

THE EFFECT OF TEMPERATURE ON Na⁺ ION TREATMENT IN BULK LIQUID MEMBRANE SYSTEMS

L'EFFET DE LA TEMPÉRATURE SUR LE TRAITEMENT DE L'ION Na⁺ EN VRAC DANS LES SYSTÈMES DE MEMBRANE LIQUIDES

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Abstract: In this study, in a bulk liquid membrane system, the effect of temperature on the transport of Na⁺ ions through a toluene-dichloromethane membrane with the use of DB18C6 as a carrier was examined. The kinetic analysis of the system was performed in accordance with non-steady state reaction kinetics and the kinetic values such as k_{1d} , k_{2m} and k_{2a} , and R_{max} , T_{max} , J_{dmax} and J_{amax} were calculated. In the experiments, four different temperatures (298°K, 303°K, 308°K and 313°K) were conducted for determining the effect of temperature on the transport of Na⁺. It was found that the k_{1d} , k_{2m} and k_{2a} parameters, without being directly attributed to temperature, decrease with the rising temperature. The best Na⁺ transport efficiency was achieved at 298°K.

Key words: Liquid membranes, Effect of temperature, Kinetic analysis

Résumé : Dans cette étude, dans un système liquide de membrane en bloc, l'effet de la température sur le transport des ions de Na⁺ par une membrane de toluène-dichlorométhane avec l'utilisation de DB18C6 comme porteur a été examiné. L'analyse cinétique du système a été exécutée selon la cinétique non - régulière de réaction d'état et les valeurs cinétiques telles que k_{1d} , k_{2m} et k_{2a} , et R_{max} , T_{max} , J_{dmax} et J_{amax} ont été calculés. Dans les expériences, les quatre températures différentes (298°K, 303°K, 308°K et 313°K) ont été conduites pour déterminer l'effet de la température sur le transport de Na⁺. On a constaté que les paramètres de k_{1d} , de k_{2m} et de k_{2a} , sans être directement attribué à la température, diminuent avec la température de montée. La meilleure efficacité de transport de Na⁺ a été réalisée à 298°K.

Mots clés: Membranes liquides, Effet de la température, Analyse cinétique

INTRODUCTION

Separation processes are of much significance in the removal of certain toxic matter from wastewater, in industrial processes and for the enrichment of precious metals. The selective separation of many metals and non-metal ions from liquid membranes is among the latest technologies being significantly dwelt upon today. Due to the advantages offered by liquid membrane separation processes, much study is being done towards the examination and advancement in this field (Noble and al, 1987; Ulbrich and al, 1994; Mulder and al, 1990). In recent years, in particularly separation operations that require chemical reactions, all influencing parameters that increase the efficiency of carrier mediated liquid membrane systems are being examined in detail (Boyadzhiev and al, 1996; Akhond and al, 1996; Aydınler et al., 2000; Calzado et al., 2001; Danesi et al.,

1981). Ligands to be able forming complex at suitable stability with the matter that is to be separated or enriched are preferred as carrier. Generally, macrocycle crown ether structures are implemented for the transport of alkali metals in liquid membrane systems (Boyadzhiev and al, 1996; Izatt et al., 1983; Gaikwad et al., 1991; Izatt et al., 1983b; Izatt et al., 1984; Lamb et al., 1980).

In the study conducted, it was investigated as to the effect of temperature on the transport of Na^+ ions through a bulk liquid membrane system. Since Na^+ ion is particularly abundant in salty water it is a cation of special significance in desalination processes. The crown ether DB18C6 proposed for alkali cations were implemented as a carrier. As membrane solvents, solvents having high dielectric constants and high boiling points with low viscosity and low solubility, such as chloroform, dichloromethane, toluene, xylene, kerosene, n-octane, mesitylene, are used (Bartcsch et al., 1987; Szpakowska and al, 1997; Strzelbicki and al, 1989; Bartsch et al., 1999). Due to allowance for better Na^+ transport efficiency as compared to other solvents, the toluene-dichloromethane binary membrane was selected within the scope of the study (He and Ma, 2000).

Much study has been done relating to aspects affecting the efficiency of transport in liquid membrane systems such as effect of the membrane solvent, effect of the carrier and effect of stirrer's speed (Altin, 2002; Behr et al., 1985; Demircioglu et al., 2000; Izatt et al., 1987; Szpakowska and al, 1991). However, there are very few investigations as to the effect of temperature on transport (Kobya et al., 1997; Izatt, et al., 1986). In former studies, with the increase in temperature alongside the rise in transport of anions (Kobya et al., 1997), there is a fall in cation transport (Izatt, et al., 1986b). In view of these results, it is not possible to judge with certainty the effect of temperature on the transport efficiency of liquid membrane systems. It is for this reason that the effect of temperature on the transport efficiency for each system ought to be examined through experimental studies.

Various approaches may be employed for the kinetic analysis of liquid membrane systems. In this study, the kinetic analysis approach that is suitable for non-steady states that was implemented by Szpakowska (1990) and He (2000) for bulk liquid membrane systems has been preferred. In this approach; it is accepted that reactions occurring during transport in the carrier medium liquid membrane systems are first-degree and irreversible.

In this approach, it was assumed that consecutive irreversible first order reaction occurred in the carrier mediated liquid membrane systems (Eq.1) [Szpakowska and Nagy, 1990; Szpakowska and Nagy, 1993; Fyles et al., 1984].



Where D, M and A represent the sodium ion (Na^+) concentration in donor, membrane and acceptor phases, respectively.

At time, T, the sodium ion concentration in donor, membrane and acceptor phases are C_d , C_m and C_a , respectively. Since the dimensionless concentration changes are very small, reduced concentrations, (R) are used for practical reasons, defined as follows.

$$Rd = \frac{Cd}{Cd_0} \quad Rm = \frac{Cm}{Cd_0} \quad Ra = \frac{Ca}{Cd_0} \quad (2)$$

Where C_{do} is the initial concentration of sodium ion in donor phase at $T = 0$. Then, the material balance equation can be written as below;

$$Rd + Rm + Ra = 1 \quad (3)$$

The following kinetic equations can be written on the basis of above kinetic analysis;

$$\frac{dRd}{dt} = -k_{1d} Rd \equiv Jd \quad (4)$$

$$\frac{dRm}{dt} = k_{d1} Rd - k_{2m} Rm \quad (5)$$

$$\frac{dRa}{dt} = k_{2a} Rm \equiv Ja \quad (6)$$

If differential Eq. (4), (5) and (6) are integrated as a result of that, the following equations are obtained; [24].

$$Rd = \exp(-k_{1d}t) \quad (7)$$

$$Rm = \frac{k_{1d}}{k_{2m} - k_{1d}} [\exp(-k_{1d}t) - \exp(-k_{2m}t)] \quad (8)$$

$$Ra = 1 - \frac{1}{k_{2a} - k_{1d}} [k_{2a} \exp(-k_{1d}t) - k_{1d} \exp(-k_{2a}t)] \quad (9)$$

The maximum value of R_m ($R_m/dt = 0$) can be written as follow;

$$R_m^{\max} = \left(\frac{k_{1d}}{k_{2m}} \right)^{-k_{2m}/(k_{1d}-k_{2m})} \quad (10)$$

If the logarithm of Eq. (10) is taken and result is rearranged the following equation will be obtained;

$$T_{\max} = \frac{\ln(k_{1d}/k_{2m})}{k_{1d} - k_{2m}} \quad (11)$$

Non-linear numerical analysis was carried out by a BASIC iteration program. The membrane entrance rate constant k_{1d} (R_d) was obtained Eq.(7) by using this program. Then, the membrane exit rate constant k_2 (k_{2m} and k_{2a}) was obtained Eq.(8) and (9).

EXPERIMENTAL

Materials

In experiment done within the scope of study was used NaCl (Merck) as donor phase, H_2SO_4 (Merck) as acceptor phase, toluene (Merck), dichloromethane (Riedel) as membrane phase, DB18C6 (Dibenzo18Crown6) as carrier. Chemical materials were used without further purification. The aqueous solutions were made up using demineralized water.

Methods

It was preferred bulk liquid membrane system, which was often used to laboratory studies for liquid membrane experiments (Fig.1). Three phases in membrane system that shown in detail in Fig.1 have been expressed the donor (D), acceptor (A) and membrane (M) phases.

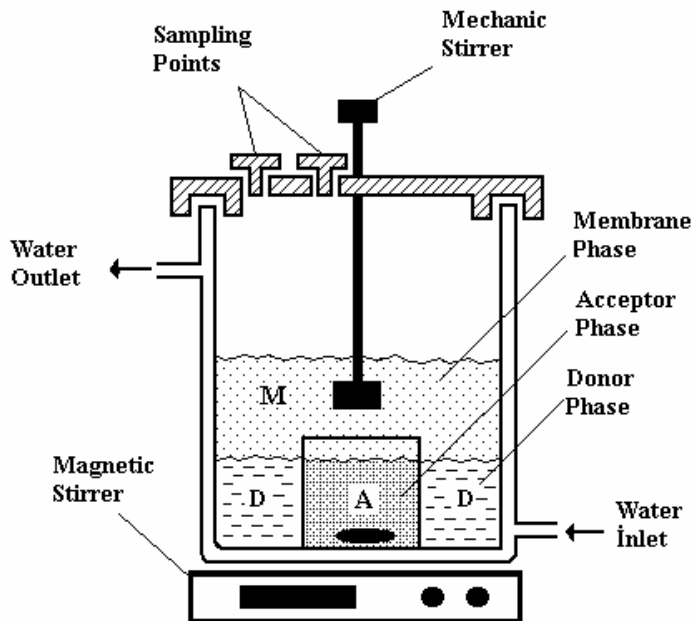


Fig. 1. The test apparatus

Density of membrane phase needs to be below of 1 due to design properties of using membrane system. In the system, organic phase is take part in the top of system. Organic phase is toluene-dichloromethane (90%-10% v/v) containing $1 \cdot 10^{-3}$ M DB18C6 as carrier. Firstly, 75 mL from 500 mg/L NaCl solution as donor phase was put into small cylinder in the inside and 75 mL from 2 M H_2SO_4 solution as acceptor phase was put into the outside part of the test apparatus. Then, 200 mL organic phase with carrier was added to reactor. Anyone of phases in the system haven't been mixed at each other. Temperature of system was kept constant during experiment by using a water circulator with digital temperature indicator (GRANT trade-mark). Membrane phase was stirred by a mechanic stirrer (IKA trade-mark), another phases were stirred by magnetic stirrer (CHILTERN trade-mark). Speed of stirrer was adjusted to speed which phases don't mix with each other. After system was started, samples were taken from both acceptor and donor phases at hours time intervals, and sodium analysis were carried out by a flame photometer (JENWAY trade-mark) [APHA, 1982].

Transport of Sodium Ions in the Bulk Liquid Membrane

The transport occurring in the bulk liquid membrane system that used in this study is carrier mediated simple transport (Fig.2). This type transport takes place in four steps.

- 1- The complex formation of carrier molecules with sodium ions at donor-membrane phase interface (D/M).
- 2- Transport of complex towards membrane-acceptor phase interface (M/A) due to concentration gradient
- 3- Decomposition of complex at membrane-acceptor phase interface (M/A)
- 4- Back diffusion of free carrier molecule to donor-membrane interface (D/M)

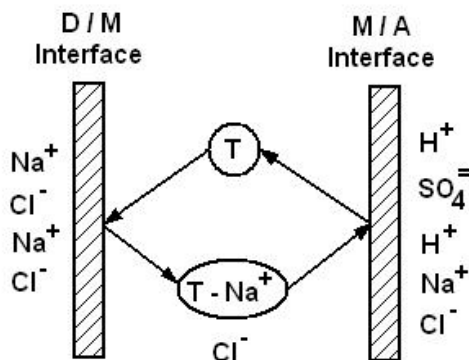


Fig. 2. The carrier mediated simple transport of sodium ion in bulk liquid membrane system

RESULTS

Within the scope of the study, towards determining the effect of temperature on the efficiency of transport of Na^+ four separate temperatures were tested. The temperature of the system was adjusted to 298°K, 303°K, 308°K and 313°K with the aid of a thermostat water circulator. As a result of tests performed, data obtained for the variation in R_d , R_m and R_a over time in the liquid membrane systems for the different temperatures has been given in Figure 3.

The kinetic analysis was performed for each system and speed constants (k_{1d} , k_{2m} and k_{2a}), flux values (J_{dmax} and J_{amax}), R_{max} and T_{max} values were determined (Table 1). Variation in membrane entry speed constant k_{1d} and membrane exit speed constant k_2 (k_{2m} and k_{2a}) in accordance with temperature are given in Figure 4.

Table 1. Kinetic parameters obtained from the systems in which different carriers were used.

Temperature (°K)	$k_{1d} \cdot 10^{-2}$ (h ⁻¹)	$k_{2m} \cdot 10^{-1}$ (h ⁻¹)	$k_{2a} \cdot 10^{-1}$ (h ⁻¹)	$R_{max} \cdot 10^{-1}$	T_{max} (h)	J_{dmax}	J_{amax}	$\log k_{1d}$
298	17,76	2,20	2,39	3,29	5,04	0,0752	-0,0724	-0,75
303	4,48	1,77	2,23	1,58	10,38	0,0299	-0,0281	-1,13
308	2,07	1,40	1,55	1,06	16,73	0,0152	-0,0148	-1,29
313	4,42	1,97	1,90	1,42	24,74	0,0278	-0,0280	-1,47

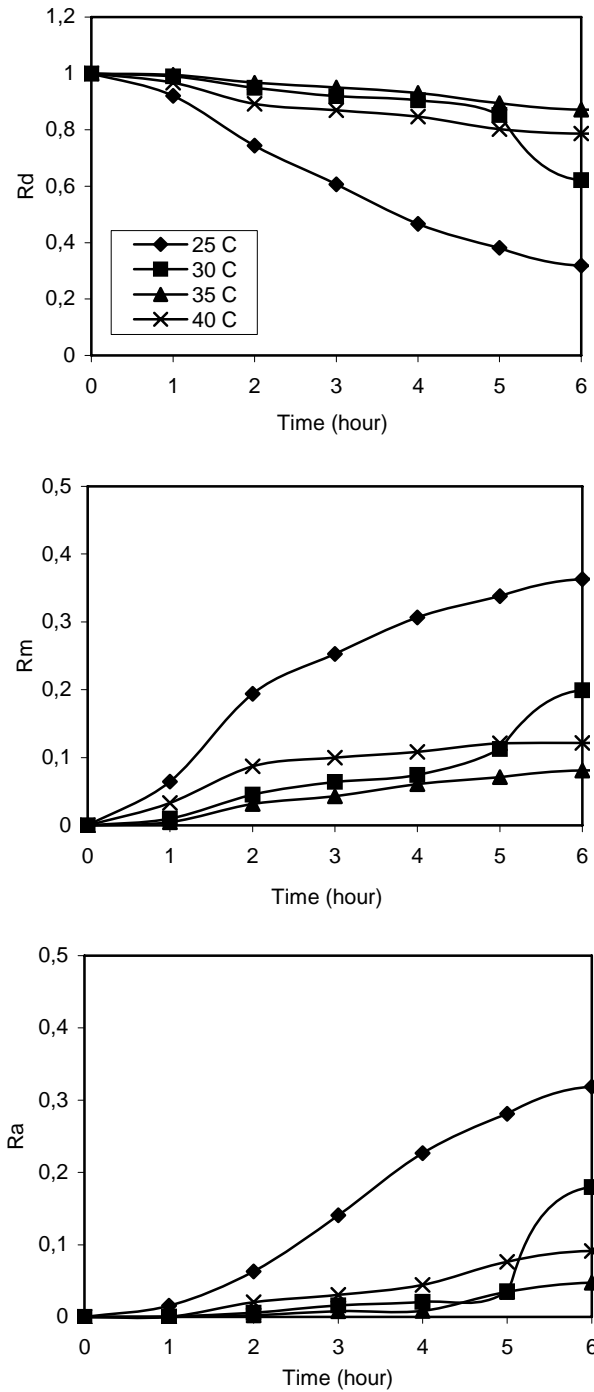


Fig. 3. In the different temperatures, the changing of the sodium ion transport ratio in donor phase (R_d), acceptor phase (R_a) and membrane phase (R_m).

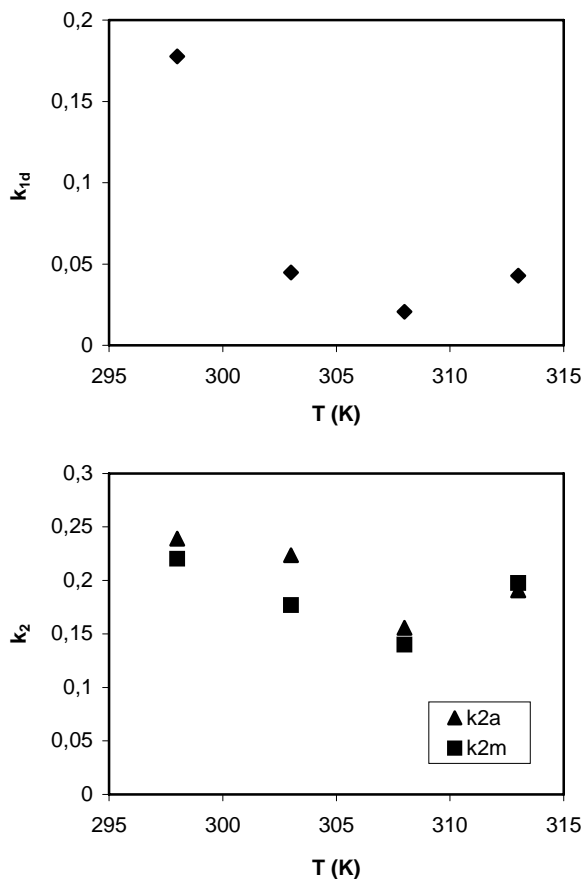


Fig. 4. Variation in membrane entry speed constant k_{1d} and membrane exit speed constant k_2 (k_{2m} and k_{2a}) in accordance with temperature

CONCLUSION

Throughout the process of testing the transport of Na^+ ion at different temperatures, it was determined that with the rise in temperature there was a corresponding fall in the membrane entry speed constant k_{1d} and the membrane exit speed constants k_{2m} and k_{2a} .

Since the solubility of the implemented carrier in the membrane phase was dependent upon temperature, 1.10^{-3} M concentration of carrier DB18C6 was completely dissolved and the initiation temperature was maintained at the lowest proposed temperature of 298°K , as given in literature. It is very important that the temperature is suitable since transport would otherwise be negatively affected had the carrier molecules not been able to dissolve completely in the membrane phase.

Maximum separation productivity for the Na^+ ions was achieved at a temperature of 298°K whereas minimum separation productivity was determined at a temperature of 308°K . With the rise in temperature the boiling point of dichloromethane was approached and it was possible that the structure of the organic membrane would be disturbed, thus higher temperatures were not tested. Furthermore, with the rise in temperature there was

an increase in the transition to the aqueous phase of the membrane matter and it was determined that the level of the membrane has fallen. At the donor phase / membrane phase interface, Na⁺-DB18C6 interaction displayed an inclination to decrease with the rise in temperature. In a similar way, at the acceptor phase / membrane phase interface, Na⁺-DB18C6 complex decomposition fell with the rise in temperature. The rise in temperature of the aqueous phase causes accelerated augmentation in the kinetic energy of the Na⁺ ions and is also a cause for the reduction in probability of Na⁺-DB18C6 complex interaction at the donor phase / membrane phase interface. Furthermore, it was determined that logk_{1d} values fell with the rise in temperature. This is to be expected in exothermic reactions, therefore, with the rise in temperature, the rate of transition from donor phase to membrane phase decreases. As can be seen from the values in Table 1, with the rise in temperature R_{max} values decrease while T_{max} values increase. The reason for the decline in R_{max} values is the decrease in complex formation at the donor phase / membrane phase interface.

The kinetic energy of the complex structures within the membrane increases with the rise in temperature, and so the complexes may transform into more stable structures. And it is for this reason that it becomes more difficult for structures at the membrane phase / acceptor phase interface to decompose and in relation to this the T_{max} values rise.

$$\log(J) = \log(A) - \frac{Ea}{2,303R} \left(\frac{1}{T} \right) \quad (14)$$

The Activation Energy (Ea) can be determined from the Arrhenius equation (eq.14). The maximum flux values (J) may be calculated according to membrane entry and exit speed constants, and Ea values can be obtained from the slope of the curve when plotted according to 1/T (Fig.5).

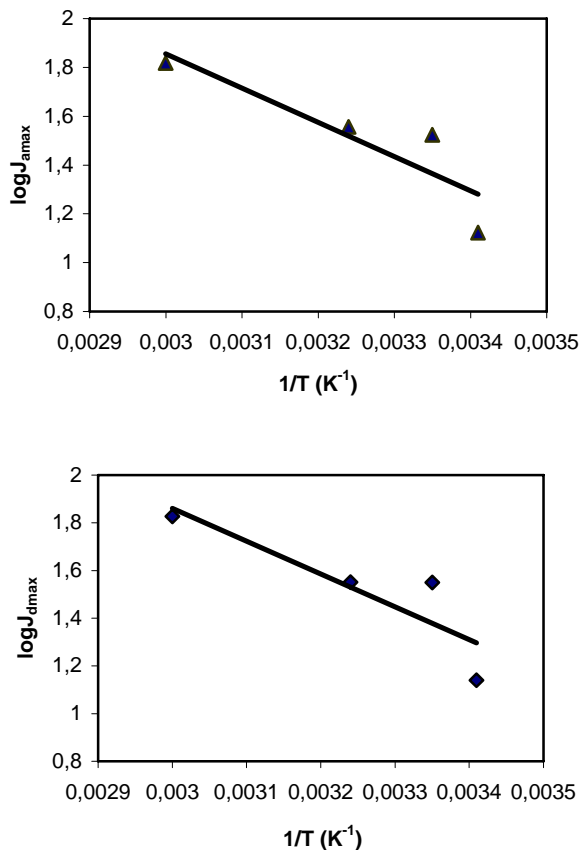


Fig. 5. In different temperatures, the changing of entry and exit flux values ($\log J_{dmax}$ and $\log J_{amax}$) in the liquid membrane system according to $1/T$

The activation energies calculated according to membrane entry and exit flux values were determined as being $E_{a_{J_{dmax}}} = 6.3 \text{ kcal.mol}^{-1}$ and $E_{a_{J_{amax}}} = 6.40 \text{ kcal.mol}^{-1}$. Effect of temperature on Na^+ ion transport speed constants can be easily seen when plotted graphics of $\log J_{dmax}$ and $\log J_{amax}$ against the $1/T$. The E_a values in diffusion-controlled processes are quite low. On the other hand, the E_a values of processes controlled by chemical reactions are high due to a strong effect of temperature on the actual speed constants. Thus, activation energy (E_a) is used as an indicator where transport occurs in fluid membrane processes with diffusion control and where controlled by chemical reactions. In diffusion controlled processes the E_a value is below 5 kcal/mol, whereas in chemical controlled processes it is above 10 kcal/mol. Hence, the system worked upon in this study may be accepted as being a diffusion controlled process when determined E_a values are taken into consideration.

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