit of tables
5
6
7
8

9 Table 1: Current efficiency vs. specific initial volume of sodium hydroxide solution, specific
10 initial volume of salt 0.14 dm, concentration of salt (base) 1.84 mol dm^{-3} (0.90 mol dm^{-3}), $T =$
11 300 K , $i = 9.95 \text{ A dm}^{-2}$
12
13
14

15
16
17
18
19 Table 2: Values of flux rates of different transfers occurring in the two-compartment
20 configuration during bipolar membrane electro dialysis of sodium formate.
21
22

23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

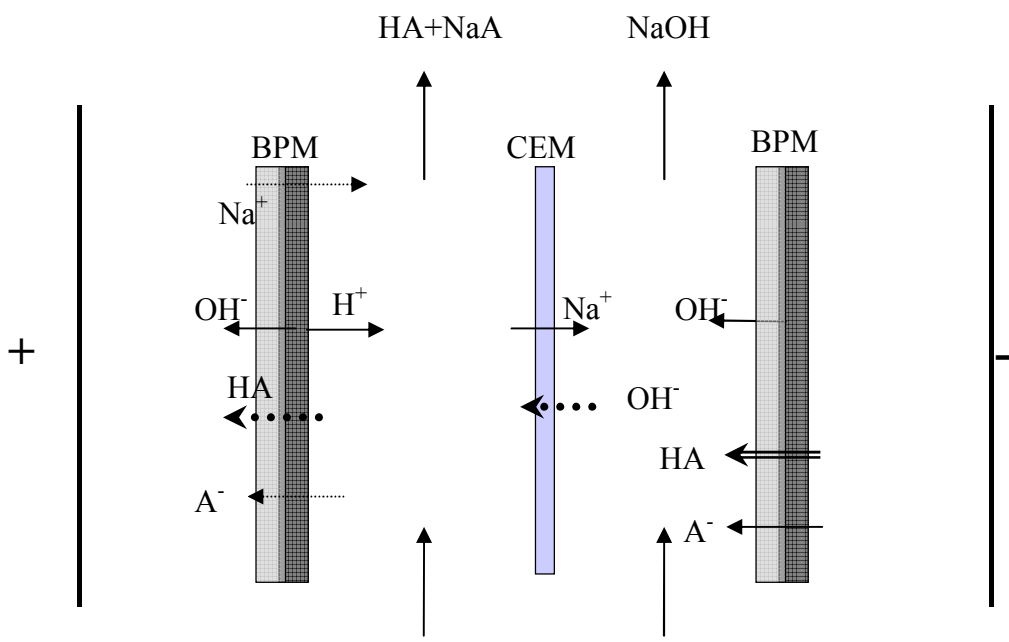


Fig. 1

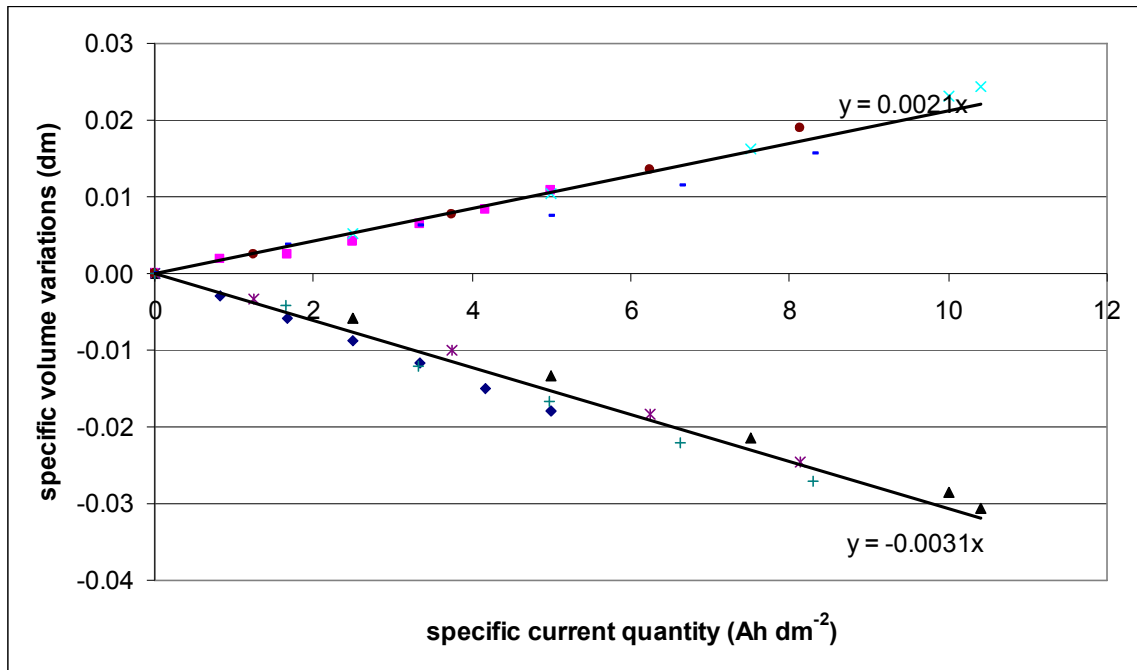


Fig.2

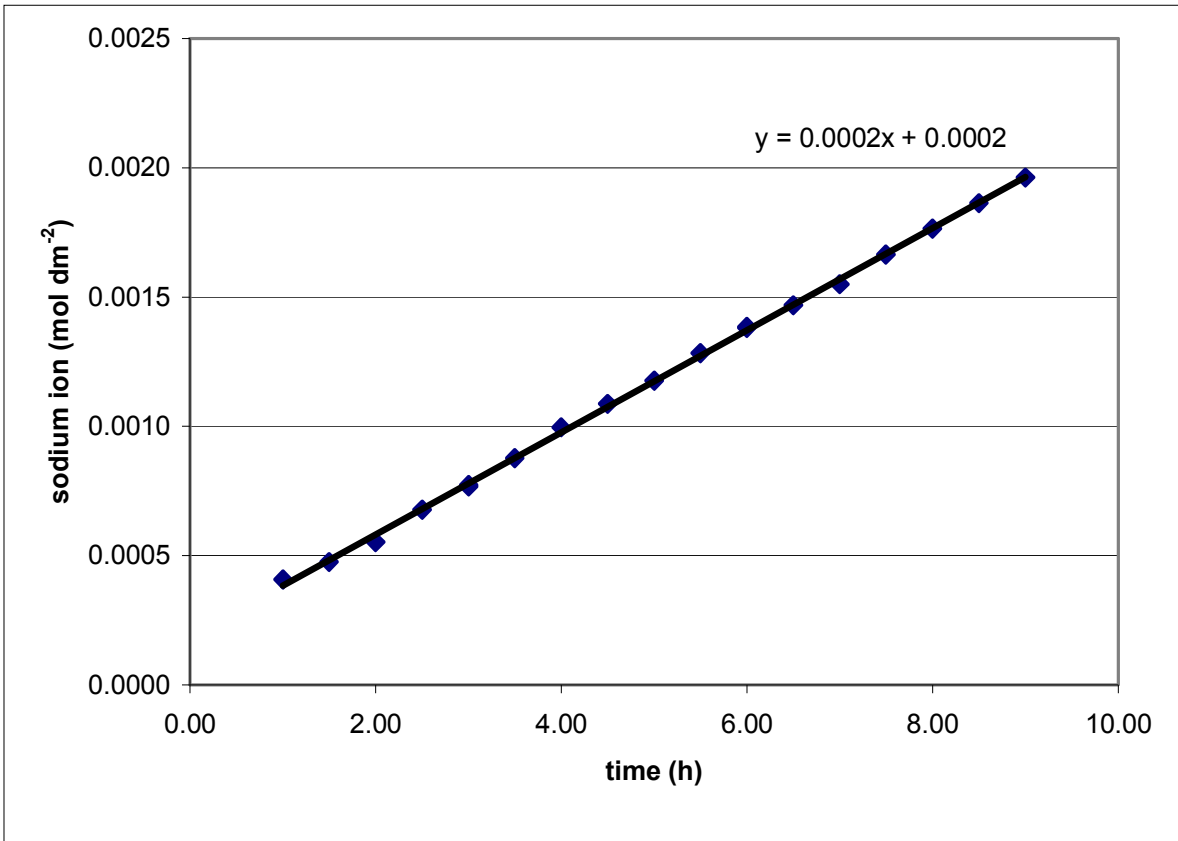


Fig. 3

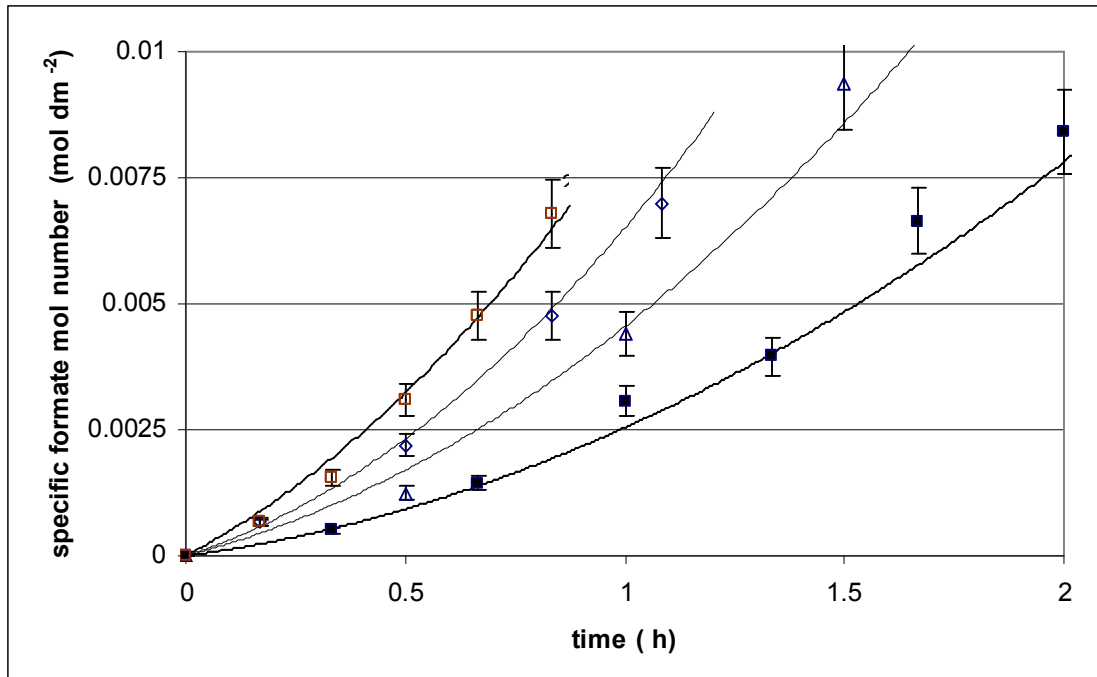


Fig. 4

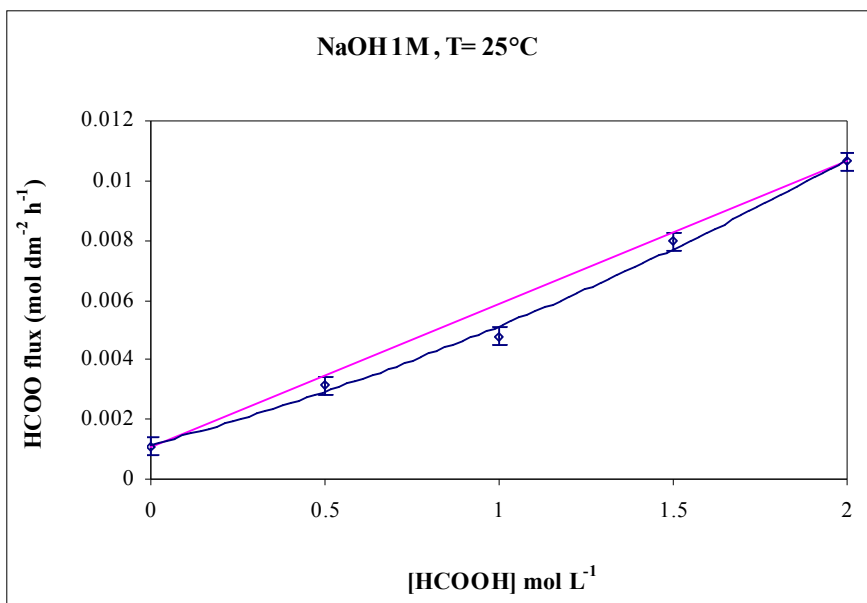


Fig. 5:

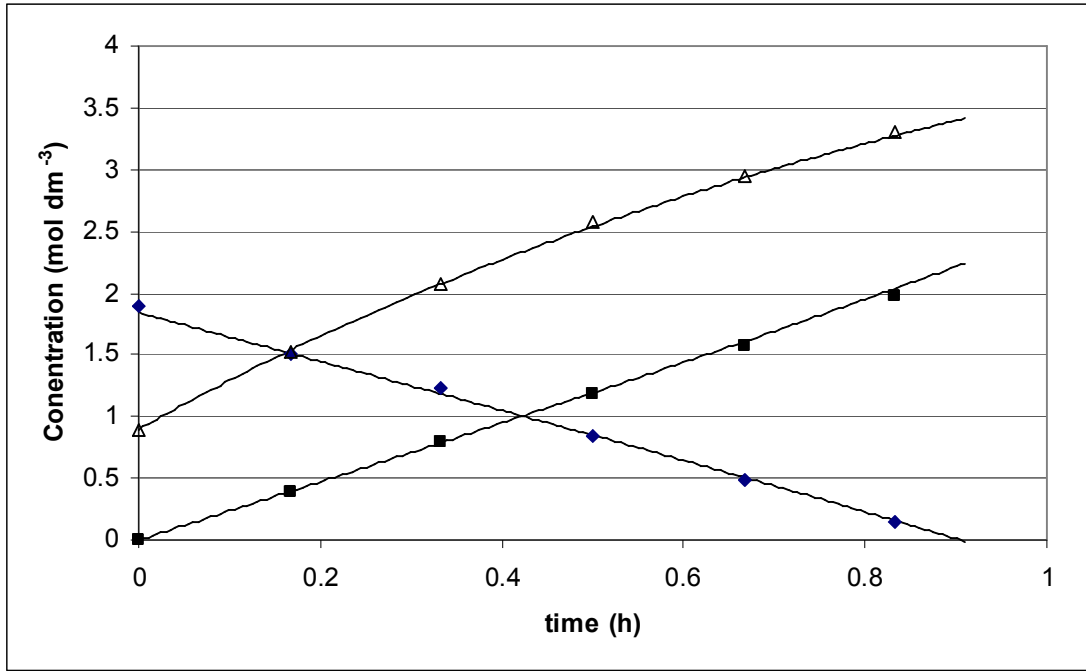


Fig. 6

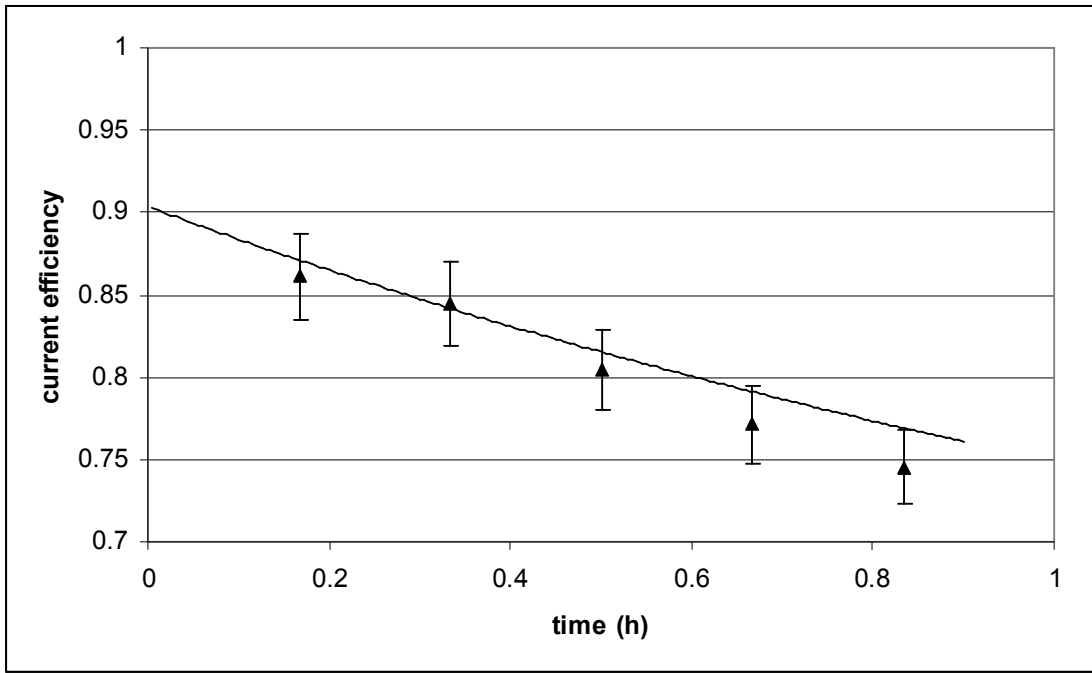


Fig. 7:

Table 1:

Specific volume of sodium hydroxide solution (dm)	Current efficiency
0.1	0.79
0.2	0.84
0.5	0.87

Table 2:

Flux rates	Values	Study
Diffusion of molecular formic acid through the bipolar membrane	4.5 to 5.0 10^{-3} dm h ⁻¹ at 298 K*	Three-compartment electro dialysis [5]
Hydroxide ion leakage through the cation-exchange membrane	3,2 10^{-3} dm ³ Ah ⁻¹ at 298K**	Three-compartment electro dialysis [5]
Formate ion leakage through the bipolar membrane	2,2 10^{-4} dm ³ Ah ⁻¹ at 300 K	This study
Sodium ion leakage through the bipolar membrane	2 10^{-5} dm ³ Ah ⁻¹ at 298K	Three-compartment electro dialysis [5] and this study
Volume variations of acid/salt compartment	3.1 10^{-3} dm ³ Ah ⁻¹	This study
Volume variations of base compartment	2.1 10^{-3} dm ³ Ah ⁻¹	This study

*Activation energy: 18 kJ mol⁻¹

**Activation energy: 23 kJ mol⁻¹