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## Separation Science and Technology

Publication details, including instructions for authors and subscription information:

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### SEPARATION OF SODIUM SULFATE AND *p*-TOLUENE SULFONIC ACID BY ELECTRODIALYSIS

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Online publication date: 10 September 2002

**To cite this Article** Shahi, Vinod K. , Thamby, S. K. , Siddhanta, A. K. and Rangarajan, R.(2002) 'SEPARATION OF SODIUM SULFATE AND *p*-TOLUENE SULFONIC ACID BY ELECTRODIALYSIS', *Separation Science and Technology*, 37: 14, 3273 – 3289

**To link to this Article:** DOI: 10.1081/SS-120006161

URL: <http://dx.doi.org/10.1081/SS-120006161>

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SEPARATION SCIENCE AND TECHNOLOGY, 37(14), 3273–3289 (2002)

## SEPARATION OF SODIUM SULFATE AND *p*-TOLUENE SULFONIC ACID BY ELECTRODIALYSIS

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### ABSTRACT

An electrodialysis process is proposed to achieve efficient separation of sodium sulfate from its mixture with *p*-toluene sulfonic acid. In this process, interpolymer type ion-exchange membranes were used due to their higher chemical stability and durability. Experiments were conducted in laboratory scale electrodialysis unit with an effective area of 65 cm<sup>2</sup> and 10 cell pairs, at different compositions of sodium sulfate and *p*-toluene sulfonic acid in its mixture, to see the effect of their concentration on the process efficiency. Batchwise electrodialysis experiment in four stages was also conducted to separate 12% (w/v) sodium sulfate from 2% (w/v) *p*-toluene sulfonic acid. Observations indicate that at higher sodium sulfate concentration, energy consumption increases while current efficiency decreases due to enhanced back diffusion from concentrate to treated compartments. Dialytic rate of sodium sulfate is also estimated under

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different experimental conditions. It is concluded that *p*-toluene sulfonic acid adsorbed or masked the surface of anion-exchange membrane, which is responsible for the increased reduction in the ionic transportation with the increase in concentration of *p*-toluene sulfonic acid. Adsorption/masking is completed up to its critical micelle concentration and beyond this concentration; further increase in *p*-toluene sulfonic acid has no more effect on ionic transportation.

**Key Words:** Electrodialysis; *P*. toluene sulfonic acid; Current efficiency; Dialytic rate; Critical micelle concentration

## INTRODUCTION

Electrodialysis is well known as a method for the desalination in which both cation- and anion-exchange membranes are used.<sup>[1–3]</sup> The earliest important industrial applications of electrodialysis was the production of potable water from brackish and seawater. Electrodialysis is also used for the purification by demineralization of solutions of widely varying industrially useful fluids encountered in the food, chemical, and pharmaceutical industries.<sup>[4,5]</sup> This method has been used, for example, to purify sugars, amino acids, proteins, etc. In this case, electrodialysis can be adopted because the nonelectrolytes do not migrate through the ion-exchange membranes. For the separation of ionic inorganics from ionic organic substance, electrodialysis can be used if the charged organic molecule is of larger molecular size. Therefore, it is of interest to see the effect on electro-driven ionic transportation due to the presence of charged organic molecule, in relation to inorganic.

*p*-Toluene sulfonic acid (TSA), which is made by sulfonation of toluene is commercially used to effect the aqueous solubility of disperse dyes. Thus azobenzene, *p*-aminobenzene, *p*-hydroxyazobenzene, *p*-dimethylaminoazobenzene, and 1-phenylazo-4-aminonaphthalene are solubilized by the addition of one or more moles of TSA per mole of disperse dye.<sup>[6]</sup> The volatilization mechanism appears to involve the formation of the sulfonic acid adduct with one mole of disperse dye by hydrophobic and nonpolar Van der Waals interactions, which supply the necessary solubilizing hydrophilic groups due to the surface active properties of TSA and is responsible for the increase in solubility of the disperse dye in water. It is also used as initiators for the catalytic polymerization of caprolactam. TSA, during its industrial production contains large amount of sodium sulfate because of the sulfonation of toluene with sulfuric acid and further



neutralization. Separation of sodium sulfate from TSA in solution phase is often achieved by precipitation process. In this paper, electro-driven membrane separation technique has been attempted for the separation and extraction of sodium sulfate from TSA. Electrodialysis experiments under different conditions have been performed and results are discussed with process efficiency (i.e., energy consumption and current efficiency) and its economic viability (i.e., loss of TSA during the separation process). Furthermore, attempts have been made to correlate the reduction in ionic transport or dialectic rate of sodium sulfate with the critical micelle concentration (CMC) value of TSA. The effects of operating conditions on desalination process are also discussed.

## EXPERIMENTAL

Toluene-4-sulfonic acid (*p*-toluene sulfonic acid) and sodium sulfate (AR grade, S. d fine Chemicals, Mumbai, India) were used in the present investigation without further purification. The cation- and anion-exchange membranes used in these studies were prepared by the method developed in our laboratory.<sup>[7]</sup> Numerous versatile industrial applications of electrodialysis process have been developed using these membranes because of its high chemical and thermal stability and high ionic conductivity due to their strong ionic character.<sup>[8–10]</sup> The basic polymer matrix of these membranes is interpolymer of polyethylene styrene–divinylbenzene copolymer. To this basic polymer, sulfonic acid groups were introduced by chlorosulfonation to make cation-exchange membrane while quaternary ammonium groups were introduced by chloromethylation and ammination for anion-exchange membrane. The membrane was conditioned by the treatment with 1*M* HCl and 1*M* NaOH successively and then equilibrated in 1*M* NaCl solution before packing in electrodialysis stack. Electrochemical properties of these membranes and stack characteristics are presented in Table 1.

A laboratory scale electrodialysis unit containing 10 cell pairs of cation- and anion-exchange membranes each having an effective cross sectional area of 65 cm<sup>2</sup> was used to study the separation of sodium sulfate from TSA in the solution phase. The electrode housings were prepared from rigid PVC sheets with built in flow distributors and outlets. A stainless steel 316 sheet and platinum coated titanium were used as the cathode and anode, respectively. A parallel-cum-series flow arrangement in three stages is employed in the stack. Pumps were used to move the outlet streams from ED stack to the respective bottles for recirculation. There were three outlet streams in recirculation mode of operation, treated, concentrated, and electrode wash. The electrode chambers were flushed with dilute sodium sulfate solution separately. Solution of known volume and composition of a mixture of TSA and Na<sub>2</sub>SO<sub>4</sub> was recirculated through the

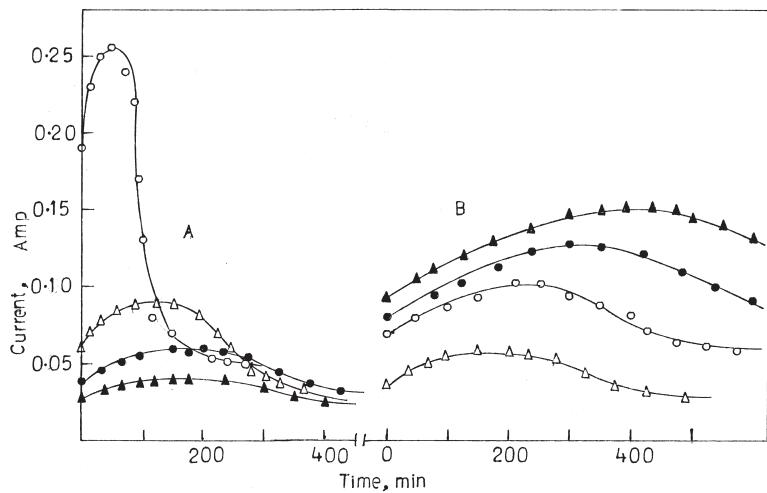
**Table 1.** Characteristics of the Electrodialysis Stack and Ion-Exchange Membranes

<i>Membranes</i>	
(a) Cation-exchange	
Membrane material and ionic group	Interpolymer type, sulfonic acid group
Aerial resistance (Ohm A m <sup>2</sup> )	1.50
Counter-ion transport number (0.1 M NaCl)	0.94
Moisture content (%)	29.80
Ion-exchange capacity (mequiv/g)	1.80
(b) Anion-exchange	
Membrane material and ionic group	Interpolymer type, quaternary ammonium group
Aerial resistance (Ohm cm <sup>2</sup> )	3.82
Counter-ion transport number (0.1 M NaCl)	0.92
Moisture content (%)	16.35
Ion-exchange capacity (mequiv/g)	1.69
Number of cell pairs	10
Effective cross-sectional area of membrane (cm <sup>2</sup> )	65.00
Cell thickness (cm)	0.20
Electrodes	
Anode	Expanded titanium metal coated with precious metal oxide
Cathode	SS 316 Sheet
Housing of electrode	Rigid PVC with built-in flow distributors and outlets
Pressing assembly	Threaded tie rods with nuts
Flow arrangements	Parallel-cum-series

treated compartments. At the same time, known volume of distilled water is fed through the concentrate compartments. The flow rates of the treated and concentrated streams were kept constant at 12.0 L/hr, while for electrode wash stream it was 7.0 L/hr for all the experiments. A predetermined DC electrical potential was applied between the two electrodes by means of an AC-DC rectifier. The recirculations of both treated and concentrate compartment streams were continued throughout the experiments. Samples were drawn at different time intervals and analyzed for Na<sub>2</sub>SO<sub>4</sub> and TSA concentrations. The Na<sub>2</sub>SO<sub>4</sub> concentration was determined by conductivity as well as by volumetric analysis method. Conductivity measurements were carried out by using microprocessor conductivity meter (Century, India Model CC 631 Chandigarh, India) at room temperature. The TSA concentrations were determined by high performance liquid chromatography (Shimadzu LC-6AD HPLC machine, Shimadzu (Asia Pacific) Pvt. Ltd., Singapore) using Shimadzu SPD-10A UV-VIS detector and Shimadzu CLC-ODS (M) (25 cm) Column (Shimadzu (Asia Pacific) Pvt. Ltd., Singapore). Measurements were performed at 40°C using methanol-phosphate buffer (pH 3.0) at flow rate of 1.4 mL/min and UV detection at 254 nm.

## RESULTS AND DISCUSSION

Electrodialysis experiments, to separate  $\text{Na}_2\text{SO}_4$  from TSA in solution phase have been carried out at different applied DC potential varying in between 0.25 and 2 V/cell pair. Concentration of  $\text{Na}_2\text{SO}_4$  and TSA in the feed solution of treated compartments was varied in between 1 and 12% and 0.5–2% (w/v), respectively. Current vs. time curves at constant applied 1.5 V/cell pair, for the experimental solutions having varied concentration of  $\text{Na}_2\text{SO}_4$  and TSA are shown in Fig. 1. Curves indicate that initially current is slightly low but progressively increases within a few minutes (depending on the composition of the solution) and after attaining the maxima, it decreases with time to a lowest limiting range. At the beginning of the experiments, the concentrate compartments through which distilled water is passed offer a high electrical resistance. With the onset of the migration of  $\text{Na}_2\text{SO}_4$  from treated to concentrate compartments, the concentration of electrolyte was built up in these compartments, while it was reduced in the other. As a result, the electrical resistances offered by the concentrate compartments are continuously being decreased in a rapid manner in comparison to the increment in electrical resistance of treated compartments. The net effect is that the overall electrical resistance of electrodialysis stack decreases with time initially, causing



**Figure 1.** Dependence of current on time at 1.5 V/cell pair applied potential for the feed of treated stream (A) -○- 2%  $\text{Na}_2\text{SO}_4$ ; -△- 2%  $\text{Na}_2\text{SO}_4$  + 0.5% TSA; -●- 2%  $\text{Na}_2\text{SO}_4$  + 1% TSA and -▲- 2%  $\text{Na}_2\text{SO}_4$  + 1.5% TSA (w/v), (B) -△- 2%  $\text{Na}_2\text{SO}_4$  + 1% TSA; -○- 3%  $\text{Na}_2\text{SO}_4$  + 1% TSA; -●- 4%  $\text{Na}_2\text{SO}_4$  + 1% TSA; and -▲- 5%  $\text{Na}_2\text{SO}_4$  + 1% TSA (w/v).



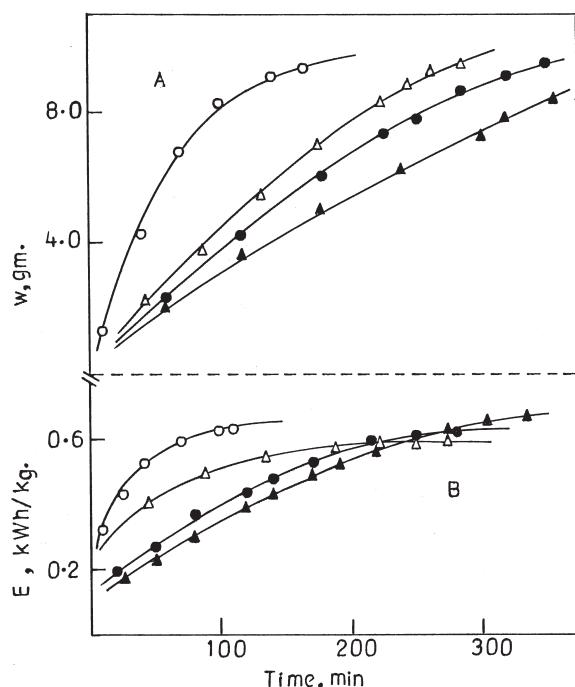
an increase in current. After reaching the maximum current, the concentration of  $\text{Na}_2\text{SO}_4$  in the treated compartments is progressively lowered, which causes an increase in the overall electrical resistance, and hence the current decreases.

Curves shown in Fig. 1A indicate that the maximum current was decreasing with the increase in TSA concentration for the same electrolyte concentration. The TSA is the surface-active agent with the hydrophilic sulfonic acid group and hydrophobic toluene moiety. Sulfonic acid group dissociates  $\text{H}^+$  in solution and thus TSA behaves as an anionic surface-active agent. The presence of surface-active materials is reported to modify the transmission characteristics of the membrane on account of the formation of adsorbed layers on the membrane interfaces.<sup>[11–13]</sup> When dissolved in aqueous solution at low concentration, it is energetically favorable for a surface-active material to migrate towards available hydrophobic/hydrophilic interface.<sup>[14,15]</sup> The orientation of a surfactant on the interface is monitored by its hydrophilic–hydrophobic balance and charge nature along with the hydrophobicity and charge nature of the interface.<sup>[16,17]</sup> In the present experimental situation, it is expected that TSA molecules migrated towards anion-exchange membranes to form adsorbed layer on it. This caused masking/fouling of anion-exchange membrane due to the presence of TSA and resulted in the reduction of ionic migrations across the ion-exchange membrane. This may be one of the reasons for reduced current obtained in the electrodialysis stack due to the presence of TSA along with  $\text{Na}_2\text{SO}_4$  in comparison to  $\text{Na}_2\text{SO}_4$  alone. Furthermore, the extent of masking/fouling and reduction in ionic transmission seems to be increasing with the TSA concentration with constant  $\text{Na}_2\text{SO}_4$  concentration. That is why current reduced progressively with the increase in TSA concentration. Curves shown in Fig. 1B, exhibit increase in current with the increase in  $\text{Na}_2\text{SO}_4$  concentration in the presence of constant amount of TSA. With the increase in electrolytic content, net electrical resistance of electrodialysis stack was decreased, which is responsible for the increase in current with the electrolyte concentration.

Energy consumption,  $E$  (kW hr/kg of  $\text{Na}_2\text{SO}_4$  removed) of an electrodialysis process is a measure of power consumed for the transportation of 1 kg of  $\text{Na}_2\text{SO}_4$  concentrate compartments. Energy consumption was estimated by Eq. (1),

$$E \text{ (kW hr/kg of } \text{Na}_2\text{SO}_4 \text{ removed}) = \int_0^t VI dt / w \quad (1)$$

where  $V$  is the voltage,  $I$ , the current,  $t$ , the time allowed for the electrodialysis experiment, and  $w$  is the weight of  $\text{Na}_2\text{SO}_4$  (kg) electro-transported from treated to concentrate compartments. Estimated energy consumption values are plotted against time in Fig. 2B for 2%  $\text{Na}_2\text{SO}_4$  (w/v) solution with TSA concentration varied in between 0.5 and 1.5% (w/v). Energy consumption progressively reduced with the TSA concentration. Since TSA is a highly water-soluble anionic surfactant, its



**Figure 2.** At 1.5 V/cell pair applied potential, (A) variation of weight of  $\text{Na}_2\text{SO}_4$  transported ( $w$ ) with time, symbols same as Fig. 1A; (B) variation of energy consumption ( $E$ ) with time, symbols same as in Fig. 1A.

presence in the aqueous solution increases the solution conductivity or the net electrical resistance of the electrodialysis stack was reduced, which is responsible for the reduced energy consumption. Moreover, weight of  $\text{Na}_2\text{SO}_4$  electro-transported plotted in Fig. 2A also exhibited the same trends. For  $\text{Na}_2\text{SO}_4$  alone, salt transportation is faster than in comparison to that in the presence of TSA and very quickly it attains the limiting value since at this stage electrolyte available for the transport in the treated compartments is very small. Due to the presence of TSA in the treated compartments,  $\text{Na}_2\text{SO}_4$  transportation was reduced by the adsorption/-masking of TSA on the anion-exchange membrane surface. The extent of reduction in ionic transmission was also increased with the increase in TSA concentration. Weight of  $\text{Na}_2\text{SO}_4$  transported from treated to concentrate compartments and energy consumption values are presented in Tables 2 and 3, for different experimental set up. With the increase in  $\text{Na}_2\text{SO}_4$  concentration in the presence of a constant amount of TSA in the feed solution, both weight of  $\text{Na}_2\text{SO}_4$  transported and power consumption are progressively increased. Weight of  $\text{Na}_2\text{SO}_4$  transported increased

**Table 2.** Data of Electrodialysis Experiments for the Separation of Sodium Sulfate of Different Concentrations in the Presence of 1% *p*-Toluene Sulfonic Acid at 1.5V/Cell Pair Applied Potential

$\text{Na}_2\text{SO}_4$ Concentration (%)	Time Allowed (min)	Analysis of Treated Compartments			Weight of $\text{Na}_2\text{SO}_4$ Transported (g)	Energy Consumption (kW hr/kg of $\text{Na}_2\text{SO}_4$ ) Transported	Current Efficiency (%)	Dialytic Rate $\times 10^9$ ( $\text{mol m}^{-2} \text{ sec}^{-1}$ )
		Feed pH (mS)	Conductivity pH (mS)	Conductivity pH				
2.0	310	22.20	2.26	14.05	2.70	8.730	0.622	91.62
3.0	390	27.31	2.48	14.36	3.17	11.760	0.699	81.54
4.0	390	32.23	2.83	18.02	3.25	13.888	0.732	77.84
5.0	390	37.45	2.90	23.15	3.29	15.410	0.761	73.24

Feed of concentrate compartments: water (1000 mL); conductivity + 0.015 mS; pH 7.05.

Feed of treated compartments:  $\text{Na}_2\text{SO}_4$  + 1% TSA solution (500 mL).



**Table 3.** Data of Electrodialysis Experiments for the Separation of 2% Sodium Sulfate (w/v) in the Presence of *p*-Toluene Sulfonic Acid of Different Concentration at 1.5 V/Cell Pair Applied Potential

TSA Concentration (%)	Time Allowed (min)	Analysis of Treated Compartments		Analysis of Treated Compartments Output		Weight of Na <sub>2</sub> SO <sub>4</sub> Transported (g)	Energy Consumption (kW h/kg of Na <sub>2</sub> SO <sub>4</sub> ) Transported	Current Efficiency (%)	Dialytic Rate × 10 <sup>9</sup> (mol m <sup>-2</sup> sec <sup>-1</sup> )
		Feed (mS)	pH	Conductivity (mS)	pH				
0	110	17.23	6.69	0.07	7.03	9.450	0.529	98.74	1.468
0.5	285	19.31	2.47	6.21	3.21	9.287	0.593	95.64	0.588
1.0	310	22.20	2.26	14.05	2.70	8.730	0.622	91.64	0.508
1.5	360	24.53	2.11	16.73	2.65	8.512	0.669	85.16	0.427
2.0	400	27.02	2.06	19.07	2.48	8.304	0.784	82.46	0.418
2.5	420	29.84	1.84	21.90	2.35	8.210	0.795	80.02	0.402

Feed of concentrate compartments: water (1000 mL); conductivity + 0.015 mS; pH 7.05.

Feed of treated compartments: TSA + 2% Na<sub>2</sub>SO<sub>4</sub> (w/v) solution (500 mL).



due to the increase in time allowed for electrodialytic separation. But energy consumption increase may be due to enhanced back diffusion of salt against its electro-transport, which plays an important role particularly when the difference in electrolyte concentration in both compartments increased in the electrodialysis experiment. Back diffusion at higher electrolyte concentration difference considerably nullifies the ionic transport under the influence of an electrical potential gradient. It is known that salt diffusion takes place through an ion-exchange membrane under the concentration and electrical gradient.<sup>[18]</sup> As the experiment is carried out in the continuous recirculation mode, the concentration of Na<sub>2</sub>SO<sub>4</sub> in the concentrate compartment reaches such a high value after some time that the diffusion of Na<sub>2</sub>SO<sub>4</sub> from the concentrate to the treated compartments becomes a predominant factor compared to the electro-transport of ions in the reverse direction. Hence, energy consumption is increased with the Na<sub>2</sub>SO<sub>4</sub> concentration. Furthermore, data presented in Table 3, indicate that for the transportation of approximately the same amount of Na<sub>2</sub>SO<sub>4</sub> in the presence of TSA, the time required for electrodialytic transport is also proportional to the TSA concentration up to certain limit. Current efficiency values presented in Tables 2 and 3 were estimated by Eq. (2),

$$CE (\%) = \frac{2wF}{MNQ} \times 100 \quad (2)$$

where  $w$  is the weight of sodium sulfate transported from the treated to the concentrate compartment (g),  $F$ , the Faraday constant (26.8 A hr),  $M$ , the molecular weight of sodium sulfate (g/mol),  $N$ , the number of cell pairs in the electrodialysis stack, and  $Q$  is the amount of electricity (A hr). Current efficiency values decreased with the increase in Na<sub>2</sub>SO<sub>4</sub> concentration in the presence of a constant amount of TSA and also with TSA concentration in the presence of a constant amount of Na<sub>2</sub>SO<sub>4</sub>. With the increase in Na<sub>2</sub>SO<sub>4</sub> concentration in treated compartments, its concentration ratio of treated and concentrate compartments increases, which is responsible for the enhanced back diffusion resulting in a decrease in current efficiency. Increase in TSA concentration at a constant concentration of Na<sub>2</sub>SO<sub>4</sub>, associated with its increased adsorption on the membrane surface and is reduction in dialytic rate of Na<sub>2</sub>SO<sub>4</sub> may be one of the reasons for the decrease in current efficiency with TSA concentration.

Since current efficiency was decreasing with the increase in transported Na<sub>2</sub>SO<sub>4</sub> amount, it was decided to remove part of solution from the concentrate stream and replace it with water in order to obtain lower energy consumption and higher current efficiency for the electrodialytic separation of a very large amount of Na<sub>2</sub>SO<sub>4</sub>. One set of experiments was performed for the separation of 12% Na<sub>2</sub>SO<sub>4</sub> from 2% TSA (w/v) in solution phase in the same electrodialysis stack at 1.5 V/cell pair of applied potential gradient, in stage IV. After each stage, 500 mL



**Table 4.** Separation of 12% Na<sub>2</sub>SO<sub>4</sub> from 2% TSA (w/v) by Electrodialysis in Four Stage Method (500 mL Solution of Concentrated Compartment Was Changed After Each Stage by the Same Volume of Water)

Stage	I	II	III	IV	Total
Time allowed for recirculation (min)	360	720	1080	1440	1440
Treated samples analysis pH	2.15	2.22	2.41	2.48	2.48
Conductivity (mS)	38.50	32.81	27.35	23.43	23.43
Na <sub>2</sub> SO <sub>4</sub> concentration (g/L)	84.85	50.68	22.32	1.67	1.67
Concentrated samples analysis Na <sub>2</sub> SO <sub>4</sub> concentration (g/L)	35.15	51.77	53.41	41.65	—
Energy consumption (kW hr/kg of Na <sub>2</sub> SO <sub>4</sub> transported)	0.34	0.78	0.80	0.93	0.71
Current efficiency (%)	91.20	86.67	72.97	70.61	80.36

Applied potential (V/Cell Pair): 1.5; initial volume of concentrate compartment (mL): 1000; initial volume of treated compartment (mL): 1000; initial pH: 2.10; initial conductivity (mS): 73.0.



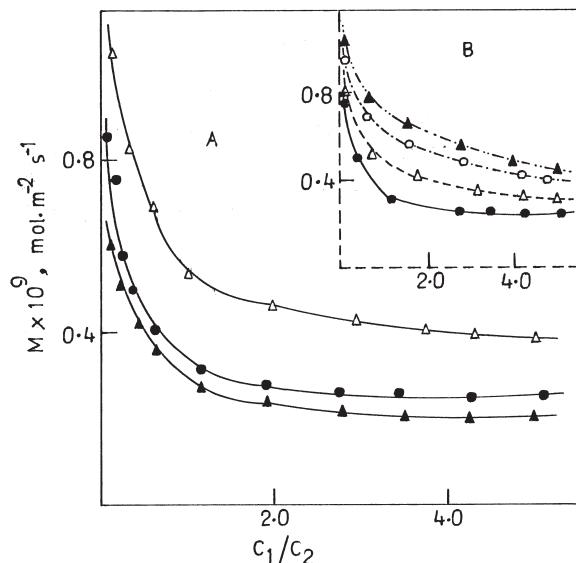
solution of the concentrate compartments was changed by the same volume of distilled water. The results obtained are presented in Table 4. Time allowed for each stage was 360 min. In stage I, 500 mL solution of the concentrate stream was replaced by distilled water after 360 min and this was repeated for the II–IV stages also. Initially, energy consumption was very low and current efficiency was around 61.20% due to the diffusion of the counter-ion across the corresponding ion-exchange membrane in addition to its electro-transport. But in the proceeding stages, energy consumption was increased while current efficiency was decreased due to back diffusion against the electro-transport of counter-ions. At the end of the stages I–IV,  $\text{Na}_2\text{SO}_4$  concentration ratios of treated to the concentrate compartment were found to be 2.40, 0.98, 0.42, and 0.04, respectively. Overall energy consumption and current efficiency for the electrodialytic separation of 12%  $\text{Na}_2\text{SO}_4$  (w/v) was found to be 0.79 kW hr/kg of  $\text{Na}_2\text{SO}_4$  transported and 50.36% which is comparable for the separation of 3%  $\text{Na}_2\text{SO}_4$  (w/v).

Next, we will consider the effect of operating conditions on the desalting process. Figure 3A and B show the effect of the  $\text{Na}_2\text{SO}_4$  concentration ratio on its dialytic rate. The dialytic rate of sodium sulfate ( $M$ ) is defined as,

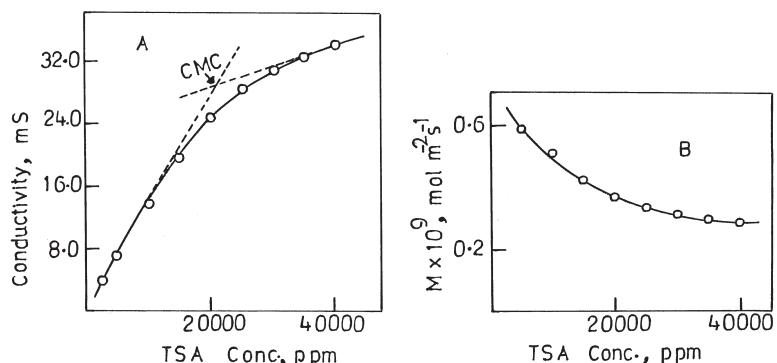
$$M = \frac{V_D}{A_{\text{eff}}} \frac{dC_{\text{Na}_2\text{SO}_4}}{dt} \quad (3)$$

where  $C_{\text{Na}_2\text{SO}_4}$  is the sodium sulfate concentration ( $\text{mol m}^{-3}$ ) in the concentrate compartment,  $t$ , the time (sec),  $V_D$ , the total volume of the solution in the concentrate stream ( $\text{m}^3$ ), and  $A_{\text{eff}}$  is effective membrane area ( $\text{m}^2$ ). The  $dC_{\text{Na}_2\text{SO}_4}/dt$  has taken the value immediately after the beginning of the desalination. In Fig. 3, with increasing  $C_1/C_2$  (where  $C_1$  and  $C_2$  are the  $\text{Na}_2\text{SO}_4$  concentrations in concentrate and treated compartments, respectively)  $M$  values decreased, which is very rapid initially or up to  $C_1/C_2 = 1$ . When  $C_1/C_2$  values increase beyond one, sodium sulfate dialytic rate tends towards limiting. This may also be because of higher back diffusion of  $\text{Na}_2\text{SO}_4$  at very high  $C_1$  and low  $C_2$  values. Furthermore, dialytic rate decreases with increase in the TSA concentration in the presence of a constant amount of  $\text{Na}_2\text{SO}_4$ , while it was found to be proportional to the  $\text{Na}_2\text{SO}_4$  concentration. With the increase in the applied potential, salt dialytic rate also increases due to higher electro-transport of  $\text{Na}_2\text{SO}_4$ .

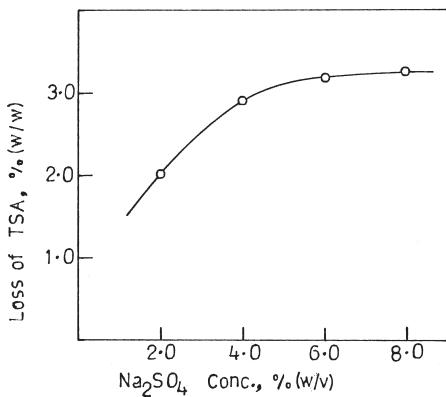
Moreover, it is reported in Refs. [13,19] that presence of additives such as surface active materials are able to modify the transmission characteristics of the membrane on account of the formation of immobilized structures or adsorbed layers. When dissolved in aqueous solution, it is energetically favorable for the surfactant to migrate to the available interface and adsorb on it. The adsorption depends upon the hydrophobic and ionic nature of surfactant along with the adsorbing surface. Variations of TSA conductivity with its concentration are shown in Fig. 4A. Critical micelle concentration, which is at the intersect of tangents of the two regions, was



**Figure 3.** Variation of dialytic rate of Na<sub>2</sub>SO<sub>4</sub> with (A)  $C_1/C_2$  at 1.5 V/cell pair applied potential in the presence of constant amount of Na<sub>2</sub>SO<sub>4</sub>, symbols same as in Fig. 1A; (B)  $C_1/C_2$  at 1.5 V/cell pair applied potential in the presence of constant amount of TSA, -●- 2% Na<sub>2</sub>SO<sub>4</sub> + 1% TSA; -△- 3% Na<sub>2</sub>SO<sub>4</sub> + 1% TSA; -○- 4% Na<sub>2</sub>SO<sub>4</sub> + 1% TSA; and -▲- 5% Na<sub>2</sub>SO<sub>4</sub> + 1% TSA (w/v).



**Figure 4.** (A) Dependence of conductivity of TSA solution on its concentration; (B) variation of dialytic rate of Na<sub>2</sub>SO<sub>4</sub> with TSA concentration in the presence of 2% Na<sub>2</sub>SO<sub>4</sub> (w/v) at 1.5 V/cell pair applied potential.



**Figure 5.** Variation of loss of TSA at 1.5 V/cell pair applied potential, with Na<sub>2</sub>SO<sub>4</sub> concentration in presence of 2% TSA (w/v).

found to be 20,000 ppm (2% w/v). Due to its anionic nature, it is expected that TSA in lower concentrations, adsorbed/masked on the anion-exchange membrane and reduces its surface charge density as well as the ionic transport across it. Variation of dialytic rate with TSA concentration in solution is shown in Fig. 4B, which shows progressive reduction in Na<sub>2</sub>SO<sub>4</sub> dialytic rate up to the CMC of TSA. Beyond the CMC of TSA, dialytic rate tends to attain a limiting value. These observations are in conformity with the expectation that a complete adsorbed layer of the surfactant in the interfacial region exists at concentration beyond its CMC.<sup>[11,13,19]</sup> The addition of more TSA beyond its CMC, has no more adverse effect on ionic transport or salt dialytic rate.

For the economical viability of any process, it may be necessary to ensure that loss of the product should be a small fraction of initial concentration. Some TSA was also transported from treated to the concentrate compartments due to its ionic nature. Loss of TSA plotted against Na<sub>2</sub>SO<sub>4</sub> concentration in Fig. 5, reveals that loss of TSA increases with the increase in Na<sub>2</sub>SO<sub>4</sub> TSA concentration and attains a limiting value at a certain concentration.

## CONCLUSIONS

From the above experimental results we can have the following conclusions.

1. An electrodialysis process using interpolymer ion-exchange membranes, can be efficiently used to separate Na<sub>2</sub>SO<sub>4</sub> from *p*-toluene sulfonic acid in the solution phase.



2. Energy consumption and current efficiency of the process is dependent on  $\text{Na}_2\text{SO}_4$  and TSA concentrations in its mixture. Lower energy consumption and higher current efficiency was obtained at lower concentrations of  $\text{Na}_2\text{SO}_4$  and TSA.
3. For the separation of very high amounts of  $\text{Na}_2\text{SO}_4$ , electrodialysis in various stages can be used with advantages.
4. Dialytic rate of the  $\text{Na}_2\text{SO}_4$  can be used to observe its transportation, which was found to increase with increase in  $\text{Na}_2\text{SO}_4$  concentration and decrease with the increase in TSA concentration.
5. Due to hydrophilic sulfonic acid groups and hydrophobic toluene ring, TSA exhibited surface-active properties, and from conductivity studies, its CMC was found to be 20,000 ppm (2% w/v).
6. With a constant amount of  $\text{Na}_2\text{SO}_4$ , its dialytic rate decreases with the increase in TSA concentration and was found to attain a limiting value beyond the CMC of TSA.
7. TSA present in the treated compartment seems to be adsorbed/masked on the anion-exchange membrane surface and is responsible for the reduction in ionic-transport. Furthermore, at the CMC value, TSA adsorption on the membrane surface was completed; this may be one of the reasons that TSA beyond the CMC has no more effect on ionic transport.
8. Dialytic rate was increased with the increase in applied DC potential. So, it is possible to operate the electrodialyzer up to 2 V/cell pair for faster transmission of  $\text{Na}_2\text{SO}_4$  from treated to concentrate compartments.
9. This process can become economically viable because the loss of TSA was always found to be less than 4% (w/w) of initial concentration.

#### ACKNOWLEDGMENTS

The authors are thankful to Prof. M. M. Sharma who posed this as an industrial problem and Dr. P. K. Ghosh, Director, CSMCRI for constant encouragement.

#### REFERENCES

1. Strathman, H. Electrodialysis and Related Process. In *Membrane Separations Technology, Principles and Application*; Noble, R.D., Stern, S.A., Eds.; Elservier Science: Amsterdam, 1995; 214.
2. Korngold, E. Electrodialysis: Membranes and Mass Transport. In *Synthetic Membrane Process*; Belfort, G., Ed.; Academic Press: New York, 1984; 192.



3. Strathman, H. Membrane Separation Processes. *J. Membr. Sci.* **1981**, *9*, 211–189.
4. Sata, K.; Sakairi, T.; Yinemoto, T.; Tadaki, T. The Desalination of a Mixed Solution of an Amino Acid and an Inorganic Salt by Means of Electrodialysis with Charge Mosaic Membranes. *J. Membr. Sci.* **1995**, *100*, 209–216.
5. Lee, H.S.; Hong, J. Electrokinetic Separation of Lysine and Aspartic Acid Using Polypyrrole-Coated Stacked Membrane System. *J. Membr. Sci.* **2000**, *169*, 277–285.
6. Kirk-Othmer *Encyclopedia of Chemical Technology*, 3rd Ed.; John Wiley & Sons: New York, 1983; Vol. 22, 49.
7. Narayanan, P.K.; Adhikary, S.K.; Harkare, W.P.; Govidan, K.P. Indian Patent No. 160880, 1987.
8. Shah, B.G.; Trivedi, G.S.; Ray, P.; Adhikary, S.K. Separation of Sodium Formate and Pentaerythritol by Electrodialysis. *Sep. Sci. Technol.* **1999**, *34* (16), 3243–3253.
9. Thampy, S.K.; Narayanan, P.K.; Chauhan, D.K.; Trivedi, J.J.; Indusekhar, V.K.; Ramasamy, T.; Prasad, B.G.S.; RaghavaRao, J. Concentration of Sodium Sulfate from Pickle Liquor of Tannery Effluent by Electrodialysis. *Sep. Sci. Technol.* **1995**, *30* (19), 3715–3722.
10. Shahi, V.K.; Thampy, S.K.; Rangarajan, R. Preparation and Electrochemical Characterization of Sulfonated Interpolymer of Polyethylene and Styrene–Divinylbenzene Copolymer Membranes. *React. Funct. Poly.* **2000**, *46*, 39–47.
11. Shahi, V.K.; Thampy, S.K.; Rangarajan, R. Studies on Transport Properties of Surfactant Immobilized Anion-Exchange Membrane. *J. Membr. Sci.* **1999**, *158*, 77–83.
12. Singh, K.; Tiwari, A.K. Membrane Potential Studies on Cholesterol Liquid Membranes. *J. Membr. Sci.* **1987**, *34*, 155–163.
13. Srivastava, R.C.; Jakhar, R.P.S. Transport Through Liquid Membranes Generated by Lecithin–Cholesterol Mixtures. *J. Phys. Chem.* **1982**, *86*, 144–1445.
14. Jones, K.L.; O'Melia, C.R. Protein and Humic Acid Adsorption onto Hydrophilic Membrane Surfaces: Effects of pH and Ionic Strength. *J. Membr. Sci.* **2000**, *165*, 31–46.
15. Shahi, V.K.; Makwana, B.S.; Thampy, S.K.; Rangarajan, R. Electrochemical Characterization of Anion Exchange Membrane with Immobilized Anionic and Cationic Surfactants. *Indian J. Chem.* **1999**, *38A*, 124–129.
16. Ray, P.; Shahi, V.K.; Pathak, T.V.; Ramachandraiah, G. Transport Phenomenon as a Function of Counter and Coions in Solution: Chrono-

SODIUM SULFATE AND *p*-TOLUENE SULFONIC ACID

3289

potentiometric Behavior of Anion Exchange Membrane in Different Aqueous Electrolyte Solutions. *J. Membr. Sci.* **1999**, *160*, 243–254.

- 17. Hoft, C.E.; Zollars, R.L. Adsorption of Single Anionic Surfactants on Hydrophobic Surfaces. *J. Colloid Interface Sci.* **1996**, *177*, 171–178.
- 18. Audinose, R.; Pichelin, G. Characterization of Electrodialysis Membranes by Chronopotentiometry. *Desalination* **1988**, *68*, 251–263.
- 19. Singh, K.; Tiwari, A.K. Studies on Characterization of Cholesterol Liquid Membranes. *J. Colloid Interface Sci.* **1987**, *116*, 42–49.

Received September 2001

Revised February 2002