

## ELECTROSMOTIC TRANSPORT OF ALCOHOL-WATER MIXTURES THROUGH ION-EXCHANGE MEMBRANES

## Part III. Efficiency of Energy Conversion

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## ABSTRACT

The efficiency of energy conversion in electroosmosis of methanol and methanol-water mixtures through a Zeokarb 225 membrane in  $\text{Na}^+$ ,  $\text{Ba}^{++}$  and  $\text{Al}^{+++}$  forms, has been estimated from the experimental data on electroosmotic effects. Results indicate that the efficiency of the maximum energy conversion increases with an increase in the magnitude of applied potential difference and decreases with the increase in the mole fraction of water in the permeant and valence of the counter ion of the ion-exchange membrane. An attempt has been made to explain the results in terms of changes in the swelling of the ion-exchange membrane and properties of the permeant in different environments.

## INTRODUCTION

THE phenomenon of electroosmosis involves the conversion of electrical energy into mechanical energy and may be taken advantage of, in the design of energy conversion devices<sup>1-4</sup>. Osterle *et al.*<sup>5-7</sup> and others<sup>8-11</sup> have discussed extensively the efficiency of electrokinetic energy conversion utilising the formalism of non-equilibrium thermodynamics. In the present communication, efficiency of energy conversion in electroosmotic permeation of methanol and methanol-water mixtures through Zeokarb 225, a sulphonic acid cation-exchange membrane in  $\text{Na}^+$ ,  $\text{Ba}^{++}$  and  $\text{Al}^{+++}$  forms has been investigated.

In electroosmosis two irreversible processes take place. The entropy production per unit time,  $\frac{d_i S}{dt}$ , has the form of a sum of two products<sup>12</sup>:

$$\frac{d_i S}{dt} = \sum_{i=1,2} J_i X_i \quad (1)$$

where  $J_i$  ( $i = 1, 2$ ) are the two fluxes and  $X_i$  ( $i = 1, 2$ ) are the conjugate forces. The sum always is positive while,  $J_i X_i$  ( $i = 1, 2$ ) separately may be positive or negative. The generalised definition of the energy conversion efficiency,  $\eta$ , in terms of thermodynamic fluxes,  $J$ , and forces,  $X$ , can be written as<sup>5,13-14</sup>:

$$\eta = - \frac{J_o X_o}{J_i X_i} \quad (2)$$

and the condition of energy conversion is  $0 \leq \eta \leq 1$ . The subscripts  $o$  and  $i$  indicate the output and input quantities respectively. The negative sign indicates that the direction of output fluxes and forces is opposite to those of input quantities.

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## EXPERIMENTAL

Zeokarb 225 in  $\text{Na}^+$  form (polystyrene resin cross-linked by 8% divinyl benzene) obtained from Permutit Company, London, was used. It had an exchange capacity of 4.8 meq/g dry resin and a moisture content was equal to 45% by weight. The resin particles were spherical and represented the size fraction between 200 and 300 mesh. Membrane was prepared from the ion-exchanger particles with the help of mechanical compression as described elsewhere<sup>15</sup>. Its thickness and cross-sectional area were 0.96 cm and  $3.15 \times 10^{-1} \text{ cm}^2$  respectively.  $\text{Ba}^{++}$  and  $\text{Al}^{+++}$  forms of the membrane were prepared by equilibrating it with one molar barium chloride and aluminium chloride solutions respectively. The experimental set up and procedure followed for hydrodynamic permeability and electroosmotic permeability measurements were the same as described earlier<sup>16</sup>. Resistance of the membrane equilibrated with the permeant and specific conductance of the permeant were measured with Toshniwal conductivity bridge at 50 cycles/sec. All the measurements were carried out in an air-thermostat maintained at  $30 \pm 0.5^\circ \text{C}$ .

## RESULTS AND DISCUSSION

In electroosmosis one conjugate force-flux pair is the imposed axial potential difference,  $\Delta\phi$ , and the electrical current,  $I$ , and the other is the resulting axial pressure difference,  $\Delta P$ , and volume flow rate,  $J_v$ . Following equation (2), the efficiency of energy conversion may be written as:

$$\eta = - \frac{J_v \Delta P}{I \Delta \phi} = - \frac{J_v \Delta P}{(\Delta \phi)^2 / R} \quad (3)$$

where,  $R$  is the resistance of the membrane/permeant system.  $\eta$  for all compositions, corresponding to various fixed values of input forces  $\Delta\phi$  have been calculated, utilising the transport data, at various

values of output forces  $\Delta P$  ranging between zero and their steady state values. A typical  $\eta$  versus  $\Delta P$  curve for Zeokarb 225 ( $\text{Na}^+$  form)/methanol system is given in Fig. 1. It is evident from the figure that:

- (i)  $\eta$  increases with increase of input force.
- (ii)  $\eta$  versus  $\Delta P$  curve passes through a maximum as  $\Delta P$  is varied from zero to the electroosmotic pressure, and
- (iii)  $\eta$  approaches maximum when  $\Delta P$  equals half the value of electroosmotic pressure.

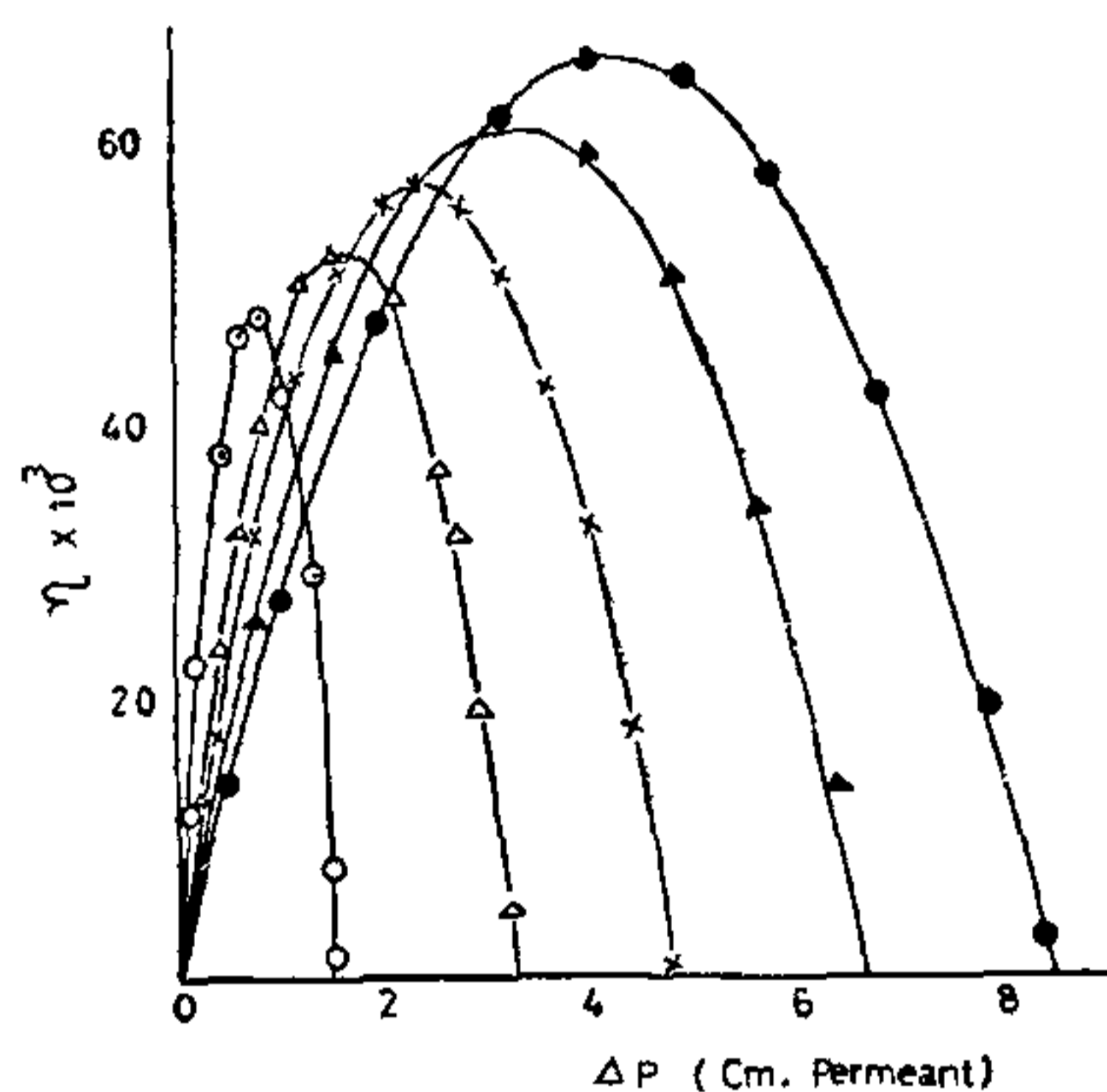


FIG. 1. Dependence of  $\eta$  on pressure difference  $\Delta P$ , at different input forces,  $\Delta\phi$ , for Zeokarb 225 ( $\text{Na}^+$  form)/methanol system.

- ( $\odot$ ),  $\Delta\phi = 100$  volts; ( $\triangle$ ),  $\Delta\phi = 200$  volts;
- ( $\times$ ),  $\Delta\phi = 300$  volts; ( $\blacktriangle$ ),  $\Delta\phi = 400$  volts;
- ( $\bullet$ ),  $\Delta\phi = 500$  volts.

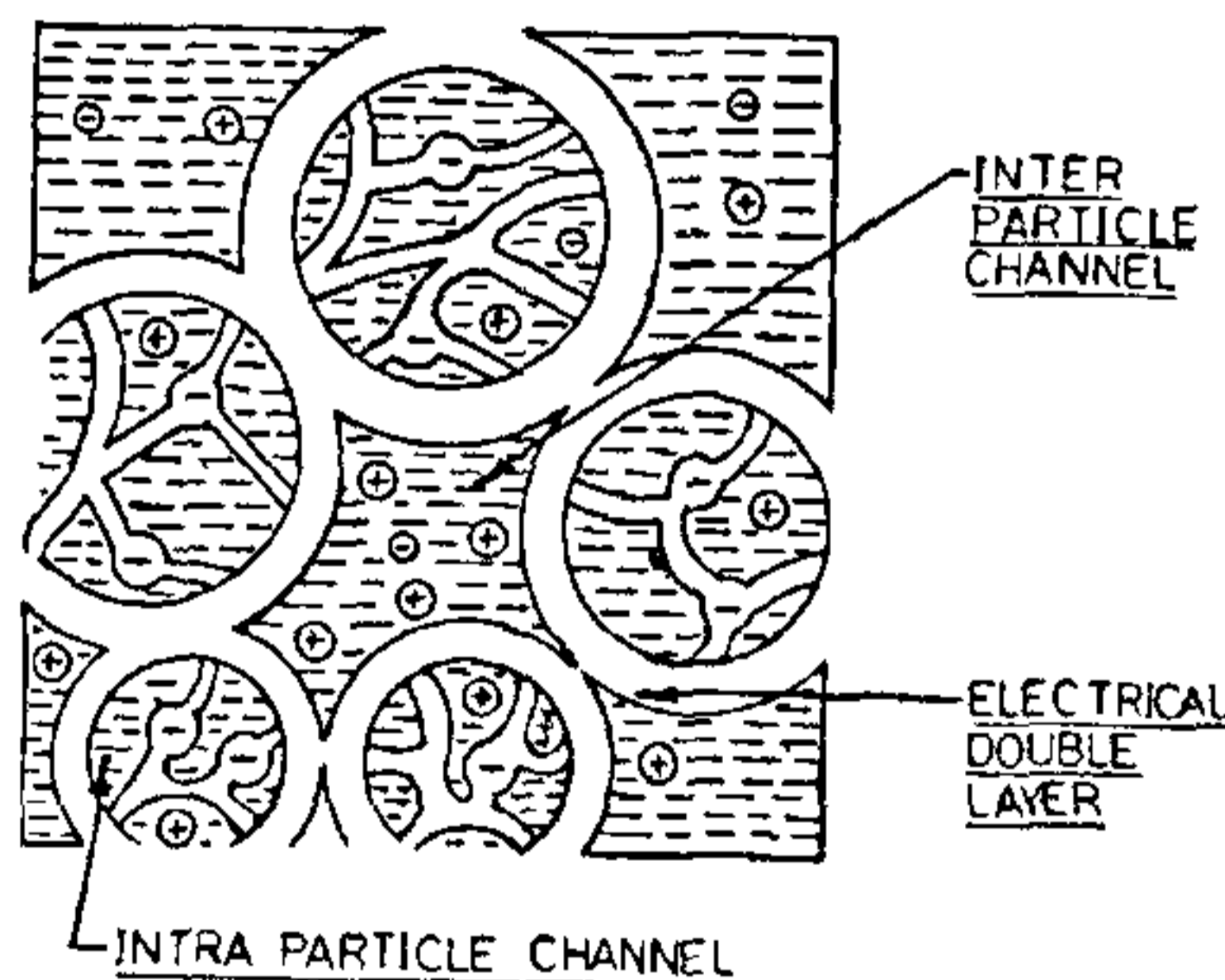
Electroosmosis involves driving of liquid uphill at the expense of electrical energy. It is obvious from equation (3) that  $\eta$  should be zero when  $J_v = 0$  or  $\Delta P = 0$ . The former corresponds to the situation when  $\Delta P$  is equal to the electroosmotic pressure difference  $(\Delta P)_{E.O.}$ , corresponding to a particular input electrical potential difference  $\Delta\phi$ , and the electroosmotic flow is just counterbalanced by the hydrodynamic flow due to the pressure difference and the net flow vanishes. Thus it is obvious that  $\eta$  would depend on  $\Delta P$  and pass through a maximum as  $\Delta P$  is varied from 0 to  $(\Delta P)_{E.O.}$  since the efficiency of energy conversion is lowered on account of hydrodynamic flow. The efficiency of maximum energy conversion,  $\eta_{max}$ , obtainable from  $\eta$  versus  $\Delta P$  plots are included in Table I. It is clear from the table that  $\eta_{max}$  decrease both with increase in the mole fraction of water in the permeant and the valence of the counter ion of the ion-exchanger membrane. The dependence can be shown to be consistent<sup>17</sup> with decrease in the average pore radius of the membrane due to enhanced swelling of the ion-exchanger and changes in the properties of the permeant in different environments.

TABLE I  
 $\eta_{max}$  for electroosmotic transport of methanol-water mixtures through Zeokarb 225 membrane in various ionic forms

Mole fraction of water $x_w$	Input force = 500 volts.		
	$\eta_{max} \times 10^3$		
	$\text{Na}^+$ form	$\text{Ba}^{++}$ form	$\text{Al}^{+++}$ form
0.0	72.0	15.0	13.6
0.1	35.5	13.2	11.2
0.2	15.0	12.6	6.2
0.3	6.2	12.2	4.2
0.4	2.0	11.0	2.8
0.5	1.0	8.8	..

The membrane used in the present investigation is heteroporous compressed plug of ion-exchange resin. Its electrochemical structure is schematically shown in Fig. 2. It is evident from Fig. 2 that there are two distinct types of capillary channels:

- (i) intra particle channels (radius  $\leq 10^{-8}$  cm) arising from random polymeric network<sup>18</sup> of resin and
- (ii) inter particle channel (radius  $> 10^{-8}$  cm) arising from heterogeneity of the plug<sup>19,20</sup>.



- ( $\odot$ ) ION EXCHANGER PARTICLE
- ( $\sim$ ) MATRIX WITH FIXED CHARGES
- ( $\blacktriangle$ ) PERMEANT
- ( $\oplus$ ) COUNTER IONS
- ( $\ominus$ ) COIONS

FIG. 2. Electrochemical structure of a porous membrane composed of cation-exchange resin (schematic).

The average pore radius of the membrane under investigation estimated from the flow data is of the order of  $10^{-4}$  cm. Hence, for the present case, the flow determining pore is the gap between the resin particles and its equivalent radius will decrease with increase in swelling of the ion-exchanger.

It is known<sup>23</sup> that polar solvents are better swelling agents than the non-polar since they interact more strongly with the ions and polar groups in the resin. Therefore, swelling of the resin in water ( $\epsilon = 81$  and  $\mu = 1.84$  Debye) and methanol-water mixtures would be stronger than in pure methanol ( $\epsilon = 32$  and  $\mu = 1.68$  Debye). This indicates that the equivalent pore radius,  $\bar{r}$ , of the membrane will decrease with increase in mole fraction of water,  $x_w$ , in the permeant. Further, alterations in the swelling of the ion-exchanger<sup>22</sup>, and hence in  $\bar{r}$ , would also occur with change in the valence of the counter ion of the ion-exchanger.

The efficiency of electroosmotic energy conversion, using kinetic molecular theory<sup>1,3</sup> based on electrical double layer, can be written from equation (3) as:

$$\eta = \left[ \frac{\pi \bar{r}^2 (\Delta P / \Delta \phi) + 2 \epsilon \xi}{4 \tau \rho k} \right] \left( \frac{\Delta \rho}{\Delta \phi} \right) \quad (4)$$

where,  $\rho$ ,  $\epsilon$  and  $k$  are coefficient of viscosity, dielectric constant and specific conductivity, respectively, of the permeant contained within the pores of the membrane.  $\xi$  is the electrokinetic potential occurring at the membrane-permeant interface. An examination of equation (4) reveals that  $\eta$  is related directly to  $\bar{r}^2$ ,  $\epsilon$  and  $\xi$  and inversely to  $\rho$  and  $k$ .

TABLE II

Dielectric constant (A), coefficient of viscosity<sup>23</sup> (B) and specific conductivity (C) of methanol-water mixtures at 30° C

Mole fraction of water $x_w$	(A)	(B) $\rho \times 10^3$ poise	(C) $k \times 10^7$ ohm <sup>-1</sup> cm <sup>-1</sup>
0.0	30.68	5.15	2.65
0.1	32.53	6.13	2.97
0.2	34.62	7.26	3.30
0.3	37.24	8.68	3.65
0.4	40.28	10.26	4.21
0.5	43.88	11.94	5.13

Data on specific conductivity,  $k$ , dielectric constant  $\epsilon$ , and coefficient of viscosity,  $\rho$ , for methanol-water mixtures are given in Table II.  $k$  was determined experimentally whereas  $\rho$  and  $\epsilon$  were taken from the literature<sup>23</sup>. It can be seen from Table II that when water is added to methanol,

(i) the increased molecular interaction in hydrogen bonded system decreases the freedom of molecular motion and therefore, tends to increase viscosity<sup>24</sup>,

(ii) ionic content of the permeant contained within the pores of the membrane increases due to the enhanced dissociation of the ion-exchanger<sup>21</sup> in medium of higher dielectric constant. Further, the self-dissociation of the permeant would also increase due to stronger proton accepting tendency of the alcoholic -OH group, and

(iii) the increased dissociation of the ion-exchanger membrane and strong interaction due to hydrogen bonding in the permeant make the electrical double layer more compact and consequently electrokinetic potential decreases<sup>25</sup>.

Although all the three,  $\epsilon$ ,  $\rho$  and  $k$  increase as mole fraction of water increases, the increase in dielectric constant is not as pronounced as the increase in coefficient of viscosity and specific conductivity. It seems, therefore, that all these factors result in a net decrease in  $\eta$  as one goes from  $x_w = 0$  to  $x_w = 0.5$ . It should be noted that the decreasing trend of energy conversion efficiency with increase in the valence of the counter ion of ion-exchanger could not be fully substantiated.

The efficiency of energy conversion of the process is extremely low which shows that a large fraction of input is being dissipated<sup>26</sup>. Therefore, electroosmotic effect cannot be used as energy conversion devices.

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## SYNTHESIS AND POTENTIAL LOCAL ANAESTHETIC ACTIVITY OF SOME 2-SUBSTITUTED THIAZOLES AND BENZIMIDAZOLES

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### ABSTRACT

The present communication deals with the synthesis and characteristics of alkylaryl-aminoacetyl-2-aminothiazoles and benzimidazoles. The results of preliminary testing of local anaesthetic activity are also reported here.

OUR investigations<sup>1-3</sup> on the synthesis and local anaesthetic activity of some derivatives of 2-amino-benzothiazoles were extended to similar class of compounds (2-aminothiazole and benzimidazole systems). Alkylaryl-aminoacetyl-2-aminothiazole and benzimidazole derivatives were synthesised by condensation of chloroacetyl chloride with 2-aminothiazole/benzimidazole followed by treatment with various primary and secondary amines. The structural formulae of the resulting compounds are shown in Tables I and II respectively.

The structures of these compounds have been established on the basis of their analytical results and infrared spectra which show characteristic strong absorption peaks at 1650-1625  $\text{cm}^{-1}$  and 1370-1360  $\text{cm}^{-1}$  corresponding to C=O and C-N bands respectively. An absorption band at 3200-3150  $\text{cm}^{-1}$  is due to the NH stretching.

### EXPERIMENTAL

Chloroacetyl-2-aminothiazole and benzimidazole were obtained by the known procedure<sup>4</sup>.

#### *Dimethylaminoacetyl-2-aminothiazole*

Dimethylamine (0.03 mole) was added slowly and with constant stirring to an ethanolic solution (20 ml) of chloroacetyl-2-aminothiazole (0.03 mole). After the addition the reaction mixture was refluxed for 5 hr and the excess of ethanol was distilled off. The residue on washing with sodium bicarbonate and crystallisation from dilute ethanol afforded the title compound, yield 3.9 g, 70%; m.p. 133°. Compound was shown to be homogeneous (single spot on TLC, silica gel); i.r.  $\sim 1630 \text{ cm}^{-1}$  (C=O);  $\sim 1365 \text{ cm}^{-1}$  (C-N);  $\sim 3150 \text{ cm}^{-1}$  (NH, stretching).

*Anal.*—Calc. for  $\text{C}_7\text{H}_{11}\text{N}_3\text{OS}$ : C, 45.40; H, 5.94; N, 22.70; S, 17.29; Found: C, 45.36; H, 5.92; N, 22.68; S, 17.26%. This base was converted into its hydrochloride for biological evaluation by passing dry hydrochloric gas in ethereal solution.

Similarly diallylaminoacetyl-, di-isopropylaminoacetyl-, N-methylanilinoacetyl-, pyrimidine-2-aminoacetyl-, pyridine-2-aminoacetyl-, N:N-dimethylanilino-*p*-aminoacetyl-, piperidinoacetyl-, piperazinoacetyl- and morpholinoacetyl-2-aminothiazoles were prepared and the elemental analyses of the compounds agreed with the calculated values (Table I).

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