CHAPTER 5

COMPLEXATION, KINETICS OF EXTRACTION
OF ALKALI AND ALKALINE EARTH METALS
AND TRANSPORTATIONS OF Na⁺ AND K⁺ ION
WITH BIS[4-(2-BENZOTHIAZOLEAZO)-(2-(o-
HYDROXYPHENOXY)-ETHYL)ETHER]
RESUME

Complexation behavior of the newly synthesised bis[4-(2-benzothiazoleazo)-(2-(o-hydroxyphenoxy)-ethyl)ether] dye with alkali and alkaline earth metal ions have been studied. The extent of complexation i.e. percentage extraction, extraction constant, distribution ratio, stability constant were determined.

The Na⁺ ion in blood serum was analysed by present method and compared with the obtained values from AAS.

The transportation study was also carried out for alkali metal ions using bis[4-(2-benzothiazoleazo)-(2-(o-hydroxyphenoxy)-ethyl)ether] dye. It’s various study viz., $t_{1/2}$, rate constant were determined.
Introduction

Crown ethers, cryptands, and open-chain polyglycol are the versatile reagents for alkali-metal ions. These compounds are used as the phase-transfer catalysts in the organic synthesis, however, their analytical applications are very limited. These have also been used as ionophores, functional groups on chromatographic packings, and to produce a cationic alkali-metal complex which can be extracted as an ion-pair with anionic dye.

There is a considerable demand for identification and separation of alkali metals in blood serum, urine and the body fluids. Therefore, the reagents must exhibit high selectivity and detection limits, adequate to deal with current therapeutic levels.

Considerable attention has been focussed on crown ether dyes, and chromogenic crown ethers with a chromophore such as picryl amine, azo and others. Some of the crown ether dyes possess a potential anionic site attached to their chromophore either inside or outside the cavity, which results in the formation of intramolecular ionpair complexes with alkali and alkaline earths. The complex formation leads to marked colour changes of dye solutions. The other type of the crown ether dyes containing the amines are incorporated in such a manner that the chromophore directly affects the complexation with metal cations, thus showing characteristic colouration in the presence of various cations. The colouration of both types of crown ether dyes is influenced considerably by the relative size of crown ether cavity and complexed cations, and the charge density of cations, so
they are often called ion-selective dyes. Thus, the crown ether derivatives bearing chromophore are promising analytical reagent for colourimetry and metal ion indicators.

Kaneda et al. have synthesised the crown ether with phenolic hydroxyl group as an integral part of the crown skeleton, which gives with crystalline lithium chloride or perchlorate yellow solution and then on addition of pyridine gives purple red colour.\textsuperscript{(13)} The colour change in organic media is no doubt related to the deprotonation of phenolic proton under combined influence of the proton removing amine and the metal cation stabilizing the resultant phenolate anion, but the complexity of the system does not seem to allow a quantitative approach to the equilibria involved.\textsuperscript{(14)} In the present investigation the bis-azo acyclic crown ether dyes and their colouration behavior on the extraction of alkali and alkaline-earth metals is described.

Complexation properties of these new ligands with alkali metal cations were studied by pH metric technique compared with the parent 18-crown-6 ligand the substituted crown demonstrate the superior selectivity for \( \text{Na}^+ \). Solvent extraction and membrane separation experiments using these new ligand were also carried out. The structural features of these new ligand have a significant influence on cation complexation selectivity and separation potential.
EXPERIMENTAL

CHEMICALS

All the chemicals used were of G.R. and AnalaR grades of E. Merck or B.D.H., respectively unless otherwise specified.

Double distilled deionized water was used. Dichloromethane was purified according to the procedure given by Vogel. DMF was purified under reduced pressure as described by Dowson et al. The buffer solutions in the pH range of 3.0 to 11.0 were prepared as described by Lange.

The dichloromethane was used as the organic solvent in all dual-module hollow – fiber (DMHF) contactor and solvent extraction experiments. The DMHF source phase and aqueous extraction phases were prepared for NaCl and KCl using distilled deionized water. The receiving phases in the membrane experiments and aqueous phases in the back extraction steps of the solvent extraction experiments were distilled deionized water.

The standard 0.001 M metal solutions were prepared by dissolving requisite amount of the chlorides into 250 ml deionized water and standardized by AAS.

APPARATUS

The UV-Visible spectra were recorded on HITACHI U-3210 spectrophotometer. Fluorescence spectra were recorded on HITACHI F-3200 spectrofluorimeter. Atomic absorption spectral measurements were made on CHEMITO 201 atomic absorption spectrophotometer (AAS).
The fluorescence lifetime was measured on SLM 4800 phase fluorimeter.

The laser effect of the dye bis[4-(2-benzothiazoleazo)-(2-(o-hydroxyphenoxy)ethyl)ether] has been tested using commercial N$_2$ laser as a pump source (Molektron UV 1000) associated dye laser (Molektron DL 400). The N$_2$ laser has a peak power of 1 MW and its pulse duration is 10 ns. The repetition rate was 20 Hz.

The activity of the uncomplexed cation was measured by potentiometry with ion selective electrodes using Radiometer Ion Meter PHM95 with Radiometers electrodes. The electrodes were conditioned to each cation by soaking overnight in a 0.01 – 0.1 M solution of its chloride. A glass cell (50 ml capacity) equipped with inlets for two electrodes and nitrogen, was used for measurement. The contents were stirred by magnetic stirrer. Titrant (tetra butyl ammonium hydroxide) 0.01 M was added from a 2.5 ml micro burette through a syringe needles. All the measurements were done at 25°C

**Fluorescence and quantum yield**

The dyes were dissolved in dioxane and introduced in a circulating cell of the dye laser. The fluorescence quantum yields were measured using quinine sulfate in 0.1 N H$_2$SO$_4$ ($\phi = 0.52$) and rhodamine 101 in ethanol ($\phi = 1.0$) as standard.

**Crown Dye**

The bis[4-(2-benzothiazoleazo)-(2-(o-hydroxyphenoxy)ethyl)ether] was synthesised according to given procedure in chapter II. The purity was
checked by melting point, HPTLC and IR Spectra. A 0.1 % solution was prepared by dissolving its requisite amount in dichloromethane.

**Solvent Extraction Experiments**

Solvent extraction experiments were performed to determine the equilibrium constant ($K_{eq}$) for the reaction

The characteristic of the extraction ability, the dependence of the distribution coefficient, $D$ of the cation between the two phases upon the bis[4-(2-benzothiazoleazo)-(2-(o-hydroxyphenoxy)ethyl)ether] dye concentration was examined. If the general equilibrium is assumed to be given by Eq. (1)

$$M^{n+}_{(aq)} + nA_{(aq)} + x L_{(org)} \rightleftharpoons [M(A)_n(L)_x]_{org}$$

Where $A$ is the cetrimide and $L$ is the crown dye.

The overall extraction equilibrium constant is expressed as

$$K_{ex} = \frac{[M(A)_n(L)_x]}{[M^{n+}][A]^n[L]^x}$$

and the distribution ratio would be defined by

$$D = \frac{[M(A')_n(L)_x]}{[M^{n+}]}$$

By introducing $D$ into equation (2) and taking the log of both sides, one obtaines

$$\log D = \log (K_{ex}[A]^n) + x \log [L]$$

(4)
With these assumptions a plot of log $D$ vs log $[L]$ should be linear, and its slope be equal to the number of ligand molecules per cation in the extraction species.

The organic diluent was dichloromethane. Equal volumes (5 ml) of aqueous phase and organic phase were shaken by a Burrell Wrist Action Shaker (model 75) until equilibrium of the organic phases (no change in phase composition) was achieved. The cations were stripped from organic phase by back extraction to an aqueous receiving phase (distilled deionized water). The measured changes in species concentration ($M^{aq+}$) were used to determine $K_{ex}$ values by the method has been used for the extraction of cations plus co anions by neutral macrocycles.

**Extraction of alkali and alkaline earth metal**

An aliquot of metal solution along with 1 ml (0.1%) cetrimide were transferred into a 60 ml separatory funnel. The volume of aqueous phase was adjusted to 10 ml with the desired pH buffer solution. The contents were shaken for 10 min with 10 ml 0.1 % crown dye in dichloromethane. The organic phase was separated, transferred into 25 ml volumetric flask and diluted up to the mark with dichloromethane. Its absorbance was measured at the $\lambda_{max}$ against reagent blank.

**Determination of stability constants**

Each emf measurement was obtained by taking reading at 5 min intervals until three successive reading differed by 0.2 mv or less. The solution was stirred for 1 min before and during each reading. The saturated calomel electrode (in 50 volume percent dioxane) was used.
A 0.001 M cation solution and 5 fold excess 0.005 M polyether in 50 % dioxane water media were titrated and the emf was noted after each addition. The thermodynamic stability constants were calculated as described elsewhere.\(^{(19)}\)
RESULT AND DISCUSSION

Infrared Spectrum of the acyclic crown ether dyes and complexes

The hydroxyl stretching vibration in the crown ether were assigned between 3445 and 3436 cm\(^{-1}\).\(^{20,21}\) In the complexation the (OH) band is disappeared, which suggests that the complexation takes place by replacing the proton and coordination with the oxygen atom. The other stretching vibration frequencies remain same except that their intensities on complexation were decreased.

The fluorescence emission spectra of the dye bis[4-(2-benzothiazoleazo)-(2-(o-hydroxyphenoxy)-ethyl)ether] is shown in Fig. 1 and the results are given in Table 1.

The laser effect of the dye has been tested using a commercial N\(_2\) laser as a pump source (Molelectron UV 1000) associated with a commercial dye laser (Molelectron DL 400). The N\(_2\) laser has a peak power of 1 MW and its pulse duration is 10 ns. The repeating rate was 20 Hz. The laser action of the bis[4-(2-benzothiazoleazo)-(2-(o-hydroxyphenoxy)-ethyl)ether] dye has been demonstrated and shows that the compound has the higher quantum yields and lasing characteristics. The variations in laser yield as a function of emission wavelength are obtained and it should be noted that owing to a very small overlap between absorption and emission spectra of the dye, the center of tuning range does not depend on concentration as observed in commercial dyes viz. rhodamine dyes. The concentration dependence of the laser yield is only due to self quenching. The optimal concentration at which the laser yield maximum is 2 \times 10^{-4} \text{ mol l}^{-1}. (Table 1) It has also been
Table 1

Fluorescence spectra and Laser characteristic of bis[4-(2-benzothiazoleazo)-(2-(o-hydroxyphenoxy)-ethyl)ether] in dioxane

<table>
<thead>
<tr>
<th>Excitation (nm)</th>
<th>Emission (nm)</th>
<th>Life time (ns) ± 0.1</th>
<th>Quantum yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>430</td>
<td>11</td>
<td>0.38</td>
</tr>
<tr>
<td>250</td>
<td>430</td>
<td>10</td>
<td>0.39</td>
</tr>
</tbody>
</table>

Laser characteristic

<table>
<thead>
<tr>
<th>λ_{max} (A^0)^a ps excitation</th>
<th>λ_{max} (A^0)</th>
<th>Tuning range A^0</th>
<th>Laser yield b</th>
<th>Optimal concentration N_2 Laser</th>
</tr>
</thead>
<tbody>
<tr>
<td>4550</td>
<td>5780</td>
<td>5500-5900</td>
<td>1.95</td>
<td>2 \times 10^{-4}</td>
</tr>
</tbody>
</table>

a. Laser wavelength at which the laser yield is maximum,
b. Laser yield relative to coumarin 480 at λ_{max},
c. Optimal concentration at which the laser yield is maximum.
Fig. 1. Excitation and Emission spectra of bis[4-(2-benzothiazoleazo)-(2-(o-hydroxyphenoxy)-ethyl)ether]
observed that the variation in the excitation wavelength also does not have any effect in the emission wavelength. (Table 1)

**Metal complexes**

The extraction was carried out from aqueous solution of alkali and alkaline earth metal hydroxide. The colour of the complex, wavelength of the maximum absorbance, molar absorptivity, Beer's law limit of the extracted complexes are given in Table 2.

The distribution of the reagent strongly favours the 1,2-dichloromethane phase and the concentration of the reagent in the aqueous phase was usually negligible throughout the present study. The absorption spectra of the extracted sodium in 1,2-dichloromethane at the various pH (6-11) is shown in Fig 2. The absorption spectra of the dye bis[4-(2-benzothiazoleazo)-(2-(o-hydroxyphenoxy)-ethyl)ether] is 400 nm and on complexation shifted to 541 nm. The crown dye is having higher extraction selectivity for sodium compared to the potassium. The selectivity for barium is more than the strontium. The metal ions were stripped into aqueous media and their concentration was determined by AAS. The percent extraction and extraction equilibria were calculated and are given in Table 3.

**Effect of pH**

The data on the effect of pH in the extraction are given in Table 3. It has been observed that below 7.0 pH the extraction is almost negligible and the extraction only possible above pH 7.0. The quantitative extraction is obtained between 9.5 pH and 11.0 pH.
Table 2
Extraction of alkali and alkaline earth metals with bis[4-(2-benzothiazoleazo)-(2-(o-hydroxyphenoxy)-ethyl)ether] dye in dichloromethane

<table>
<thead>
<tr>
<th>Metal</th>
<th>pH of extraction</th>
<th>Colour of the Complex</th>
<th>$\lambda_{\text{max}}$, nm</th>
<th>Beer's Law (ppm)</th>
<th>Molar Absorptivity, $\varepsilon$ (1 mol$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>10.5</td>
<td>Red</td>
<td>545</td>
<td>0.10-5.00</td>
<td>5.5 x 10$^3$</td>
</tr>
<tr>
<td>K$^+$</td>
<td>10.5</td>
<td>Red</td>
<td>545</td>
<td>0.25-15.00</td>
<td>3.0 x 10$^3$</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>10.5</td>
<td>Red</td>
<td>545</td>
<td>0.30-15.50</td>
<td>2.9 x 10$^3$</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>10.5</td>
<td>Red</td>
<td>551</td>
<td>1.20-28.00</td>
<td>5.0 x 10$^2$</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>10.5</td>
<td>Red</td>
<td>551</td>
<td>1.3-30.00</td>
<td>3.0 x 10$^2$</td>
</tr>
</tbody>
</table>

The $\lambda_{\text{max}}$ of the bis[4-(2-benzothiazoleazo)-(2-(o-hydroxyphenoxy)-ethyl)ether] in dichloromethane is 400 nm.
Table 3

Distribution ratio and percent extraction of metals by crown ether dye bis[4-(2-benzothiazoleazo)-(2-(o-hydroxyphenoxy)-ethyl)ether] at various pH

<table>
<thead>
<tr>
<th>pH</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Cs⁺</th>
<th>Ba²⁺</th>
<th>Sr²⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%E</td>
<td>D</td>
<td>%E</td>
<td>D</td>
<td>%E</td>
</tr>
<tr>
<td>6.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>7.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>8.0</td>
<td>70.0</td>
<td>2.3</td>
<td>65.2</td>
<td>1.8</td>
<td>60.2</td>
</tr>
<tr>
<td>8.5</td>
<td>91.0</td>
<td>10</td>
<td>69.0</td>
<td>3.2</td>
<td>65.5</td>
</tr>
<tr>
<td>9.0</td>
<td>99.0</td>
<td>99</td>
<td>85.0</td>
<td>5.6</td>
<td>80.5</td>
</tr>
<tr>
<td>9.5</td>
<td>99.4</td>
<td>165</td>
<td>99.2</td>
<td>185</td>
<td>99.0</td>
</tr>
<tr>
<td>10.0</td>
<td>99.7</td>
<td>1800</td>
<td>99.9</td>
<td>1400</td>
<td>99.8</td>
</tr>
<tr>
<td>10.5</td>
<td>99.8</td>
<td>1805</td>
<td>99.9</td>
<td>1500</td>
<td>99.9</td>
</tr>
<tr>
<td>11.0</td>
<td>99.9</td>
<td>1805</td>
<td>99.9</td>
<td>1500</td>
<td>99.9</td>
</tr>
</tbody>
</table>

shows no extraction,

% E percentage of extraction,

D distribution ratio
Fig. 2. Effect of pH on the absorption spectra of sodium with bis[4-(2-benzothiazoleazo)-(2-(o-hydroxyphenoxy)-ethyl)-ether] in dichloromethane
Structure of Coordination Complex

The extraction constant ($K_{ex}$), the aqueous ion-pair formation ($K_{MLA}$) and the formation constant of bis[4-(2-benzothiazoleazo)-(2-(o-hydroxy-phenoxy)-ethyl)ether] dye with alkali metal ($Na^+$, $K^+$, $Cs^+$) and alkaline earth metal ($Ba^{2+}$, $Sr^{2+}$) were determined in $25^0C$. (Table 4) The extraction constant is the highest for $Na^+$ while minimum for $Sr^{2+}$. The order of the stability constant is $Na^+ > K^+ > Cs^+$ and $Ba^{2+} > Sr^{2+}$.

It is well known that potassium ion is the most easily complexed with dibenzo-18-C-6 type reagents because of the ionic size just fits the cavity of this type. In the present experiments, the extraction constants for sodium is highest, compared to potassium and cesium although the differences in values are small. The relative ease of extraction of sodium can be explained by the protonation of phenolate group and then the coordinate through the oxygen of the alkyl ether. This probably completes a lipophilic skin assumed the sodium ion, if the pairing citramide comes in contact with the complex from the opposite (axial) direction. The order of the extraction, shows that smaller the ionic size of the cation, the greater the ionic interaction thus easing the extraction of these cations. The same order is obtained for their stability constant as well as the selectivity constant. The most of the transition metals and other associated ions except the alkali and alkaline earth metals are not interfering in the extraction and determination of sodium, potassium, cesium, barium and strontium.
Table 4

Extraction and Stability constants in 50% dioxane – water medium at 25°C

<table>
<thead>
<tr>
<th>Metal ions</th>
<th>Cation radius A₀</th>
<th>log K₁⁺ᵃ</th>
<th>log K₂⁺</th>
<th>log K₁ / log K₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>0.95</td>
<td>5.7</td>
<td>5.50± 0.02</td>
<td>-</td>
</tr>
<tr>
<td>K⁺</td>
<td>1.33</td>
<td>4.9</td>
<td>4.87± 0.05</td>
<td>-</td>
</tr>
<tr>
<td>Cs⁺</td>
<td>1.35</td>
<td>4.7</td>
<td>4.60± 0.04</td>
<td>-</td>
</tr>
<tr>
<td>Ba²⁺</td>
<td>1.35</td>
<td>4.3</td>
<td>5.90± 0.03</td>
<td>2.95± 0.04</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>1.13</td>
<td>3.9</td>
<td>4.98± 0.02</td>
<td>2.52± 0.03</td>
</tr>
</tbody>
</table>

ᵃ in dichloromethane
The structure of metal complexes were evaluated by the mole ratio method and plotting the log $D_m$ against the log crown dye concentration (Figs. 3-7). The mole ratio method shows that the metal to the ligand ratio for the Na$^+$, K$^+$ and Cs$^+$ metal is 2:1 whiles in case of the divalent ions (Ba$^{2+}$, Sr$^{2+}$) it is 1:1. Similarly the slope of the straight lines for monovalent and divalent metals are 0.5 and 1, respectively. The complexes between anionic crown ether derivatives and alkali and alkaline earth metal ions are stabilized by a chelating interaction between the crown ether bound metal and the anionic group in addition to the stabilization provided by the ordinary metal-crown ether interaction.\(^{(22)}\)

**Stability constants**

The stability constants ($\log K_1$, $\log K_2$) are given in Table 4. The selectivity for Na$^+$ is more than K$^+$ and Cs$^+$ while for divalent ions Ba$^{2+}$ > Sr$^{2+}$. The selectivity of the crown dye bis[4-(2-benzothiazoleazo)-(2-(o-hydroxy- phenoxy)-ethyl)ether] for these two cation over other in their respective groups in the periodic table is well established.\(^{(23,24)}\) The stability constant of alkali and alkaline earth metals are inversely proportional to their ionic radii. A linear relationship is obtained when stability constants are plotted against the ionic radii (Fig. 8). It has also been observed that the stability constant decreases with the increase of the atomic number. The selectivity of Na$^+$ over K$^+$ and for Ba$^{2+}$ over Sr$^{2+}$ (Table 4, Fig. 8) is almost entirely enthalpic in origin, probably corresponding to the close approach of the cation to the ring donor atoms without the need to strain any ring bonds.
Fig. 3. The plot of log D vs -log C
Fig. 4. The plot of log D vs -log C
Mole ratio method for Cs$^+$ ion

Fig. 5. The plot of log D vs $-\log C$
Fig. 6. The plot of log D vs –log C
Fig. 7. The plot of $\log D$ vs $-\log C$
Fig. 8. The plot of log $K_1$ vs cation radius ($A^0$)
Determination of Sodium in blood serum

Human blood serum (0.2 ml) was mixed with an aqueous perchloric acid and dichloroacetic acid to precipitate the protein and centrifuged. An aliquot of 0.1 ml from the supernatant solution, mixed with aqueous buffer (to adjust the pH 10) and cetrimide (1 ml) added. The aqueous solution was then shaken with a 10 ml solution of dye in dichloromethane. After phase separation the absorbance of the organic layer was measured at 545 nm against reagent blank. A calibration curve was prepared with NaCl solution and the conc. of sodium was computed. The data are given in Table 5.

Table 5
Determination of Sodium in Human Blood Serum

<table>
<thead>
<tr>
<th>Sample</th>
<th>Present method</th>
<th>AAS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Child</td>
<td>4.9 ± 0.2</td>
<td>4.85 ± 0.05</td>
</tr>
<tr>
<td>Men I</td>
<td>5.4 ± 0.3</td>
<td>5.48 ± 0.07</td>
</tr>
<tr>
<td>Men II</td>
<td>5.2 ± 0.2</td>
<td>4.98 ± 0.08</td>
</tr>
<tr>
<td>Women</td>
<td>5.5 ± 0.2</td>
<td>5.47 ± 0.06</td>
</tr>
</tbody>
</table>

Average of 20 determination in each categories

Child between the age of 3 – 6 years.
Men I between the age of 25 – 40 years.
Men II between the age of 35 – 55 years.
Women between the age of 25 – 45 years.
Membrane Transport of Sodium and Potassium

The DMHF membrane system consisted of a glass – 250 ml reservoir containing the source phase and another of equal volume containing the receiving phase. These aqueous phases were circulated by means of C – Flex or Norpene tubing and peristaltic pump through the lumen of a hallow – fiber bundle. Each fiber bundle was constructed of 60 lengths of polypropylene micro porous hollow – fibers, secured using polyethylene tubing connectors and silicon glue.

The fibers used, celgered X 20 (Hoechst Celanese), have an inside diameter of 400 μm, an effective pore size 0.03 μm and 40 % porosity. Each fiber bundle was 15 cm in length, excluding the polypropylene tubing connectors. Two fiber bundle were holed in a U – shape and immersed in 60 ml membrane reservoir containing 25 ml of the membrane solvent / macracyclic solution. The average outside surface area of each bundle in 500 ml of pure and dry THF was added dropwise. The reaction mixture was stirred at rt of 1 d and then refluxed for 4 d. The solvent was evaporated under reduced pressure, and was exposed to the solvent was 71 cm². Solvent and aqueous reservoirs were continuously stirred with Teflon – coated magnetic stirring bars and synronous stirring motors at 600 rpm.

Each membrane experiment was run for at least 10 h. Samples for analysis were taken periodically (usually hourly) from the receiving phase. New hollow – fiber bundles were made for each experiment. The samples were analysed for metal cation content using AAS. All experiments were performed in triplicate. Membrane and solvent extraction blank experiments,
Transport experiments were performed using a liquid membrane system the sodium and potassium concentration in aqueous compartment were monitored as a function of time, concentration of reagent (bis[4-(2-benzothiazoleazo)-(2-(o-hydroxyphenoxy)ethyl)ether] and alkali metals by means of colourimetric method and also by AAS. The transport data are an average of at least three runs where experimental error is less than 3 %.

A typical concentration of sodium and potassium vs time is shown in figs 9,10. The mass balance of alkali metals in the source and strip phase obeys all time, t, indicating that there is no accumulation of alkali metal in or on the membrane. The sodium and potassium concentration in the strip phase varies linearly with time upto 6 h and 8 h, respectively.
Assuming that metal transport is diffusion limited, the flux can be determined from the initial slope using the flux equation based on Fick’s law (25) as

\[
J = \frac{V}{A} + \left( \frac{dc}{dt} \right) = \left[ \frac{\delta}{D_{aq}} + \frac{L}{D_M K_D} + \frac{1}{K_{i+}} \right] C_{s_0}^{t=0}
\]  

(5)

Where \( V \) = strip solution volume, \( A \) = effective membrane area, \( \delta \) and \( L \) are Nerst aqueous diffusion layer and membrane thickness, \( D_{aq} \) and \( D_M \) are the diffusion coefficient of metal in aqueous solution and the effective diffusion coefficient in the membrane phase, \( K_D \) is the distribution coefficient, \( K_i \) is the pseudo-first order rate constant for the transfer of sodium or potassium at the source/membrane interface and \( C_{s_0} \) is the time-dependent bulk concentration of sodium or potassium species in the source solution.

If the interfacial chemical reaction are very fast (\( K_i \rightarrow \infty \)) then eqn (5) can be written as

\[
\frac{1}{P} = \frac{C_{s_0}^{t=0}}{1} = \left[ \frac{\delta}{D_{aq}} + \frac{L}{D_M K_D} \right]
\]  

(6)

Where \( P \) is the permeability of sodium/potassium combining eq. (5) and (6) and integrating the equation between \( t = 0 \) and \( t = t \) we obtaine

\[
\ln \left[ \frac{C^{t=0} - C_{st}}{C^{t=0}} \right] = \frac{A}{V} \cdot pt
\]  

(7)
Table 6
Values of the $D_m$, $J$ and $P$

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>$D_m$ ($10^{-8}$ cm$^2$S$^{-1}$)</th>
<th>$J$ ($10^{10}$ cm$^2$S$^{-2}$)</th>
<th>$P$ ($10^{-3}$ cmS$^{-1}$)</th>
<th>K mole$^{-1}$ cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>7.9</td>
<td>1.5</td>
<td>3.4</td>
<td>$6.243 \times 10^{-3}$</td>
</tr>
<tr>
<td>K$^+$</td>
<td>5.2</td>
<td>1.10</td>
<td>2.1</td>
<td>$1.880 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Table 7
Rate constant at various metal concentrations.

<table>
<thead>
<tr>
<th>Metal conc. (ppm)</th>
<th>K mole$^{-1}$ min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
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Fig. 9. $\text{Na}^+$ transportation with variation in metal conc.
Fig. 10. $K^+$ ion transportation with change in metal conc.
Fig. 11. Na⁺ ion transportation with reagent variation.
Fig. 12. $K^+$ ion transportation with reagent variation
Where $C_{so}^0$ initial metal concentration, in the source solution and $Cst$ time dependent bulk concentration of metal species in the strip solution. $P$ can be evaluated from the slope of the plot of the left-hand term of the equation (7). The values of the $D_M$, $J$ and $P$ can be obtained from typical concentration vs time profile for sodium and potassium transport are given in Table 6.

The transportation of the metal of the pseudo-unimetal reaction of the first order which can be represent as

$$K = \frac{2.303}{t} \log \frac{C_{so}^0}{C_{so}^0 - Cst}$$  \hspace{1cm} (8)$$

The variations in the concentration of sodium and potassium keeping the reagent concentration constant, with respect to time is shown in Fig 9,10. It has been observed that the maximum transportation is observed at 6.0 and 8 h, respectively. The $t_{1/2}$ for sodium and potassium is 3 and 5 h, respectively. The rate constant at the various concentrations of metals is given in Table 7. It has been observed that as the concentration of the metal increases the rate constants are also increases.

The transportation of sodium and potassium ion with the variation of time and with the variation of the reagent concentration is shown in Fig 11 and 12. The optimum time for the transportation of sodium and potassium is 6 and 8 h, respectively at various concentration of the dye.
REFERENCES


