Application of Conducting Polymer Membranes
Part 1: Separation of Nitric and Phosphoric Acids

Abdolreza Mirmohseni and Azizollah Sae'edi

Department of Applied Chemistry, Faculty of Chemistry, University of Tabriz, Tabriz, I.R.Iran

ABSTRACT

The development of membrane systems that are dynamic in structure can attribute a new dimension in separation technology. The paper presents separation of two inorganic acids (HNO_3/H_3PO_4) using conducting polyaniline membrane. The inherent dynamic and controllable properties of the conducting polymers are used to exploit a new method of separation. In this method the transport of each species can be switched on/off during separation. The acids (HNO_3/H_3PO_4) are successfully separated using the polyaniline membrane.

Key Words: membrane, conducting polymer, polyaniline, acid separation, selective transport

INTRODUCTION

Membranes are the basis of many important applications including purification of water, concentration of aqueous solutions and protein recovery. In conventional membranes, separation is usually achieved on the basis of permeability differences between chemicals. The selectivity of the membrane is ruled by its characteristics (such as morphology) which are established at the time of their synthesis [1].

In recent years it has been shown that a new family of membranes with dynamic properties can be prepared. These are the membranes which are able to respond to specific stimuli [2].

In the pursuit of such dynamic systems we have previously [3] described transport of acids across the polymer membranes. The group of materials we have selected to develop as membranes are conducting electroactive polymers.

These materials are known to respond to electrical stimuli [4]. The inherent reversible electroactivity of the conducting polymer means that the membranes made from such materials are dynamic. Also these materials offer the ability to be switched from an oxidized (conducting) to a reduced (less conducting) form, and the chemical changes which accompany them can be used as an advantage towards selective transport of chemicals across the materials.

Various characterization methods including cyclic voltammetry [5] scanning electron microscopy [6], atomic force microscopy [7], and quartz crystal microbalance [8] have been employed to demonstrate dynamic structure of the conducting polymers.

The species selected for the study are acids. Waste waters carry predominantly acids and metals

[9]. Most catalyzed reactions involved in industrial applications (e.g. polymerization and cracking) make use of acidic species [10]. Even a careful chemical neutralization leaves a high content of acidic materials in the effluent. The separation of acids using a dynamic membrane that can be doped by acids is expected to be of economical interest.

EXPERIMENTAL

Reagents and Materials

Analytical reagent (AR) grade chemicals were used throughout, unless otherwise stated. Ammonium persulphate, aniline, methanol, hydrochloric acid, *ortho*-phosphoric acid 85%, ammonia solution (25%), sodium acetate trihydrate, anhydrous sodium sulphate, barium chloride dihydrate, potassium nitrate, resorcinol and *N*-methyl-2-pyrrolidone (NMP) were all purchased from Merck chemicals. Nitric acid was purchased from Fluka chemicals.

Instrumentation

A Shimadzu UV-120-01 spectrophotometer was used to determine the acidic anions. Measurement of solution pH was carried out using a Philips PW 9422 pH meter. To apply electrical stimuli a Farnel Instrument Ltd. model E 30/2 potentiostat was used. The different electrical set up used is described as methods A and B in the next section.

Mechanical properties were determined by stress-strain technique using a Shimadzu SB-25-TB testing machine at room temperature. A strain rate of 1 mm/min was employed. An ASTM standard method was employed. Each specimen of the polymer membrane was cut with the dimensions of 10×10×0.01 mm. The specimen was held in the jaws of a 20 Newton cell using adhesive tape. Then the measured force was converted to the tensile strength and Young's modulus.

Analytical Procedures

Determination of Nitrate and Phosphate Ions
Spectrophotometric methods for the determination of nitrate and phosphate ions were used. The methods are rapid with good reproducibility and

low interference from common inorganic ions. In the case of nitrate, resorcinol reagent was employed [11]. In the presence of sulphuric acid, a rapid reaction occurs between resorcinol and the nitrate ion. The nitro compound formed gave an absorption spectrum with a maximum at 347 nm. Measurement at 360 nm was preferred because of the smaller absorbance of resorcinol.

A linear calibration curve was obtained for concentrations up to 4 ppm nitrate ion. The relative standard deviation, calculated by 10-fold analysis of 0.05, 0.2, 1 and 4 ppm samples, was 4, 1, 0.2 and 0.2%, respectively. The phosphate ion was determined using stannous chloride and ammonium molybdate as the reagents.

Molybdophosphoric acid was formed and it was reduced by stannous chloride to intensely coloured molybdenum blue. This method was sensitive, and feasible measurements were made down to 0.007 ppm phosphate ion by using increased light path length [12]. The determination was carried out at 690 nm. The calibration curve was linear between 0.3 to 2.0 ppm.

Cell Design
The cell utilized in the transport studies (Figure 1) consisted of two compartments (source and receiv-
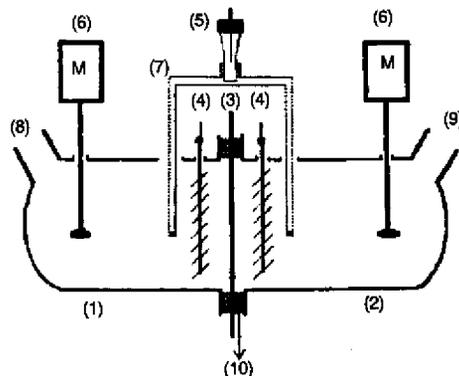
(1) source solution, (2) receiver solution, (3) membrane, (4) auxiliary electrode (platinum mesh), (5) reference electrode (Ag/AgCl), (6) stirrer motors, (7) salt bridge, (8) feed injection, (9) sampling place, (10) plastic O-ring.
Figure 1. The cell used for separation of acids.

ing side) separated by the membrane (A=11.34 cm²). Source compartment contained feed solution, usually mixture of acids, whereas in the receiving side a double distilled water was used. 0.01 M NaClO₄ was used as a background electrolyte in both compartments whenever any potential was applied. Samples were withdrawn from the receiving compartment of the cell as a function of time and were analyzed.

To obtain homogeneous samples, the solution in each side was stirred using small stirrers, driven by 12 V DC motors. The rate of stirrers was held between 150−180 cycle/min.

Membrane Preparation

The chemical preparation of polyaniline membranes was carried out in three distinct stages:

−powder preparation.

−solution preparation.

−casting and drying.

Fine polyaniline powder was prepared in an aqueous acidic solution as described previously [1]. Ammonium persulphate of 45.6 g was dissolved in 250 mL of 1.70 M HCl solution. This was then added to 20 mL of aniline dissolved in 250 mL of 1.70 M HCl. The oxidant was added slowly over a period of 1 h to keep the temperature of polymerization below −3 °C. This is the recommendation of many workers to increase the molecular weight of the prepared polymers [1, 3, 13]. The polymer was collected and washed several times with double distilled water until the solvent became colourless.

It was previously shown that the removal of the THF-soluble fractions from emeraldine base leads to a significant increase in the molecular weight of the remaining powder [13]. The polymer was therefore, washed several times with THF. Finally the emeraldine acid form was converted to the base form by leaving the powder in 1.70 M NH₄OH solution. This had to be implemented because the base form was being more soluble in solvent, NMP.

The powder was dried in an oven (60 °C for 12 h), then it was ground with an agate mortar and pestle before being passed through a 60 mesh sieve

to obtain a very fine powder.

One gram of the fine powder was then slowly added to 40 mL of NMP solution. The solution was finally filtered and used to prepare polyaniline membrane according to a casting method. The details of the method have been already described [1]. The films prepared from 4 mL of solution cast over a piece of glass (8×8 cm) gave a membrane with the thickness of 15−16 μm.

RESULTS AND DISCUSSION

Characterization of the Membranes

Mechanical properties of the polymer membrane were measured as described in the experimental section. The values obtained for the Young's modulus of the polyaniline membrane compared with some other materials suggest that the polymer was less rigid than polyacrylates, ABS resins (acrylonitrile-butadiene-styrene copolymers) and steel (Table 1). Considering the results obtained, the films are strong enough to be used as a separator in the transport and separation studies.

Transport and Separation of Acids

All separation and transport studies were carried out across the polyaniline membranes using the transport cell as described in the experimental section (Figure 1). Both anion and proton concentrations were determined in the receiving

Table 1. Range of mechanical properties for some engineering materials and polyaniline films.

Materials	Elastic modulus (Gpa)	Tensile strength (Mpa)
Ductile steel [14]	200	350−800
Glasses [14]	40−140	10−140
ABS [14]	2.5	45
Polyacrylate [14]	2.16	69
Polyethylene [15]	0.20	25
Polypyrrole/		
Nafion [2]	0.30−0.37	40−55
Polyaniline	0.43−0.45	70−80

Figure 2. Transport of 0.4 M HNO₃ without any external applied potential.

Note that no transport obtained for 0.2 M H₃PO₄.

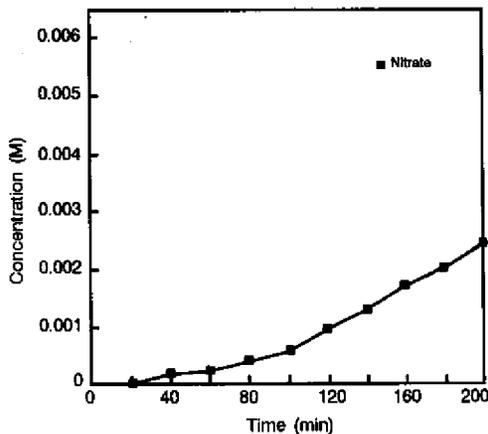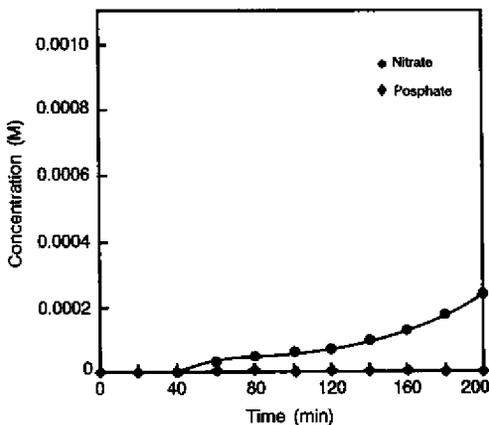**Figure 3.** Separation 0.2 M HNO₃ and 0.2 M H₃PO₄ without any external applied potential.

compartment as a function of time.

When no external driving force was applied, it was found that in the first 20 min no acid transport took place (Figure 2). However after this period of time, the concentration of nitric acid was linearly increased in the receiving compartment solution. It is believed that this delay time, is the period required for the membranes to be protonated (anions are also involved to maintain charge neutrality). This process is quite feasible because, the polymer was initially in the emeraldine base form. The corresponding reaction can be shown as follows:
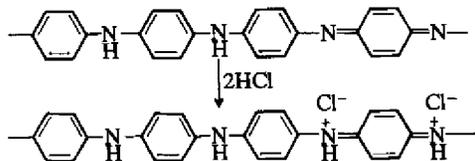
When all −N= sites were protonated the diffusion of nitric acid began (Figure 2). The protons, as equal concentrations with the nitrate anions, were transported across the membrane.

The transport of phosphoric acid under the same conditions was investigated. However, no

H_3PO_4 (phosphate ion) transport was observed.

Therefore, it is expected that a mixture of HNO_3/H_3PO_4 can be separated using the membrane. It is assumed that the low affinity between the membrane and phosphate species (H^+, $H_2PO_4^-$) decrease the rate of protonation. However, mechanistic studies still are under investigation.

Separation of a mixture of HNO_3/H_3PO_4 was carried out using the membrane. Equal concentration of the acids in source and distilled water in receiving compartments were employed, respectively. The flux obtained for transport of HNO_3 (nitrate ion) was 0.121×10^{-9} mol cm⁻² s⁻¹ (after 200 min) while for phosphoric acid (phosphate ion) it was negligible (Figure 3). Selectivity of the membrane for the acids was therefore, 100%. Note that in all the experiments anion and proton concentrations were equal.

In an attempt to improve the rate of transport while maintaining the selectivity, an external driving force was applied. This was carried out in two different manners.

Method A

An electrical field was applied between two platinum electrodes across the polymer membrane
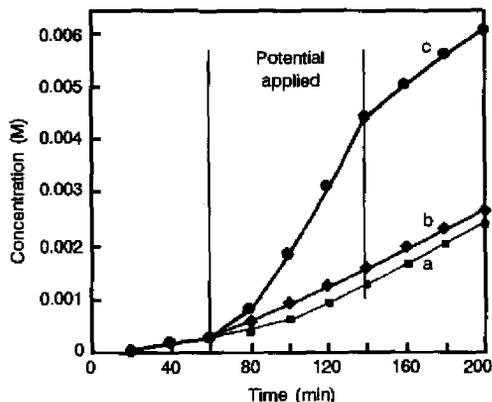
a: No potential applied; b: An electrical field of 1V was applied as described (method A); c: An electrical field of 2V was applied as described (method A).

Figure 4. Influence of electrical field (method A) on transport of 0.4 M HNO_3.

Note that the transport obtained for 0.4 M H_3PO_4 slightly increased.

Figure 5. Influence of electrical field (method A, 2V) on separation of acids (0.2 M HNO_3 and 0.2 M H_3PO_4).

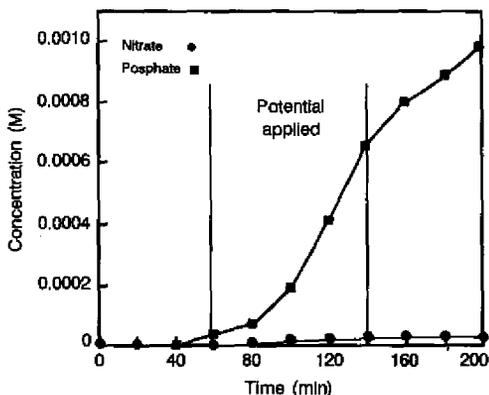with the positive electrode exposed to the receiving compartment solution.

Method B

A three electrode system was used with the membrane acting as the working electrode. A platinum auxiliary electrode and an Ag/AgCl reference electrode were the other two electrodes. In such a configuration polymer membrane is to be expected to involve directly in the electrochemical reactions.

Using set up A potential difference of 1.0 and 2.0 V applied between two Pt electrodes. The oxidative potential exposed to the receiving solution to encourage anion transport. Application of an electric field of 1.0 V had no significant effect on transport of HNO_3 (Figure 4). However, application of 2.0 V potential caused an increase in the flux rate. It was approximately increased by 70 times.

$$\text{Flux rate} = \frac{\text{Flux (2V)}}{\text{Flux (No potential)}} =$$

$$\frac{3.700 \times 10^{-9} (\text{mol.cm}^{-2}.\text{S}^{-1})}{0.053 \times 10^{-9} (\text{mol.cm}^{-2}.\text{S}^{-1})} \approx 70$$

Considering the results obtained, separation of HNO_3/H_3PO_4 was carried out using potential difference of 2V (method A). It was found that, the rate of transport of HNO_3 (nitrate ion) increased while the selectivity factor (α) was reduced (Figure 5).

$$\alpha = \frac{\text{Flux (nitrate)}}{\text{Flux (phosphate)}} =$$

$$\frac{0.800 \times 10^{-9} (\text{mol.cm}^{-2}.\text{s}^{-1})}{0.021 \times 10^{-9} (\text{mol.cm}^{-2}.\text{s}^{-1})} \approx 38$$

It should be noted that under the same condition, when no potential was applied, the flux obtained for H_3PO_4 (phosphate ion) was negligible and the selectivity was therefore, 100%.

We have previously shown [3] that application of a positive potential (0.6 V) to the polyaniline membrane increased the rate of transport of HNO_3. By the same trend of thought the separation of HNO_3/H_3PO_4 was considered.

It was found that when a positive potential of 0.6 V was applied (method B), the rate of transport of HNO_3 increased (Figure 6). The transport was halted by application of a negative potential (-0.2 V). Then it restarted by application of the positive potential. The switching behaviour
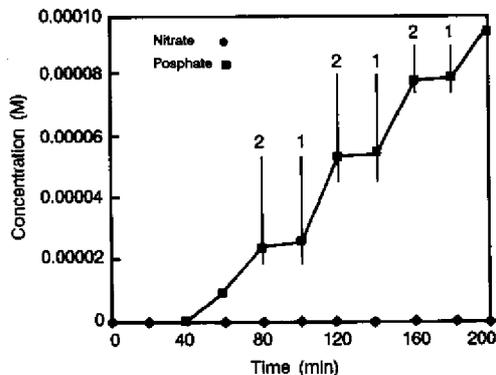
(1) A constant potential of 0.65 V was applied for 15 min.

(2) A constant potential of −0.02 V was applied for 15 min.

Note that no transport obtained for H_3PO_4.

Figure 6. Influence of electrical stimuli (method B) on separation of acids.

was quite reversible. These simulations had no effect on the transport of phosphate. The results show that the rate of transport of nitrate ion, compared with the case of no potential, was increased.

$$\frac{\text{Flux (method B.HNO}_3)}{\text{Flux (No potential. HNO}_3)} =$$

$$\frac{0.156 \times 10^{-9} (\text{mol.cm}^{-2}.\text{s}^{-1})}{0.053 \times 10^{-9} (\text{mol.cm}^{-2}.\text{s}^{-1})} \approx 3$$

Flux obtained for H_3PO_4 was negligible. Therefore, introducing this method improves the magnitude of flux by 3 times while the selectivity factor was not reduced.

CONCLUSION

The results presented in this paper show that the polyaniline membrane is permeable to some inorganic acids including HNO_3 and H_3PO_4. It is found, however, that the rate of transport varies depending on the acid employed. In this work, for instance, the flux obtained for HNO_3 is some hundreds of times greater than H_3PO_4.

On the basis of the above observations separation of HNO_3/H_3PO_4 using the polymer membranes, is considered practical. The separation is successfully carried out with 100% selectivity. In order to improve the rate of transport a conventional driving force employing an electrical field is applied. The rate of separation is improved by 38 times.

When the membrane acts as a working electrode in a three electrode cell, an improvement in the rate of separation is obtained while the selectivity factor is maintained. This could be a novel application in the field of separation technology and membrane science which offers the possibility of selective and controllable transport. In this method, the membrane characteristics can be modified by application of external stimuli.

ACKNOWLEDGEMENTS

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