

## Potential Measurements on Rubber Surfaces in Electrolyte Solutions

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### ABSTRAK

Beberapa filem getah yang nipis disediakan daripada getah asli dan getah-getah ubah-suai dan digunakan sebagai membran elektrod. Keupayaan yang terhasil bergantung kepada kepekatan ion dalam larutan dan dibincangkan mengikut sebutan penjerapan ion-ion itu ke permukaan membran.

### ABSTRACT

Films of natural and modified rubber were prepared and used as electrode membranes. The potential developed varied with the concentration of ions in solution and is discussed in terms of adsorption of the ions onto the membrane.

**Keywords:** rubber film, electrode membrane, adsorption potential

### INTRODUCTION

A number of materials other than glass have been used as the membrane for electrodes where ion exchange can occur. Polyvinyl chloride (PVC) has been widely used in conjunction with an additive showing a specific affinity for ions in solution. Garibi *et al.* (1990) and Palepu *et al.* (1990), for example, used cationic surfactants to neutralize the negative charges on the surface of their membranes. Hampton *et al.* (1987) used 12 crown-4 as a neutral carrier for some cations, while Fung and Wong (1980) used crown ethers for a similar purpose.

No attempt seems to have been made to construct an electrode membrane based on natural rubber, NR. The reason for this is not apparent. It could be due to the unavailability of fresh raw rubber in non-producing countries or the unavailability of the polymer in a pure form. NR, being an agricultural product, contains many organic and inorganic impurities. On the other hand, the question of wettability of a rubber surface is perhaps the most important practical reason why its use as an electrode membrane has yet to be explored. Rubber and synthetic polymers are hydrophobic (Noda 1991a); however, methods have been found for the modification of rubber and polymers to produce a hydrophilic surface, thus eliminating the wetting problem. For example, Noda (1991b) coated the surface of latex elastomer with a pretreated hydrophilic polymer. Ramussen *et al.* (1977) used chromic

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acid for the treatment of the surface of low density polyethylene film, PE-H, in order to develop carboxylic groups, and this rendered the film wettable. It was later found that at  $\text{pH} < 4$ , the carboxylic groups were protonated and this rendered the surface hydrophobic. However, at  $\text{pH} > 10$  the groups were ionized, making the surface hydrophilic (Wilson and Whiteside 1988).

Thus it is apparent that, to a certain extent, ionization of the functional groups and adsorption of ions by the active centres on the surface of rubber do take place when it is in contact with an aqueous medium. Similar phenomena have been observed to occur on the surface of an activated carbon; a detailed discussion on the theory and mechanism has been described in a previous communication (Badri *et al.* 1990). Together they point to the possibility of a new scope of research in this area as modifications of rubber, either on the surface or in bulk, have been investigated extensively. Examples can be found in many publications, e.g. Barnard *et al.* (1975); Gelling and Porter (1988) and the references therein. In this paper it is the authors' intention to introduce the subject through some preliminary findings from experiments which explored the possibility of using NR and other modified rubbers as electrode membranes.

## MATERIALS AND METHODS

All laboratory chemicals used were of analytical grade. A sample of NR (SMR 20) about one year old was cut into small pieces; 13 g were added to 100 ml THF to form a viscous mixture which imparted a colloidal appearance due to incomplete solubility. Eight drops of the mixture were used directly (unfiltered) to form a membrane of about 1 mm thickness at the end of a borosilicate glass tube of 5 mm i.d. When the membrane was dry, the seal was strengthened by Araldite epoxy resin. The membrane was tested for leakage by filling the tube with 1M HCl saturated with AgCl to a depth of about 3 cm. When in use, an Ag/AgCl electrode was inserted into the tube and the assembly was connected to a LEVEL DC microvoltmeter type TM8 with an impedance of 100 Gohm. The reference electrode used in the experiment was also Ag/AgCl in 1M HCl. The reference solution was separated from the test solution by a porous carbon junction made from coconut shell activated carbon (Badri *et al.* 1989). The activated carbon junction was used to ensure minimal contamination of the test solution by the reference solution.

The two electrodes were coupled together and dipped into a test solution of a known concentration. The system was thermally equilibrated at  $30^\circ\text{C}$  in a water bath. The stable potential developed was recorded (stabilization required about 10 min). After each measurement, the electrodes were rinsed with distilled water and dried gently with soft tissue paper. The test solutions used were HCl, NaOH, KOH, and NaCl of various concentrations.

### *Membrane Oxidation with Permanganate*

An electrode, A, was left soaking in a solution of 0.5M concentration in both  $\text{KMnO}_4$  and NaOH for about 16 h. It was then dipped several times into 6M

H<sub>2</sub>SO<sub>4</sub> to remove any deposited MnO<sub>2</sub>. It was washed thoroughly with distilled water and used for potential measurements (Table 2).

#### *Membrane Doping with Iodine*

Iodine solutions of three different concentrations were prepared by dissolving 0.2, 0.3, and 0.4 g I<sub>2</sub> in 100 ml THF. Twenty ml of each solution were thoroughly mixed with 20 ml NR solution and left to stand in a fume hood for 72 h. NR thus doped was used to form the membranes for electrodes B, D, and E respectively. Electrode C was made from the mixture containing 0.2 g I<sub>2</sub> left to react for 30 days.

#### *Fresh NR and Modified NR Membranes*

Fresh samples of SMR 10, DPNR, ENR 10 and ENR 50 were obtained from the Rubber Research Institute of Malaysia, and a sample of skim rubber was secured from a local company. Similar electrodes were prepared using these rubbers, but the solution used contained only 5 g rubber in 100 ml THF.

All electrodes were soaked in distilled water for 1 week before use to ensure full swelling of the membrane surface.

#### *IR Study*

A drop of NR rubber solution containing various amounts of I<sub>2</sub> was placed on the surface of NaCl window. The spectra were recorded on a Perkin Elmer FTIR spectrophotometer.

## RESULTS

The magnitudes of the surface potential that developed across the NR membrane of the electrode when it was dipped into HCl solution of various concentrations are given in Table 1 and plotted in *Fig. 1* as a function of -log concentration, pC. The potential increased steeply as the concentration of the acid decreased from 1M to 10<sup>-4</sup>M. At concentrations lower than 10<sup>-4</sup>M, the increase was more gradual, and in fact might have been negative. These results were very encouraging and prompted us to continue with the subsequent experiments.

TABLE 1  
Surface potential of NR membrane in HCl (mV)

- log (HCl)	0	1	2	2	4	5	6	7
Potential	15	31	54	82	126	123	125	135

The oxidation of the membrane surface with KMnO<sub>4</sub> was found to have a deleterious effect on the performance of the electrode (Table 2). The electrode became less sensitive to the changes in pC than the original and thus this method of modification was not pursued any further. Similarly, doping the membrane with iodine

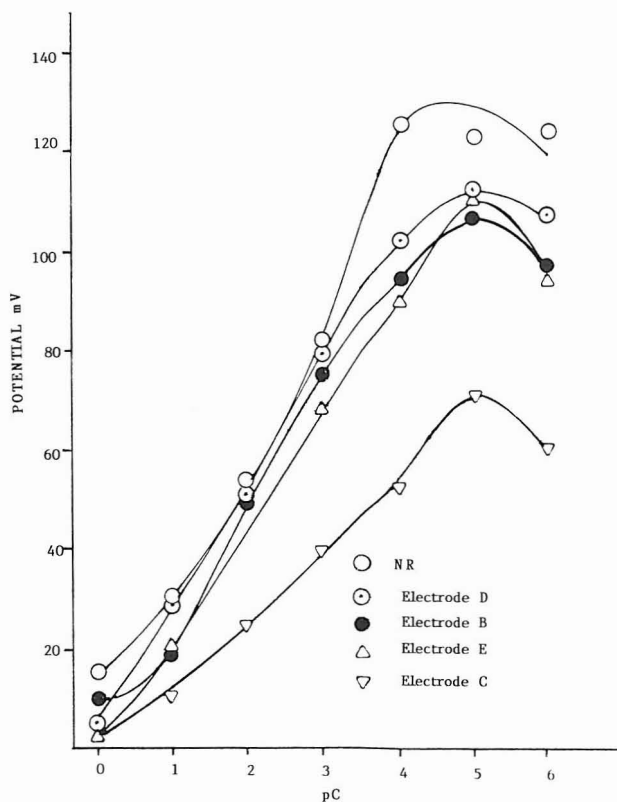


Fig. 1. Surface potential of NR and I-doped NR membranes in HCl

TABLE 2  
Surface potential (in Mv) of NR membrane oxidized by  $KMnO_4$  in HCl: variation with soaking time - Electrode A

Soaking time (days)	- log (HCl)						
	0	1	2	3	4	5	6
1	6	10	15	23	30	42	38
4	4	11	15	28	37	46	40
6	7	12	30	38	42	47	45
15	5	10	29	37	45	48	47

did not in any way improve the sensitivity of the electrodes. The values obtained for the membranes doped with various amounts of  $I_2$  are given in Table 4 for HCl solution. By extending the mixing period the performance of electrode C became worse (Table 3). However, as can be seen from Table 3, the sensitivity of electrode

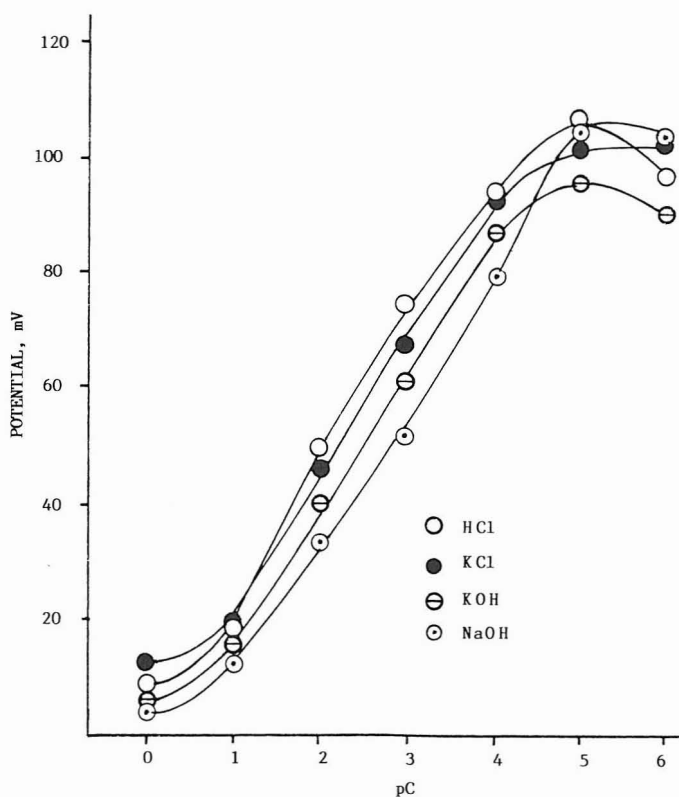


Fig. 2. Surface potential of NR membrane doped with I – Electrode B

B improved with time of soaking in distilled water. The optimum soaking time seemed to be about 1 week, and this was used as a standard procedure in all subsequent experiments.

The surface potential of electrode B in acid, salt and base is given in Table 5 and plotted in Fig. 2. It is obvious that the increase in the potential as pC was increased was the same as that described earlier for the unmodified NR membrane, except that the sensitivity might have been slightly lower.

The surface potential for the electrodes made with fresh SMR 10, ENR 10, ENR 50, DPNR and skim rubber membranes are given in Tables 6-10. All membranes showed an increase in sensitivity towards changes in ionic concentration compared to the aged NR membrane. For better comparison, the values are plotted as a function of pC for each solution HCl, NaCl and NaOH in Fig. 3, 4, and 5.

The IR spectra of NR and NR with I<sub>2</sub> left to react for 72 hours and 30 days in THF are given in Fig. 6. Only C-H and O-H stretching frequencies are shown for ease of comparison. The samples of NR and NR + I<sub>2</sub> in ThF showed weak OH vibration, indicating the presence of either water or hydroxyl groups in the rubber.

TABLE 3  
Surface potential (mV) of NR membrane doped  
with iodine – variation with soaking time in water

Soaking time (days)	– log (HCl)						
	0	1	2	3	4	5	6
<b>Electrode B</b>							
2	5	15	39	56	71	76	70
4	7	19	42	66	76	78	90
10	10	26	50	75	95	108	98
<b>Electrode C</b>							
2	14	23	38	51	68	73	65
4	10	19	32	48	65	70	60
6	5	13	19	38	50	56	60
10	3	11	25	40	53	71	61

Electrode B: NR + I<sub>2</sub> for 72 hrs

C: NR + I<sub>2</sub> for 30 hrs

TABLE 4  
Surface potential (mV) of NR membrane doped with I<sub>2</sub> after  
soaking in water for 10 days

Electrode	– log (HCl)						
	0	1	2	3	4	5	6
B	10	20	50	75	95	108	98
C	3	11	25	40	53	71	61
D	5	30	51	80	103	113	108
E	3	21	50	68	90	101	95

TABLE 5  
Surface potential (mV) of NR + I<sub>2</sub> membrane in  
various solutions - electrode B.

Solution	– log (HCl)						
	0	1	2	3	4	5	6
HCl	10	20	50	75	95	108	98
KCl	14	22	46	67	94	102	10
NaOH	4	15	34	52	80	105	10
KOH	7	19	40	61	87	96	91

TABLE 6  
Surface potential (mV) of SMR 10 membrane in various solutions

Solution	- log conc., PC						
	0	1	2	3	4	5	6
HCl	16.7	106.3	174.5	245.6	247.4	259.9	253.4
NaCl	22.2	87.5	166.2	234.2	245.7	255.9	259.7
NaOH	43.6	74.1	94.3	155.6	254.5	253.7	256.3

TABLE 7  
Surface potential (mV) of ENR 10 membrane in various solutions

Solution	- log conc., PC						
	0	1	2	3	4	5	6
HCl	19.8	114.0	183.6	252.1	181.7	277.6	277.9
NaCl	7.2	112.7	182.9	246.4	250.6	264.3	266.8
NaOH	44.3	91.9	104.4	173.8	280.1	278.2	282.0

TABLE 8  
Surface potential (mV) of ENR 50 membrane in various solutions

Solution	- log conc., PC						
	0	1	2	3	4	5	6
HCl	8.2	99.3	155.2	212.9	263.7	276.0	263.8
NaCl	42.2	71.6	82.4	120.1	212.5	258.7	273.1
NaOH	4.8	78.5	161.7	221.8	229.9	242.0	240.1

TABLE 9  
Surface potential (mV) of DPNR membrane in various solutions

Solution	- log conc., PC						
	0	1	2	3	4	5	6
HCl	19.8	111.2	174.2	237.2	261.1	266.0	256.0
NaCl	25.5	97.6	170.5	237.6	253.3	252.7	250.6
NaOH	45.3	80.5	85.9	136.8	328.6	233.2	247.9

However, the spectrum for NR + I<sub>2</sub> left to react for 30 days showed a considerable increase in the intensity of OH vibrational frequencies, indicating the influence of THF in self-degradation of rubber.

TABLE 10  
Surface potential (mV) of skimmed rubber membrane in various solutions

Solution	- log conc., PC						
	0	1	2	3	4	5	6
HCl	10.2	85.1	165.3	207.2	238.2	247.5	238.6
NaCl	43.7	92.8	268.6	236.2	265.2	266.8	254.9
NaOH	15.9	108.6	125.8	183.4	247.9	262.3	261.8

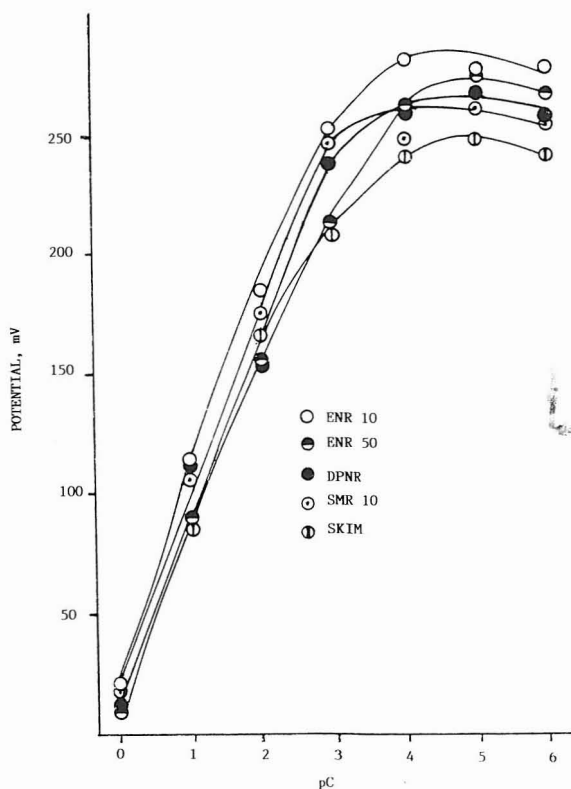


Fig. 3. Surface potential of fresh and modified natural rubber membranes in HCl

## DISCUSSION

The latex obtained from *Hevea brasiliensis* can be separated roughly into three fractions under ultracentrifugation (Moir 1959). The three fractions are rubber cream, C-serum and the so-called bottom fraction. Rubber cream is the main non-aqueous component that, when processed, yields NR. The main component of NR is rubber hydrocarbon which makes up about 95% of the cream, the rest being



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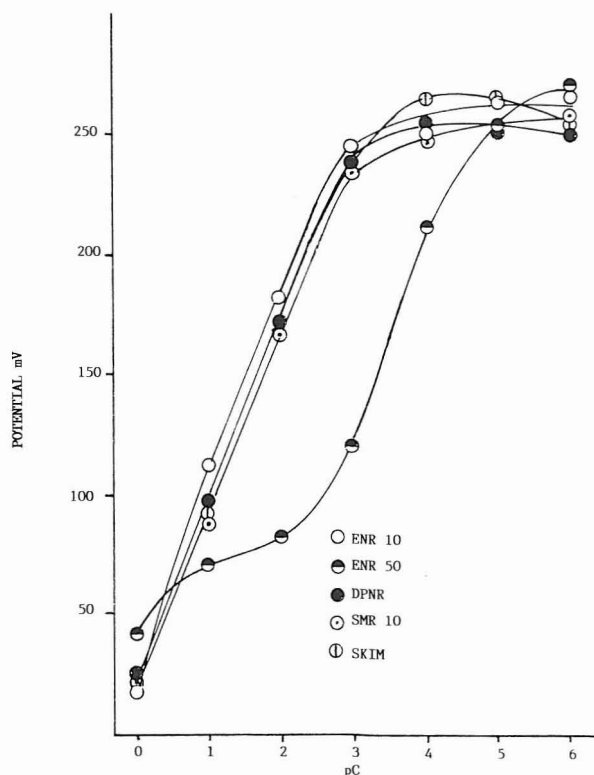
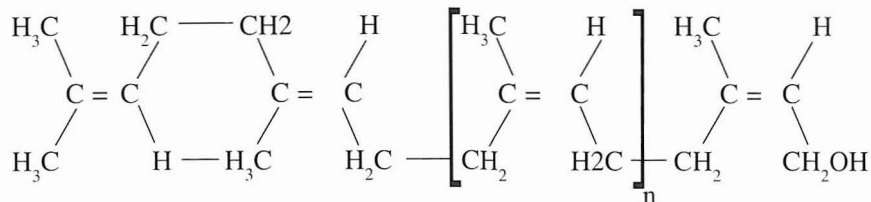


Fig. 4. Surface potential of fresh and modified natural rubber in NaCl

protein, amino acids, glycerides, fatty acids and others including traces of metal ions (Hasma and Othman 1990).

Rubber hydrocarbon is cis-1,4-polyisoprene



with n running into thousands of units. In NR, the polymer contains a high degree of long chain branching which is associated with the presence of non-hydrocarbon groups distributed along the chains (Angulo-Sanchez and Caballevo-Mato 1981). One of the most important of these groups is the aldehyde group, which is thought to be responsible for cross-linking between the chains in NR (Sekhar 1961). It was

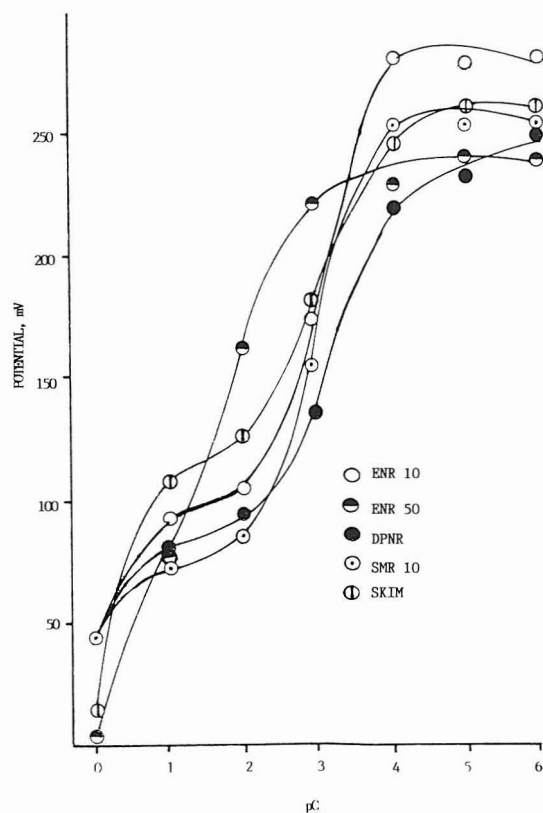


Fig. 5. Surface potential of fresh and modified natural rubber in NaOH

estimated that the concentration of this group was in the range of  $1.6-5.4 \times 10^{-6}$  mole per gram of rubber, varying from clone to clone (RRIM 1973; Subramaniam 1975). Others, such as lipids, neutral glycolipids and phospholipids, amounted to 1.4-3.2%. Natural rubber latex contains 0.95% protein. Upon centrifugation, 27.2% of this stays in the rubber fraction (Tata 1980).

With all these non-rubber constituents present in NR, certainly the surface of an NR film would have a moiety of functional groups resembling that of activated carbon (Hassier 1974), which explains why carbon black is a good filler for NR (Hallum and Drushel 1958). When the NR film is brought into contact with an aqueous medium, adsorption and desorption equilibria would be established between the film surface and the medium. The result of these equilibria would be an accumulation of charges on the surface of the film balanced by the counter ions in the vicinity on the solution side. Such arrangement of opposite charges produces what is termed an electrical double layer. The presence of an electrical double layer was postulated to explain why water reduced the coefficient of friction of a wet rubber

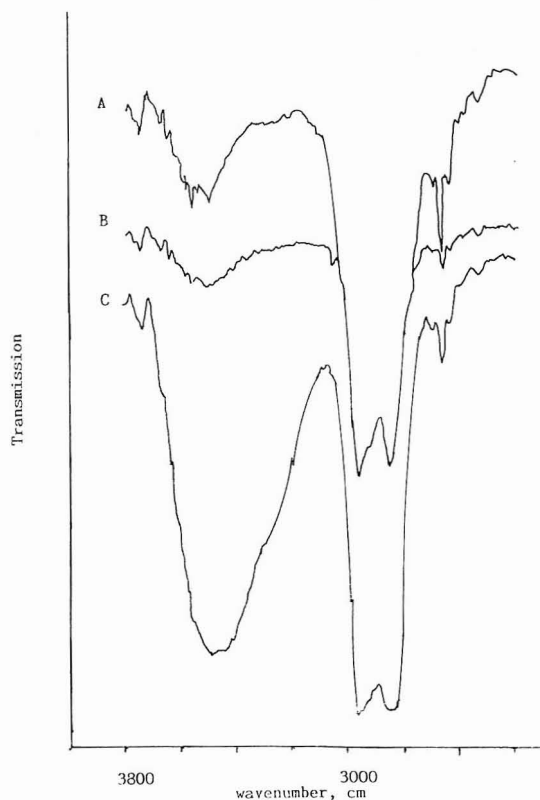


Fig. 6. IR spectra for NR and I-doped NR  
 A NR, B I doped for 3 days, C I - doped for 30 days

surface sliding on a glass plate (Richards and Roberts 1988). As for the carbon electrode (Badri *et al.* 1990), the electrical potential for the system could be measured.

It could be envisaged that when the surface came into contact with water, to a certain extent the oxygen atoms on the aldehyde groups would be protonated. Such an electrostatic reaction would also occur on other oxygen atoms of hydroxyl groups, ethereal groups, epoxy groups and the nitrogen atoms of the amino groups in amino acids and proteins. This was especially so on the internal surface of the membrane in contact with 1M HCl. On the other hand, the carboxylic and other acidic groups that might be present on the main chain and fatty acids would undergo ionization to form hydrogen ions in the aqueous medium, leaving the negative charges on the surface of the membrane. This was especially likely to happen on the outer surface of the membrane when the test solution was of high pH or neutral. The nett potential measured was then the difference between these two double layers on the opposite surfaces of the same membrane. Since the concentration of HCl in the internal surface was constant, the variation in the potential measured was assumed to be essentially due to the variation in the concentration of the test solu-

tions. This is shown in Table 1 and *Fig. 1* for the case of NR membrane dipped in HCl at various concentrations.

An attempt was made to increase the surface concentration of the hydroxyl groups on the outer surface of the membrane by  $\text{KMnO}_4$  oxidation. Unfortunately, the attempt was not successful (Table 2). Instead, the membrane became less sensitive to the  $\text{H}^+$  concentration of the test solution. This was perhaps due to the phenomena of preadsorption discussed previously for the case of  $\text{Li}^+$  in activated carbon membrane (Badri and Crouse 1989). However, it could also have been due to the nature of the aged rubber itself. It is well known that rubber, when left in air, can form a skin made up of a highly cross-linked polymer that is impervious to oxygen. It is a slow process resulting in high viscosity rubber due to cross-linking of oxygen-containing groups attached to the main chain. Even in the absence of air, such an event could still take place due to dissolved oxygen in the rubber (Morris 1991). The result of this phenomenon has been well observed in a 50-year-old rubber sample (Kaneko 1975) and in a 100-year-old rubber sample (Ab Malek and Stevenson 1992). The action of permanganate was perhaps to enhance oxidation and consequently cross-linkages of the main chain.

When soaked in  $\text{KMnO}_4$ , a rubber sample acquired a purplish, patchy coating and a black residue that could be rubbed off easily (Roberts and Brackley 1989). At the same time, polyglycol was formed at the surface but such a large functional group reduced the hydrophilicity of the surface (Holmes-Farley *et al.* 1988) compared to small functional groups such as epoxide and ethers. Therefore, oxidation of the surface with  $\text{KMnO}_4$  did not enhance the sensitivity of the membrane. It has also been observed that in the case of latex particles the effect of ageing is to increase the resistance of the inner part of the rubber particles to oxidation by permanganate (Hamzah *et al.* 1989). Thus soaking the membrane in  $\text{KMnO}_4$  might have introduced only small amounts of oxidation products on the surface, and these products might have caused the surface to be more hydrophobic.

It was thought that due to this impervious skin the electrical conductivity of the aged rubber might have been reduced, and thus the sensitivity of the electrode would have been lowered. Rubber doped with iodine was reported to have enhanced electrical conductivity (Thakur 1988). However, it was found in this investigation that  $\text{I}_2$  doping did not improve the sensitivity of the electrode (Table 3, 4). In fact, the sensitivity was further reduced when doping time in THF was extended to 30 days. This could be clearly seen in *Fig. 1*, where the potential observed for each electrode (B, C, D and E) is plotted as a function of pC.

The marked decrease in the sensitivity of electrode C could have been due to the destruction of the epoxy rings on the surface of the membrane. The epoxy group is one of the products of air oxidation of NR (Burfield 1974). It was shown to undergo ring opening in the presence of THF to form diols (Gelling and Porter 1988). Evidence to substantiate this can be seen in the IR spectra of the rubber solutions given in *Fig. 6*. Spectrum I was for SMR 20 in THF, spectrum II for SMR 20 +  $\text{I}_2$  72 h and spectrum III for SMR 20 +  $\text{I}_2$  30 days. It is obvious that the intensity

of OH vibration frequency increased markedly as the doping time was increased from 3 to 30 days. Hence, even though rubber could have been oxidized by permanganate solution to produce hydroxyl groups on the surface of the membrane, the present results indicate that the hydroxyl groups further reduced the sensitivity towards  $H^+$  in the test solution.

The results tabulated in Table 2 and 3 indicate that the membranes must be soaked for at least a week in water to ensure their stability. This is probably the time-lag required by water to flow into the pores and crevices on the surface of the membrane and subsequently activate sites for adsorption and desorption of ions. Being hydrophobic, the surface of pure polyisoprene should not be swollen by water but the presence of non-rubber constituents in NR imparts a slight hydrophilic nature to NR, thus making it imbibe water (Muhr 1992). The amount of imbibed water is not large, indicating a high degree of cross-linking in NR (Melville 1964).

The sensitivity of the  $I_2$  doped membrane to the changes in the ionic concentration of the test solutions was comparable for all the test solutions used (Table 5, Fig. 2). A similar observation was made earlier for the activated carbon membrane (Badri *et al.* 1989). The explanation proposed was that the adsorptivity of these ions onto the surface was the same. Thus the membrane was not selective enough to differentiate between various species in solution.

Even though they are also non-selective, the membranes made from fresh rubber were found to be more sensitive than the aged SMR 20 to the changes in the concentration of the ions in solution, (Figs. 3-5 and Tables 6-10). In Fig. 3, the potential was plotted as a function of HCl concentration. All the membranes showed roughly the same sensitivity, with ENR 10 being the most sensitive while skim rubber was the least sensitive. Hence it is difficult to identify the principal surface groups that are active sites for adsorption and desorption of ions on a rubber film. ENR 10 membrane was consistently the most sensitive, but an increase in the degree of epoxidation (ENR 50) did not result in a corresponding increase in sensitivity. It is possible, however, that the epoxide oxygen was indeed an active site for adsorption when present at a certain concentration on the surface of the membrane, the maximum being that found for ENR 10. All the non-epoxidised rubbers, SMR 10, DPNR and skim rubber, contained fewer epoxide groups, and thus showed an inferior sensitivity compared to ENR 10 and ENR 50 membranes.

It seems that protein and amino acid impurities in rubber cannot be considered as active sites for the adsorption of ions. Skim rubber was shown to have high fatty acid, protein and ash contents (Bristow 1990), yet its membrane was found to be the least sensitive (Fig. 2). When proteins and amino acids were removed from rubber to obtain deproteinized natural rubber, DPNR, the derived membrane did not show very much improvement over the others.

The electrode potential in NaOH showed a slightly different relationship to pC in that the increment between pC2 and 3 was minimal for all membranes except that of ENR 50. Similar behaviour was also seen in the case of the ENR 50 membrane in NaCl and, to a lesser extent, ENR 10 (Fig. 1). Thus NaCl behaved similarly to

NaOH against ENR rubber membranes. Since  $\text{Na}^+$  was the common ion in both solutions, there must be a component in ENR rubbers that reacts strongly with  $\text{Na}^+$  ions once they are adsorbed.

The very reactive species could have been the carboxylic groups of the fatty acids. It has been estimated that the fatty acid concentration in NR is about 1%, and even higher (2.77%) in skim rubber (Arnold and Evans 1991). In concentrated NaOH solution the carboxyl groups would be ionized. The negatively charged surface would favour the adsorption of  $\text{Na}^+$ . As the concentration of the base is lowered, these acids, being weak, would be ionized less and less until a point is reached when ionization stops completely. At this point,  $\text{pC} = 2$  in Fig. 5, the adsorption process becomes similar to those that take place in acidic and neutral media (HCl and NaCl solutions). Holmes-Farley *et al.* (1985) have shown that the oxidized surface of low-density polyethylene film had carboxylic acid, ketone and aldehyde groups developed on its surface. The acids could be neutralized by bases, and showed a wide range of  $\text{pK}_a$  values. The arrest in the potential rise at  $\text{pC} = 2$  to 3 in Fig. 5 can probably be attributed to this. The carboxylic groups with a surface concentration of  $1.6 \times 10^{15}/\text{cm}^2$  imparted a certain degree of hydrophilicity to the PE surface (Holmes-Farley and Whiteside 1986). About 30% of the carboxylic groups resided on the surface, while the rest were thought to be subsurface groups (Holmes-Farley and Whiteside 1987). This could explain the time lag required by the electrode to achieve stability. In addition, the adsorption of  $\text{Na}^+$  by the subsurface carboxylic groups amounted to insolubilization of the salt, leaving the  $\text{H}^+$  confined and free to be adsorbed deep inside the surface. This gave the apparent picture of high  $\text{H}^+$  concentration of the basic solution, hence the potential developed was similar to that of an acidic medium. It is obvious that the concentration of  $\text{Na}^+$  in the subsurface was much less than the bulk concentration. Thus the subsurface groups ceased ionization well in the region of low  $\text{pC}$  of bulk NaOH. In this instance, at bulk concentration of 0.1M, some of the carboxylic groups had already ceased ionization, just as has been found for low density polyethylene above.

### CONCLUSION

Natural rubber film shows considerable affinity for dissolved ions in solution. The response is linear over a limited range of concentrations. Aged rubber may not be as sensitive as fresh rubber. The choice of rubber grades did not seem to be of any great consequence, except for the epoxidized samples. Selectivity towards either the cations or anions tested was not apparent and therefore the electrode may be useful only for detecting the total ionic concentration in solution. Further efforts to chemically modify the rubber and study the surface phenomena are necessary so that its characteristics can be better understood with a view to its utilization as an electrode membrane.

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