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Non-steady state kinetics of the coupled transport of nitrite (NO_2^-) ions through liquid membranes (n-hexane 85% + chloroform 15%) containing tetraoctylammonium chloride as a carrier was examined at temperatures ranging from 273-308 °K. In this study, the influence of temperature on the kinetic parameters (k_{1d} , k_{2m} , k_{2a} , t_{\max} , R_m^{\max} , J_d^{\max} , J_a^{\max}) was investigated. The membrane entrance (k_{1d}) and exit rates (k_{2m} , k_{2a}) were increased with temperature. For maximum membrane entrance and exit fluxes, the activation energies were calculated from the slopes of the two linear relationships: $E_{ad} = 6.62 \text{ kcal/mol}$ and $E_{aa} = 6.63 \text{ kcal/mol}$, respectively. The values of the calculated activation energy indicate that the process is diffusionaly controlled.

Kinetic Analysis of Coupled Transport of Nitrite Ions Through Liquid Membranes at Different Temperatures

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Liquid membranes are effective systems for the separation of different species from dilute solutions and they play an important role in separation technology and processes^[1,2]. Their efficiency and economic advantages mean that they are viable options for use in precious-metal recovery^[3,4], toxic product (heavy metals, organic molecules) treatment^[5-7], the separation of anions, weak acids and bases, biologically important compounds and in the elimination of gaseous mixtures from wastewaters. They are also especially suited to the treatment of low concentrations of ions in water, below some hundreds of ppm^[8]. Scientific research in this field continues to be active despite the fact that at present the large-scale application of liquid membranes in industry is not yet a viable option. Detailed investigation of kinetic analysis of ion transport of liquid membranes is important in view of their selective, efficient and low-cost application in science and technology.

Besides the hundreds of cation separation systems published in the literature, only a few examples are known for the separation of anions. Liacona, et al.^[9] used a counter-transport of chloride

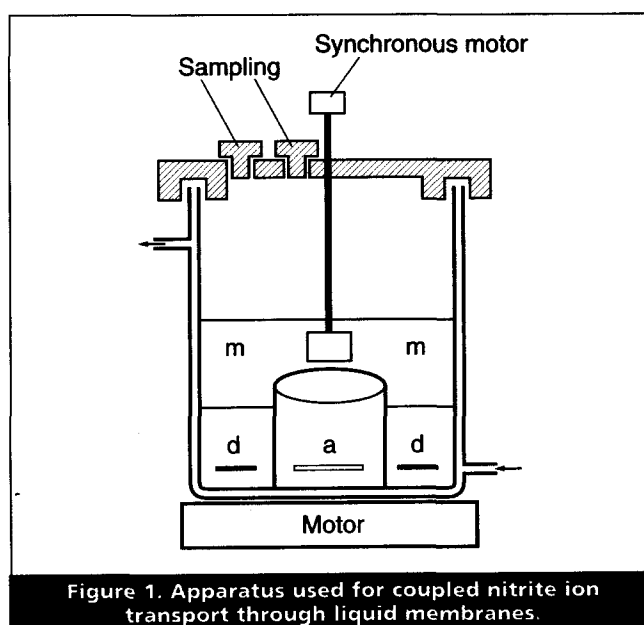
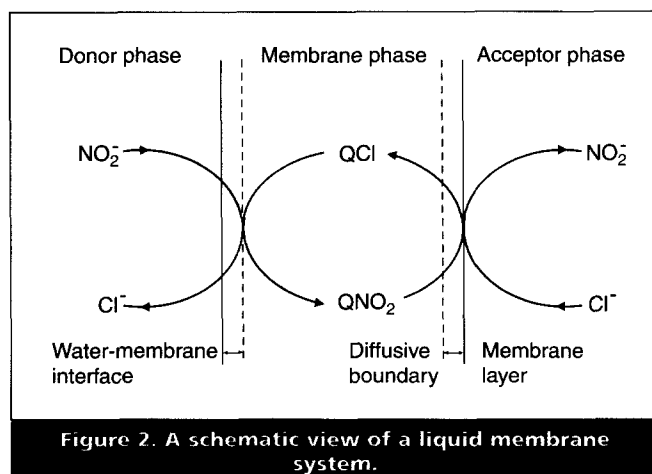


Figure 1. Apparatus used for coupled nitrite ion transport through liquid membranes.



ions to remove chromate anions from a water phase. Another example of a counter-transport process, between chloride and hydroxide ions, is given by Molnar, et al.^[10]. In this latter article the transport mechanism was not entirely clear and some complexities in the chemistry of diffusion were observed. Anions can also be removed by a co-transport mechanism. In this way, systems were developed for the concentration of nitrite ions^[11], nitrate ions^[12] and chloride ions^[13]. In these cases, transport depends on the concentration of the co-ions (usually protons) in the feed solution.

Liquid membrane technologies represent a potentially important method for industrial application including wastewater treatment and pollution removal^[14,15]. The quantity of nitrite ions in ground water is reaching levels where it is becoming a problem for preparing drinking water. For removing nitrite and nitrate from drinking waters, some treatment techniques have been developed such as chemical precipitation, ion exchange, distillation, reverse osmosis, electrodialyses, biological denitrification, solvent extraction, ultrafiltration, and liquid membrane processes^[16, 17 and 18]. According to the results of these studies, it was considered that use of liquid membranes for wastewater treatment provide more advantages than other nitrite treatment methods^[18].

In this study, the coupled transport kinetics of nitrite ion transport through liquid membranes was studied at different temperatures in the range of 293-308 °K. The kinetics of nitrite ion transport were analyzed in the form of two irreversible first order reactions. The influence of temperature on the kinetic parameters was also investigated.

EXPERIMENTAL

Materials

The chemical reagents used in these experiments were sodium nitrite, NaNO_2 (Merck, > 99.5 %), tetraoctylammonium chloride, $[\text{CH}_3(\text{CH}_2)_4\text{N}(\text{Cl})]$ (Fluka, > 99 %), n-hexane, C_6H_{14} (Fluka, > 99.7 %), chloroform, CHCl_3 (Fluka, > 99 %) and hydrochloric acid, HCl (Merck, 37 %). The aqueous solutions were prepared using demineralised water.

KINETIC PROCEDURE

Coupled transport experiments were conducted using a thermostated (TECHNE mark, model TE-8D) apparatus shown in Figure 1. The donor (d, 75 ml) and acceptor (a, 75 ml) water

phases were stirred at variable speeds by a mechanical stirrer (IKA mark, model RE 166). The membrane phase (m, 200 ml) which has a density less than 1 was stirred magnetically (HEIDOLPH mark, model MR 3003 SD). Stirring speeds for the donor, membrane and acceptor phases were 150, 200 and 150 rpm, respectively.

The initial compositions of the phases consisted of the donor phase which was an aqueous NaNO_2 solution (initial nitrite ion concentration, $C_{d0} = 50 \text{ mg/l}$ or $8.1 \times 10^{-4} \text{ M}$) and the acceptor phase which was an aqueous 2 M HCl solution. The organic membrane phase was made up by dissolving carrier (tetraoctylammonium chloride, $C_{\text{carrier}} = 10^{-3} \text{ M}$) in the chloroform and n-hexane solution. The duration of a kinetic run was about 600 minutes.

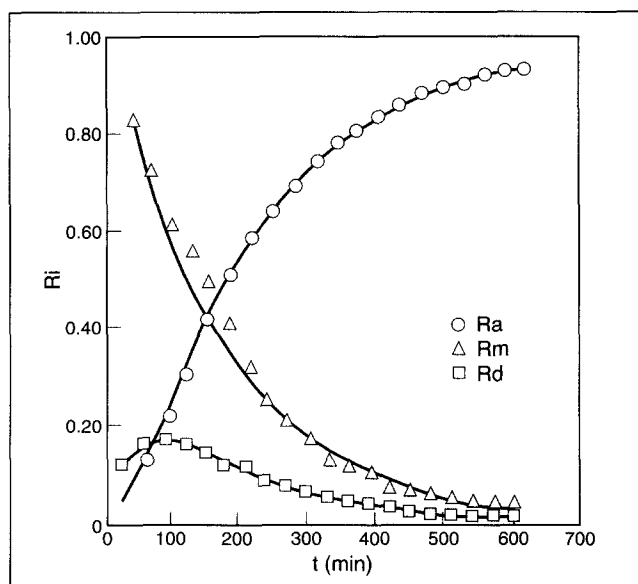


Figure 3. Time dependence of reduced concentration of nitrite ions, R_d , R_m , R_a phases in coupled transport through liquid membranes ($T = 298 \pm 0.1$ °K). Theoretical curves are calculated from Eqns. (7), (8) and (9), respectively.

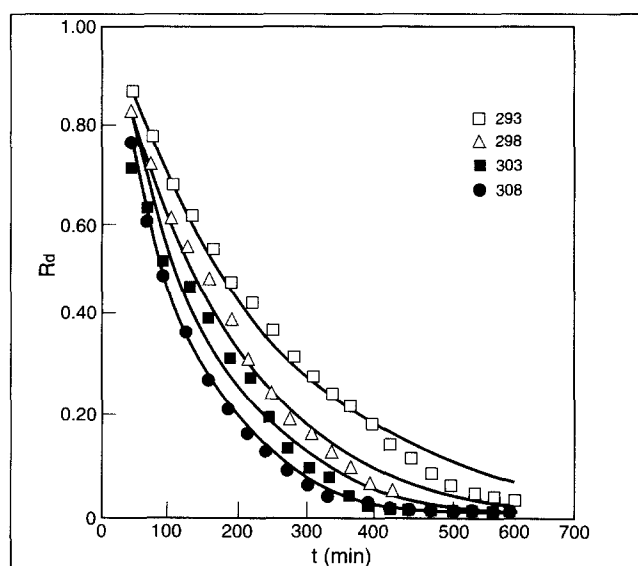


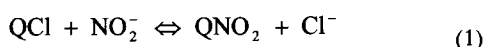
Figure 4. Time variation of reduced concentration of nitrite ions in the donor phase (R_d) during coupled transport through liquid membranes at different temperatures. Theoretical curves are calculated by Eqn. (7).

Samples (0.5 ml) were taken from both water phases (acceptor and donor phases) at regular time intervals and the nitrite ion concentration was analyzed by a spectrophotometric method [19].

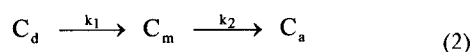
RESULTS AND DISCUSSIONS

If a membrane is considered as a semipermeable barrier between two phases, then an immiscible liquid can serve as a membrane between two liquid or gas phases. Different solutes will have different solubilities and diffusion coefficients in this liquid and the product of these two terms is an expression of the permeability. A liquid membrane can yield selective permeabilities and, therefore, result in a separation. Because the diffusion coefficients in liquids are typically of an order of magnitude higher than in polymers, so a larger flux can be obtained. Further enhancement can be accomplished by using a nonvolatile complexing agent (carrier) in the liquid. This carrier molecule can selectively and reversibly react with the solute, and this reversible reaction provides a means of enhancing the solute flux and improves the selectivity at the same time.

There is a basic mechanism for this enhanced coupled transport. In coupled transport the carrier agent couples the flow of two or more species, e.g. nitrite ion and chloride. In this case the carrier must contain, of course, ionizable-chloride groups. Thanks to this coupling, the nitrite ion can be transported against its concentration gradient provided that the concentration gradient of chlorides is sufficiently large. The mechanism of coupled transport of nitrite ion is given in Figure 2. QCl represents the chloride carrier. At the interface d/m, nitrite ion reacts with one chloride ionizable carrier molecule(QCl), liberating one chloride ion. Then, the QNO_2 complex diffuses through the membrane. At the interface, m/a, the carrier molecules are protonated and nitrite ions are liberated into the receiving phase. Finally, the neutral carrier diffuses back across the membrane. Thus, nitrite ions move from left to right and electrical neutrality is maintained by the movement of chloride ions in the opposite direction. A simple theoretical approach can be used to obtain kinetic equations for a coupled transport system, the equilibrium existing at the two interfaces (membrane-water phases) should also be considered.



In this study, it was considered that two consecutive irreversible first-order reactions were formed at coupled transport with a liquid membrane system of nitrite ions and so the kinetic equations were written as follows:



where C_d , C_m and C_a are the NO_2^- concentrations in donor, membrane and acceptor phases, respectively and C_{d0} is the initial(at $t = 0$) NO_2^- concentration in the donor phase.

Since the concentration changes are very small, it was thought that writing in R notation is more practical, and so dimensionless reduced concentrations are used for practical reasons: $R_d = \text{C}_d / \text{C}_{d0}$, $R_m = \text{C}_m / \text{C}_{d0}$ and $R_a = \text{C}_a / \text{C}_{d0}$ can be written. Samples were taken from the acceptor aqueous phase and thus, nitrite analysis was made. NO_2^- concentration in the organic phase was determined from the mass balance equation. The mass balance equation with R notation may be written as follows:

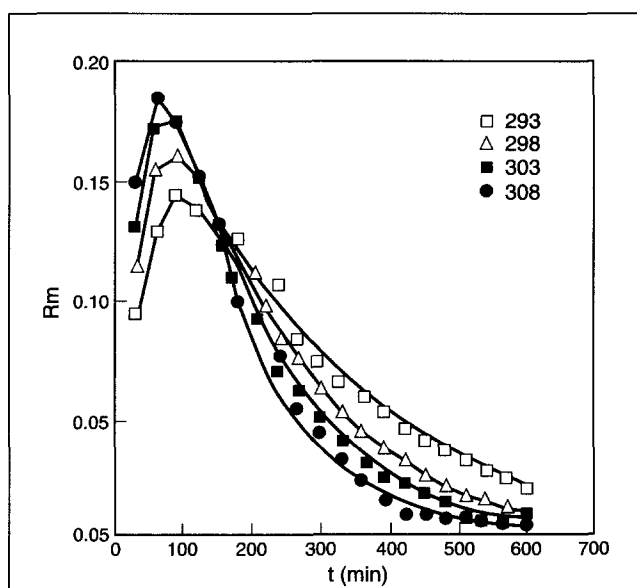


Figure 5. Time variation of reduced concentration of nitrite ions in the membrane phase (R_m) during coupled transport through liquid membranes at different temperatures. Theoretical curves are calculated by Eqn. (8).

$$R_d + R_m \frac{V_m}{V_d} + R_a \frac{V_a}{V_d} = 1 \quad (3)$$

where V_a , V_d and V_m are the volumes of the acceptor, donor and membrane phases, respectively.

Figures 3 and 6 show that the nitrite ion accumulates in the membrane phase during the transport process. As a consequence, the concentration gradient of the nitrite ion varies permanently and therefore non-steady state kinetics will govern the whole transport process. Such kinetic behaviour may be observed whenever the amounts of carrier and anions are comparable with each other [20,21], using reduced concentrations, the following rate equations may be written for the above-proposed kinetic scheme (Eq.2):

$$\frac{dR_d}{dt} = -k_1 R_d \equiv J_d \quad (4)$$

$$\frac{dR_m}{dt} = k_1 R_d - k_2 R_m \quad (5)$$

$$\frac{dR_a}{dt} = k_2 R_m \equiv J_a \quad (6)$$

From this transport system, if differential equations (4), (5), (6) are integrated and rearranged (when $k_1 \neq k_2$), the following equations are obtained [22]:

$$R_d = \exp(-k_1 t) \quad (7)$$

$$R_m = \frac{k_1}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)] \quad (8)$$

$$R_a = 1 - \frac{1}{k_2 - k_1} [k_2 \exp(-k_1 t) - k_1 \exp(-k_2 t)] \quad (9)$$

where the k_1 (k_{1d}) and k_2 (k_{2m} , k_{2a}) values are the apparent membrane entrance and exit rate constants, respectively. It is

apparent that R_d decreases mono-exponentially with time, R_a follows a monotonically increasing sigmoid-type curve while the time variation of R_m presents a maximum. Then, the maximum value of R_m (when $dR_m/dt = 0$) and t_{max} may be written as follows:

$$R_m^{max} = \left(\frac{k_1}{k_2} \right)^{-k_2 / (k_1 - k_2)} \quad (10)$$

$$t_{max} = \left(\frac{1}{k_1 - k_2} \right) \ln \frac{k_1}{k_2} \quad (11)$$

R_a versus t yields an increasing sigmoid curve. It has an inflection point (when $d^2R_a / dt^2 = 0$)

$$R_a^{infl} = 1 - \left(\frac{k_1}{k_2} \right)^{-k_2 / (k_1 - k_2)} \left(1 + \frac{k_2}{k_1} \right) \quad (12)$$

occurring at [23] :

$$t_{infl} = t_{max} \quad (13)$$

First order time differentiation of Eqns. (7) to (9) leads to the final forms of flux equations:

$$\frac{dR_d}{dt} = -k_1 \exp(-k_1 t) \quad (14)$$

$$\frac{dR_m}{dt} = \frac{k_1}{k_2 - k_1} \cdot [\exp(-k_1 t) - \exp(-k_2 t)] \quad (15)$$

$$\frac{dR_a}{dt} = \frac{k_1 k_2}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)] \quad (16)$$

The complexity of these equations prevents the simple comparison of kinetics which were observed for different membrane materials. Therefore, it is useful to examine and compare maximum release rates which can be attained in a given experimental condition. Substituting t in Eqns. (14) to (16) by its maximum value (Eqns. (17) and (19)) one obtains[23] :

$$\left. \frac{dR_d}{dt} \right|_{max} = -k_1 \left(\frac{k_1}{k_2} \right)^{-k_2 / (k_1 - k_2)} \equiv J_d^{max} \quad (17)$$

$$\left. \frac{dR_m}{dt} \right|_{max} = 0 \quad (18)$$

$$\left. \frac{dR_a}{dt} \right|_{max} = k_2 \left(\frac{k_1}{k_2} \right)^{-k_2 / (k_1 - k_2)} \equiv J_a^{max} \quad (19)$$

We see that at $t = t_{max} = t_{infl}$, the system is in steady state since the concentration of nitrite ions in the membrane (R_m) does not vary with time (Eqn. 18) because the maximum penetration (J_d) and exit (J_a) fluxes are equal but having opposite signs[23]:

$$-J_d^{max} = +J_a^{max} \quad (20)$$

The actual numerical analysis was carried out by non-linear curve fitting using a BASIC iteration program. The first rate constant, k_1 , was obtained from eq. (7) using the donor phase

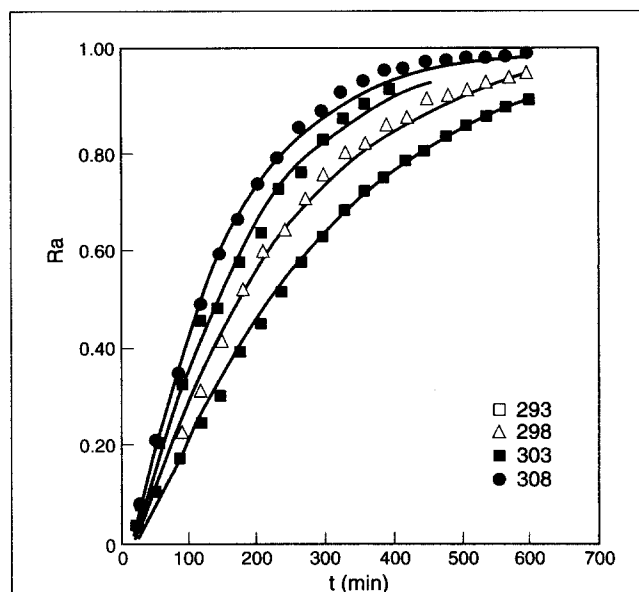


Figure 6. Time variation of reduced concentration of nitrite ions in the acceptor phase (R_a) during coupled transport through liquid membranes at different temperatures. Theoretical curves are calculated by Eqn. (9).

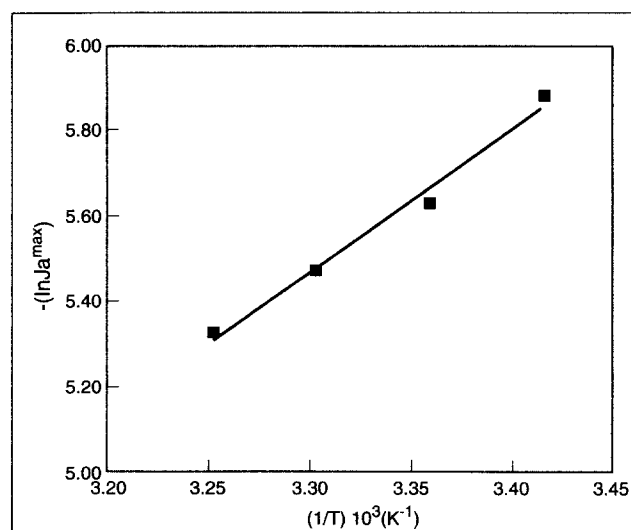


Figure 7. Arrhenius plot of nitrite ion transport at J_a^{max} .

data (k_{1d}), while the membrane exit rate constant, k_2 , may be obtained either directly from the acceptor phase kinetic data (k_{2a}) using eq. (9) or indirectly from the membrane phase data calculated on the basis of eq. (8) (k_{2m}). In both cases the k_{1d} value, obtained from eq. (7) was used in the calculations. The obtained kinetic parameters k_{1d} , k_{2m} , k_{2a} , R_m^{max} , t_{max} , J_d^{max} and J_a^{max} are given in Table 1.

The variation of reduced nitrite ion concentrations with time in donor, membrane and acceptor phases were shown in Figures 3, 4, 5 and 6, respectively. Coupled transport of nitrite ion experiments was executed at a temperature range of 293-308 °K and the membrane entrance(k_{1d}) and exit rates(k_{2m} , k_{2a}) increased with increasing temperatures. A numerical analysis between membrane exit rates k_{2m} and k_{2a} can be expressed with R_p values. Membrane entrance rate k_{1d} is obtained from $\ln(R_d)$ versus t curves. Reduced NO_2^- ion concentrations are given in Table 2, and according to this table R_d values get close to zero. At the end

308	3.34±0.01	2.60±0.01	2.55±0.01	0.19	64.38	4.88	4.85
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Table 1. Non-steady state kinetic parameters for coupled transport of nitrite ions through liquid membranes at different temperatures (k_{1d} , k_{2m} , k_{2a} , R_m^{max} , t_{max} , J_d^{max} and J_a^{max}).

of the reaction time if R_a is expressed as R_d , then permeate degree values $R_p = 1 - R_d^{fin}$ can be determined. As R_p approaches 1, k_{2m} and k_{2a} are approximately equal at all studied temperatures and thus, $R_p > 0.88$ values are obtained. The difference between k_{2a} at 308 °K is due to a little increasing of standard error at this temperature. The possible cause of this is the saturation of the donor intersection. If R_d values are small, this situation can be reduced with suitable mixing velocity. In addition to temperature, mixing velocity should be optimized at different experimental conditions for NO_2^- ions transport with liquid membranes.

The highest transport efficiency was reached at 303-308 °K. At 293 °K lower membrane efficiencies are present. Moreover, the nitrite ion concentrations are relatively high in the membrane. Furthermore separating efficiency may be characterized with R_a values. At all temperatures, except 193 °K, it is observed that R_a is greater than 0.98. At coupled transport of nitrite ions, the highest R_a values are obtained at 308 °K as seen in Table 2. Activation energies are calculated which take into consideration J_d^{max} and J_a^{max} from experiments which were carried out at four different temperatures (293, 298, 303 and 308 °K).

For diffusion controlled processes, the activation energy (E_a) values are quite low, while there is a strong effect of temperature on actual rate constants (Figure 7). E_a values are rather higher at chemically controlled processes. For this reason the activation energy (E_a) is used as an indicator of diffusion or chemical reaction control steps of a reaction during membrane processes. For diffusion controlled processes, E_a values are lower than 10 kcal/mol. But according to the literature at chemically controlled processes, E_a values are higher than 10 kcal/mol. Thus, it is considered that the transport of nitrite ions is diffusion controlled^[24].

It was concluded that temperature has an affect on the kinetic constants which were obtained for the coupled transport of nitrite ions. Since the coupled transport of nitrite ions, was formed with the consecutive irreversible reactions, calculating the activation energy of the transport process with respect to membrane entrance and exit rates is not the correct procedure. Thus, maximum membrane entrance flux (J_d^{max}) and membrane

exit permeate flux (J_a^{max}) values were used for the transport process including k_1 and k_2 (Eq. 21). Activation energy values were obtained from the maximum membrane exit flux (J_a^{max}) versus $(1/T)$ plots which are given in Figure 7.

$$\ln(J) = \ln(A) - \frac{E_a}{R} \left(\frac{1}{T} \right)$$

(21)

Calculated activation energies for membrane entrance and exit permeate rates for nitrite ions are $E_{ad} = 6.62$ kcal /mol and $E_{aa} = 6.63$ kcal /mol, respectively. Those calculated activation energies indicate that temperature has an affect on the transportation rate constants of nitrite ions. It may be assumed that the temperature effect is mainly exerted on the maximum membrane entrance and exit fluxes of the coupled transport reactions which are taking place in the reaction zones of ionic interfaces. The values of the activation energy obtained for the two transport stages revealed that the first and second steps are most probably controlled by both species diffusion.

CONCLUSIONS

With liquid membrane processes, nitrite ions are effectively and successfully removed from aqueous solutions. Temperature has an important affect on the transport of nitrite ions and especially, it is observed that transport rate constants are increased with temperature. In addition to temperature, an investigation on mixing velocity, the pH of different organic solvents and physicochemical specialties of phases may be useful. Moreover, as the temperature is increased, R_m^{max} increases, t_{max} decreases, and nitrite ions are rapidly transported into the membrane, and so less cumulation appears in the membrane. For maximum membrane entrance and exit fluxes, the activation energies for membrane entrance and exit permeate rates were calculated as 6.62 and 6.63 kcal/mol, respectively. The values of the apparent activation energy indicate that the process is diffusionally controlled.

NOMENCLATURE

C	nitrite ion concentration (M)
C_a	nitrite ion concentration in the acceptor phase (mol/l, M)
C_d	nitrite ion concentration in the donor phase (mol/l, M)
C_{d0}	nitrite ion concentration in the donor phase at t = 0 moment (mol/l, M)
C_m	nitrite ion concentration in membrane phase (mol/l, M)
$C_{carrier}$	carrier concentration (mol/l, M)
E_a	activation energy (kcal/mol)
E_{ad}	activation energy for membrane entrance rate (kcal /mol)
E_{aa}	activation energy for exit permeate rate (kcal /mol)

308	0.002	0.003	0.995	0.998
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Table 2. Distribution of nitrite ions in donor, membrane and acceptor phases in coupled transport (t ≈ 600 min.).

J_a^{\max}	maximum value of membrane exit flux (mol /m ² .min)
J_d^{\max}	maximum value of membrane entrance flux (mol /m ² .min)
k_1	membrane entrance rate constant (min ⁻¹)
k_2	membrane exit rate constant (min ⁻¹)
k_{1d}	membrane entrance or leak to membrane rate constant (min ⁻¹)
k_{2a}	membrane exit rate constant (min ⁻¹)
k_{2m}	membrane exit rate constant (min ⁻¹)
R	reduced nitrite ion concentration (dimensionless)
R_a	reduced nitrite ion concentration in the acceptor phase (dimensionless)
R_d	reduced nitrite ion concentration in the donor phase (dimensionless)
R_m	reduced nitrite ion concentration in the membrane phase (dimensionless)
R_p	permeability degree (dimensionless)
R_a^{\inf}	reduced nitrite ion conc.in acceptor phase corresponding to inflection point of the function (dimensionless)
R_d^{\inf}	R_d at the end of reaction time(dimensionless)
R_m^{\max}	max. reduced nitrite ion concentration of membrane phase(dimensionless)
t	time (min.)
t_{\inf}	time corresponding to inflection point of the function (min)
t_{\max}	time which nitrite ion concentration reaches maximum (min.)
T	temperature (°K)
TOACl	tetraoctylammonium chloride
V_a	volume of acceptor phase (cm ³)
V_d	volume of donor phase (cm ³)
V_m	volume of membrane phase (cm ³)
Subscripts	
a	acceptor phase
d	donor phase
d_0	initial nitrite ion concentration
m	membrane phase

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