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Transport of methylene blue through bulk liquid membrane containing calix[8]arene derivative

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ABSTRACT

In this study, an experimental study on the transport of methylene blue (MB) through bulk liquid membrane (BLM) is done and thereby best set of solvent, operating conditions, and mode of transport that would yield optimum performance of the BLM are identified. Therefore, a kinetic study of MB transport from an aqueous donor phase into an aqueous acceptor phase through a BLM containing calix[8]arene octacarboxylic acid (COCA) derivative as a carrier was studied. The influence of type of solvent, stirring speed, effect of NaCl weight in feed phase and temperature were investigated. The kinetic parameters (k_1, k_2, R_m^{max}, t_{max}, J_d^{max}, J_a^{max}) were calculated for the interface reactions assuming two consecutive, irreversible first-order reactions. In this study, the experiments demonstrated that COCA derivative is a good carrier for MB transport through liquid membranes.

Keywords: Bulk liquid membrane; Calixarene; Kinetic study; Methylene blue

1. Introduction

Fifteen percent of the total world production of dyes is lost during the dyeing process and is released in the textile effluents. The release of those colored wastewaters to the ecosystem is a dramatic source of aesthetic pollution, eutrophication, and perturbations in aquatic life [1]. Methylene blue (MB) is an important dye, and it is used in some medical applications in large quantities, but it can also be widely used in industrial practices such as textile and printing. MB is a cationic dye and used extensively for dying cotton, wool, and silk. The main source of aquatic pollution with colored compounds is textile dyes [2]. It is important to find cheap and efficient methods to clean industrial wastewater due to the growing emphasis on environmentally friendly industry. Physical, chemical, and biological methods are presently available for the treatment of textile wastewater [3]. Madeni et al. [4] studied bulk liquid membrane (BLM) containing Cyanex 301 as a carrier for the removal of MB in their studies. However, their transport of MB was longer time than ours [4, Table 9]. Muthuraman et al. [5] have studied recovery of MB, but they did not used membrane transfer system. In their study, they extracted MB solution. A membrane system is a continuous system, but extraction is a batch system. Thus, membrane systems are used for industrial applications on a large scale.

Utilization of membrane technology for carrier and facilitated transport through liquid membranes

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(LM) is a well-known technique for the separation of metal ions and organic matters [6]. Attention on the usage of various types of LM for separation processes has been increasing in recent years. A number of successful researches involving the transport of metal ions [7,8], rare earth elements [9], drugs [10], phenols [11], and the treatment of waste water [12] through the liquid membrane have been carried out. Certain advantages of this class of separation techniques are low capital costs, space requirements, and energy consumptions. Different LM have been studied according to their geometrical configurations, such as BLM, supported liquid, emulsion liquid membranes [13,14]. One of the simplest designs to perform liquid membrane processes is BLM, which is often used for the investigation of the complexation and transport properties of synthetic and natural ionophores with salts [15]. BLM has been studied for preconcentration and separation of different metal ions with a variety of liquid membrane phases. In addition to the crown ethers, cryptands, and cyclodextrins, the calixarenes are an important class of supramolecular hosts. Its ability of recognizing cationic and anionic species, as well as neutral molecules, is an important property of calixarene [16]. Calix[8]arene, which has a relatively large cavity, is an useful receptor for recognizing organic compounds, and it is used as a carrier for various amines and amino acid esters due to its large cavity [17,18]. Confirmation of its large cavity size in the solid state made it an attractive alternative to crown ethers for the potential binding of large cationic species [19]. Inazumi and Sueishi studied with calix[8] arene derivative compound for complexation with MB [20]. They mentioned that inclusion ability for the upper main cavity of calix[8]arene compound is effectively controlled by inserting cations into the ester carbonyl groups on the lower rim; in other words, cavity size of the calix[n]arene compound is an important parameter for the transport study. Yoshimi et al. studied p-sulfonatocalix[n]aren derivatives with MB. Their studies shows calix[8]aren cavity is better than calix[6]aren and calix[4]aren. Calix[4]aren cavity is too small to make complex with MB [21].

In the present study, investigation about the transport of MB through the BLM by a calix[8]arene octacarboxylic acid, (5,11,17,23,29,35,41,47-octa-ter-butil-49,50,51,52,53,54,55,56 octaethoxycarbonilmethoxy calix[8]arene), as the mobile carrier is done. Several important parameters such as time dependency, NaCl concentration, temperature, and stirring rate that affect the transport rate in the liquid membrane system were elucidated.

2. Experimental

2.1. Chemicals and procedure

Analytical reagent-grade chemicals were used for the preparation of all of the solutions. Dichloromethane, chloroform, and carbon tetrachloride (Merck) were used as organic diluents. All aqueous solutions were prepared with ultrapure water obtained from a Millipore Milli-Q Plus water purification system. The carrier used in the study was synthesized according to the literature methods [22]. The molecular structures and abbreviations of the carrier membrane used in the study are shown in Fig. 1. The membrane phase was prepared by dissolving an appropriate amount of the carrier in each solvent so that the concentration of calixarene derivative in the each solution was $1 \times 10^{-3}\,\mathrm{mol\,dm^{-3}}$. A stock solution of $1 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$ MB was used as a sorbate and was not purified prior to use. pH was fixed during the study, and pH of water was adjusted to 3.00 ± 0.01. Besides pH value was measured at the beginning and at the end of the study.

2.2. Transport experiments

The experimental setup was a U-Type glass cell (the contact area between the donor and the membrane, and the membrane and the acceptor phases of the BLM system were $1.5\,\mathrm{cm^2}$) used for separating the two aqueous phases (Fig. 2). The temperature of the cell contents was kept constant at $298\,\mathrm{K} \pm 1$ by placing the cell in a thermostated water bath. The aqueous feed solutions ($10\,\mathrm{cm^3}$) consisted of MB ($1 \times 10^{-5}\,\mathrm{mol\,dm^{-3}}$) and sodium chloride (at different weights) adjusted to pH 7.0. It was confirmed that in the absence of NaCl in the feed phase, transfer of MB across the membrane did not take place. The stirring rate was 150 rpm for both the feed and the stripping phase.

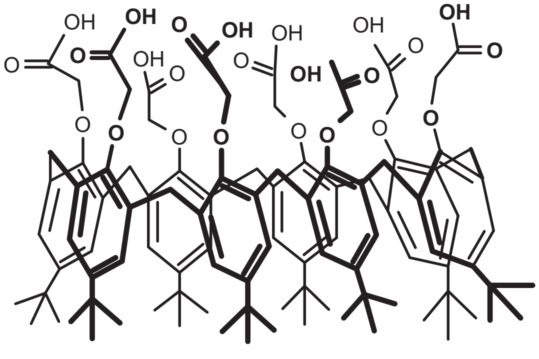

Fig. 1. Calix[8]arene octacarboxylic acid (5,11,17,23,29,35,41,47-octa-ter-butil-49,50,51,52,53,54,55,56 octaetoksicarbonilmetoksi calix[8]aren) (COCA).

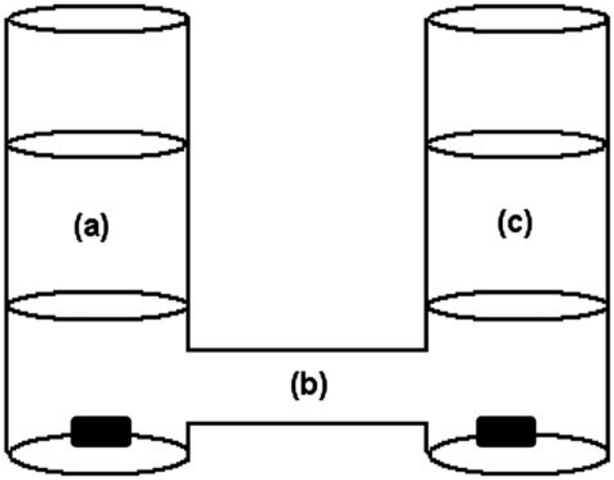

Fig. 2. Experimental setup for the transport experiments; (a) donor phase ($10\,\mathrm{cm}^3$): $1\times10^{-5}\,\mathrm{mol\,dm}^{-3}$, pH = 7.00 ± 0.01. (b) Membrane phase ($7\,\mathrm{cm}^3$): $CHCl_3$, CCl_4 and CH_2Cl_2, membrane; COCA derivative ($1\times10^{-3}\,\mathrm{mol\,dm}^{-3}$). (c) Acceptor phase ($10\,\mathrm{cm}^3$): ultrapure water pH = 3.00 ± 0.01.

The organic phase was stirred at variable speeds magnetically (Arex mark). In the BLM transport experiments, the samples ($2\,\mathrm{cm}^3$) were taken from the feed solution and receiving solution at scheduled time intervals and analyzed for MB content with a spectrophotometer. Afterwards, it was added to both sides immediately to maintain a constant volume in the solutions. Experiments were performed at the existence of the membrane resulting in no transport of MB. Determinations were repeated more than twice for each set of experimental conditions. The measurements were performed with a UV-160A Model Shimadzu Spectrophotometer.

3. Results and discussion

3.1. Transport mechanism of MB by calix[8]arene octacarboxylic acid

The mechanism of transport of MB through calix [8]arene derivative BLM is illustrated in Fig. 3. pH values in the donor and acceptor phases crucially affect the transport efficiency due to the dependence of extraction on the proton-exchange mechanism. MB in the donor phase diffuses to the interface and forms a complex with calix[8]arene octacarboxylic acid (Fig. 3). In this step, one proton is released from calix [8]arene octacarboxylic acid accompanying the complexation. The complex diffuses toward the opposite interface through the BLM. The stripping reaction takes place with hydrogen ions at the interface with the acceptor phase.

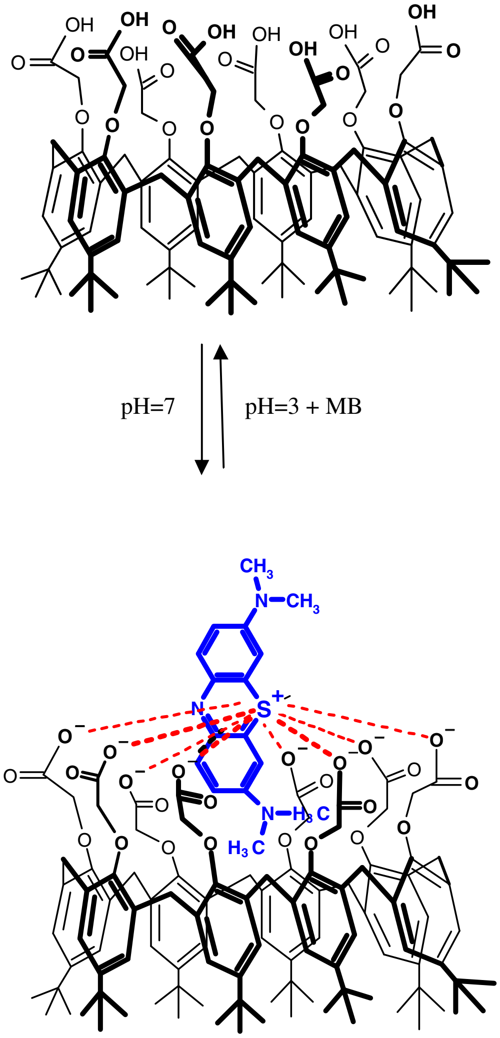

Fig. 3. Proposed complexation model between MB and calix[8]arene octacarboxylic acid.

3.2. Kinetic study

Kinetic study measurements were performed under exactly the same experimental conditions in each time period. In the experiments, variation of MB concentration with time was directly measured in both donor (C_d) and acceptor (C_a) compartments. The corresponding change of concentration in the membrane (C_m) can be obtained from the material balance by considering reduced dimensionless concentrations.

$$R_d = \frac{C_d}{C_{d0}} \quad R_m = \frac{C_m}{C_{d0}} \quad R_a = \frac{C_a}{C_{d0}} \tag{1}$$

According to Eq. (1), the material balance with respect to reduced dimensionless concentrations can be written as $R_d + R_m + R_a = 1$.

The kinetic behavior of the consecutive irreversible first-order reactions from the above given expressions are described at the following relation:

$$C_d \xrightarrow{k_1} C_m \xrightarrow{k_2} C_a \tag{2}$$

where k_1 and k_2 are the apparent membrane entrance and exit rate constants, respectively. The derived equations of kinetic procedure for consecutive reaction systems were previously described in detail [23,24]. The kinetic scheme can be described by considering the reduced concentrations as follows:

$$\frac{dR_d}{dt} = -k_1\,R_d \equiv J_d \tag{3}$$

$$\frac{dR_m}{dt} = k_1\,R_d - k_2\,R_m \tag{4}$$

$$\frac{dR_a}{dt} = k_2\,R_m = J_a \tag{5}$$

where J represents the flux. Taking integral of Eqs. ((3)–(5)) and assuming that $k_1 \neq k_2$ leads to the differential equation forms given as follows:

$$R_d = \exp\,(-k_1\,t) \tag{6}$$

$$R_m = \frac{k_1}{k_2 - k_1}\,[\exp\,(-k_1\,t) - \exp\,(-k_2\,t)] \tag{7}$$

$$R_a = 1 - \frac{k_1}{k_2 - k_1}\,[k_2\,\exp\,(-k_1\,t) - k_1\,exp\,(-k_2\,t)] \tag{8}$$

Maximum value of R_m and t_{max} when $dR_m/dt = 0$, can be evaluated as:

$$R_m^{max} = \left(\frac{k_1}{k_2}\right)^{-k_2/(k_1-k_2)} \tag{9}$$

$$t_{max} = \left(\frac{1}{k_1 - k_2}\right)\,\ln\frac{k_1}{k_2} \tag{10}$$

First-order time differentiation of Eqs. ((6)–(8)) leads to the following forms:

$$\left.\frac{dR_d}{dt}\right|_{max} = -k_1\left(\frac{k_1}{k_2}\right)^{-k_1/(k_1-k_2)} \equiv J_d^{max} \tag{11}$$

$$\left.\frac{dR_a}{dt}\right|_{max} = k_2\left(\frac{k_1}{k_2}\right)^{-k_2/(k_1-k_2)} \equiv J_a^{max} \tag{12}$$

$$\left.\frac{dR_m}{dt}\right|_{max} = 0 \tag{13}$$

$$-\frac{dR_d}{dt}|_{max} = \frac{dR_a}{dt}|_{max} \tag{14}$$

Steady-state kinetics requires equality in magnitude in the total permeation and exit fluxes of two phases (J_d and J_a, respectively, in min^{-1} units) with opposite signs, during the transport process:

$$-J_d^{max} = +J_a^{max}$$

The time dependency experiments performed for the investigation of the effect of time resulted in increase in the quantity of MB, transported from donor phase into the organic phase as well as those released in the acceptor phase increased with time. A quantitative transport of MB ions took up time more than 8 h. Variation of the reduced concentrations of MB with time in the donor, membrane, and acceptor phases for the carrier are shown in Fig. 4.

3.3. Effect of sodium chloride concentration in the feed phase

The effect of the weight of NaCl on the MB transports in feed phase was investigated and results are shown in Table 1 and Fig. 5. As can be seen in Fig. 5,

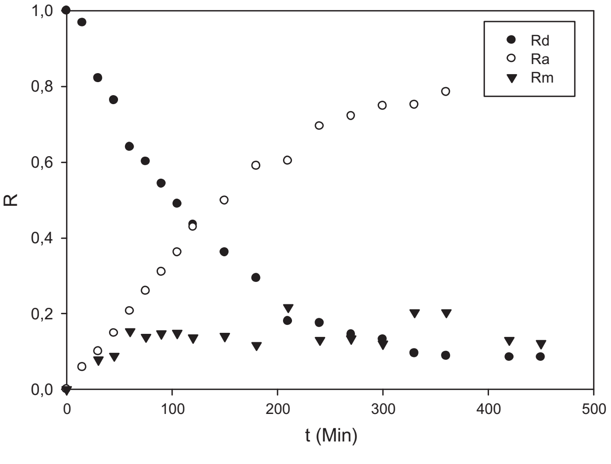

Fig. 4. Time dependence of R_d in donor phase, R_m in membrane phase, and R_a in receiving phase ($t = 25$°C, stirring speed = 150 rpm, COCA derivative 1×10^{-3} mol dm^{-3} and solvent $CHCl_3$).

Table 1
Kinetic parameters of MB for various NaCl weights in the donor phase (Solvent, $CHCl_3$; Temperature, 25℃; Stirring rate. 150 rpm and COCA derivative 1×10^{-3} mol dm^{-3})

NaCl Weight (g)	$k_1(\times 10^{-3})$ (min^{-1})	$k_2(\times 10^{-3})$ (min^{-1})	$k_m(\times 10^{-3})$ (min^{-1})	R_m^{max} (min^{-1})	t_{max} (min^{-1})	J_d^{max} (min^{-1})	J_a^{max}
0.18	6.89	19.1	18.6	0.20	83.50	−3.87	3.87
0.09	6.18	4.76	4.88	0.42	183.80	−1.98	1.98
0.045	6.09	2.37	2.78	0.55	253.70	−1.30	1.30

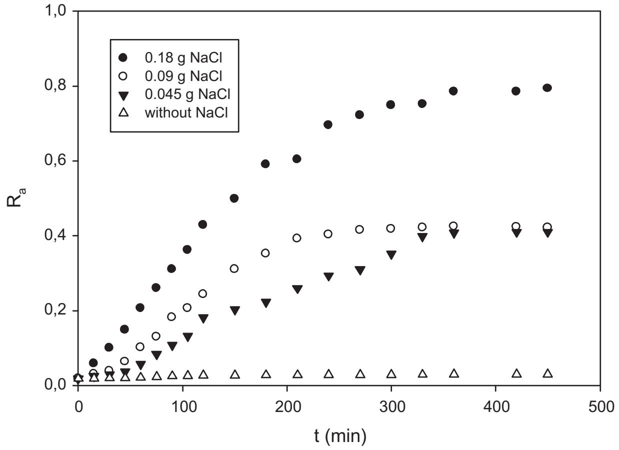

Fig. 5. Effect of NaCl weight on transport of MB through liquid membrane using COCA ($t = 25$℃, COCA derivative 1×10^{-3} mol dm^{-3} and volume of the donor and acceptor phases 10 cm^3).

efficiency of MB transport in the membrane increased by increasing NaCl weight in the feed phase. First, experiments were carried out without NaCl addition to the feed phase. The results obtained showed almost no transport to the organic phase (Fig. 5). This situation reveals the importance of NaCl content within the solution, because NaCl provides an ionic balance between the two phases and affects the transport efficiency [25]. The transport through the membrane is expected to be dependent on the ion balance. Maximum transport occurred when the NaCl amount was about 0.18 g. Because k_1 value is higher and t_{max} value is lower than that of the others. This shows the importance of protons in the feed phase [26]. A weight of 0.09 and 0.045 g of NaCl can be considered as insufficient to allow the dissociation of the complex formed between MB and the ionic liquid at the membrane receiving phase interface and thus the not release of MB in the receiving aqueous phase [27]. And also, both k_1 and k_2 decrease with NaCl weight decrease in the feed phase. Thus, 0.18 g NaCl was selected in the feed phase for the MB transport in the study.

3.4. Stirring rate effect

Hydrodynamic conditions have an important role in mass transfer at the interface between two liquid phases [28]. In order to investigate the effect of hydrodynamics on the MB transport, experiments were carried out with different stirring rates, 50, 100, 150, 200, and 300 rpm at 25℃. Data obtained from experiments are given in Table 2 and Fig. 6. It was found that the transport of MB increases with increasing the stirring speed from 50 to 300 rpm. However, MB transport rate remain stable and not changed after a time interval at stirring speeds 200 and 300 rpm, as seen in Fig. 6. According to this result, 150 rpm was selected

Table 2
Kinetic parameters of MB at different stirring rates (Solvent, $CHCl_3$; Temperature, 25℃ and COCA derivative 1×10^{-3} mol dm^{-3})

Stirring Rate (rpm)	$k_1(\times 10^{-3})$ (min^{-1})	$k_2(\times 10^{-3})$ (min^{-1})	$k_m(\times 10^{-3})$ (min^{-1})	R_m^{max}	t_{max} (min^{-1})	J_d^{max} (min^{-1})	J_a^{max} (min^{-1})
50	2.58	6.27	6.06	0.22	240.64	−1.42	1.42
100	2.64	6.58	7.39	0.21	231.78	−1.43	1.43
150	6.89	19.1	18.6	0.20	83.50	−3.87	3.87
200	8.84	5.25	7.24	0.47	145.14	−2.45	2.45
300	9.34	4.40	6.66	0.51	152.36	−2.25	2.25

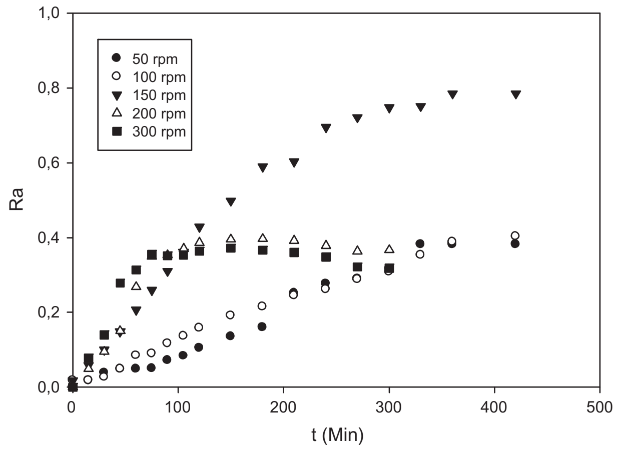

Fig. 6. Stirring effect on transport of MB through liquid membrane using COCA (COCA derivative 1×10^{-3} mol dm^{-3} and $t = 25$℃).

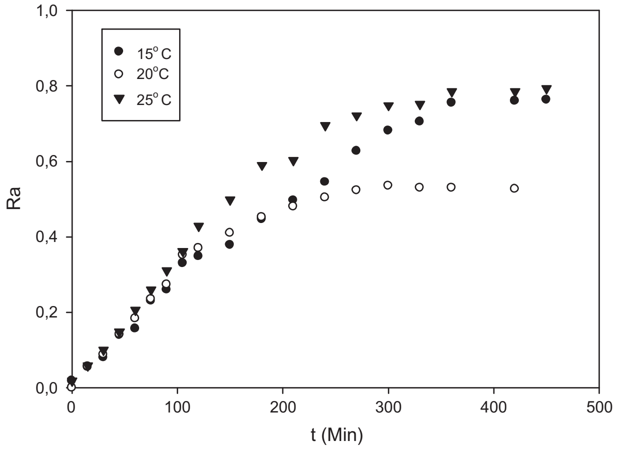

Fig. 7. Effect of the temperature on MB transport through COCA carrier (COCA derivative 1×10^{-3} mol dm^{-3}, stirring speed = 150 rpm, and solvent $CHCl_3$).

as the best stirring speed in this study and maximum permeation of MB was obtained at this speed (Table 2). The higher values of k_1 than k_2 obtained throughout different stirring rates suggest that the MB transport across COCA-based LM was governed by the stirring effect.

3.5. Temperature effect

The effect of temperature on the transport of MB through the BLM was examined at 15, 20, and 25℃. Experimental results are given in Table 3 and Fig. 7. Kinetic parameters in Table 3 show that the value of k_1 was maximum at 25℃ and minimum at 15℃ which indicates that the membrane transport rate increases by increasing temperature. The effect of temperature on the MB transported through the liquid membrane, due to the temperature dependency of the membrane viscosity, is another effect of temperature on the transport process [29]. In this section, results show that k_1 values are larger than k_2 values throughout the temperature range studied and k_1 value increase with temperature. This condition can be also clearly seen in Fig. 7.

3.6. Type of solvent effect

Selection of a right solvent is the prime issue in all kinds of liquid membrane separation processes. Solvent is an important parameter for the stabilization of BLM because it influences the transport efficiency. The solvents are mainly responsible for the lifetime of the liquid membrane and for the solubility of the complex formed [30]. The effect of organic diluents on the rate of transport in membrane was evaluated by using chloroform, dichloromethane, and carbon tetrachloride. Kinetic parameters of COCA in these solvents are reported in Table 4. It is observed that separation of MB is negligible when CCl_4 was used as a solvent for the membrane phase. The results are shown in Fig. 8. Considerable separation occurs in chloroform solution, followed by dichloromethane, resulted in the selection of chloroform as the suitable solvent for the subsequent studies.

Table 3
The kinetic parameters of MB transport through membrane at different temperatures (solvent, $CHCl_3$; stirring rate 150 rpm and COCA derivative 1×10^{-3} mol dm^{-3})

Temp. (℃)	$k_1(\times 10^{-3})$ (min^{-1})	$k_2(\times 10^{-2})$ (min^{-1})	$k_m(\times 10^{-2})$ (min^{-1})	R_m^{max}	t_{max} (min^{-1})	J_d^{max} (min^{-1})	J_a^{max} (min^{-1})
15	6.20	3.45	3.44	0.12	60.64	−4.25	4.25
20	6.21	1.20	1.16	0.25	113.77	−3.06	3.06
25	6.89	1.91	1.86	0.20	83.50	−3.87	3.87

Table 4
Kinetic parameters on MB in different solvents ($t = 25$℃, stirring rate is 150 rpm and COCA derivative 1×10^{-3} mol dm^{-3})

Solvent	$k_1 (\times 10^{-3})$ (min^{-1})	$k_2 (\times 10^{-2})$ (min^{-1})	$k_m (\times 10^{-2})$ (min^{-1})	R_m^{max}	t_{max} (min^{-1})	J_d^{max} (min^{-1})	J_a^{max} (min^{-1})
$CHCl_3$	6.89	1.91	1.86	0.20	83.50	−3.87	3.87
CH_2Cl_2	8.46	1.10	1.15	0.304	103.36	−3.52	3.52
CCl_4	There was no transport of MB						

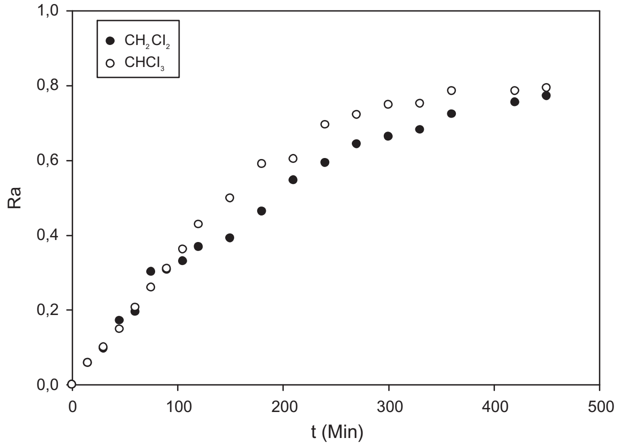

Fig. 8. Type of solvent effect on the MB transport through liquid membrane using COCA (COCA derivative 1×10^{-3} mol dm^{-3}, stirring speed = 150 rpm and $t = 25$℃).

4. Conclusions

There are too many studies about membrane transport done by using calix[4]arene in literature; however, investigation of literature shows that studies done with calix[8]arene are negligible. As a result of this investigation, this study could not be compared with another studies used compounds of calix[8]arene derivatives. However, when compared with membrane studies done by using calix[n]arene compounds, in this study, especially t_{max} time is observed to be too low which means MB component that is required to be removed from environment is removed in a relatively short time and effectively from the environment. The originality of this study lies in the fact that a study done by using MB and calix[8]arene was not found.

In this study, facilitated transport of MB through BLM using calix[8]arene derivative as mobile carrier is studied. In transport experiments, the samples were taken out from the feed phase and receiving phase at scheduled time intervals and analyzed for MB content by using spectrophotometry. The efficiency of the method depends on various parameters such as the effect of NaCl weight in feed phase, type of solvent, stirring speed, and temperature. A kinetic model, based on the kinetic laws of two consecutive irreversible first-order reactions, was used to describe the mass transfer process successfully. By fitting the experimental data, the apparent rate constants (k_1, k_2) are obtained, and the maximum accumulation of MB in the liquid membrane phase (R_m^{max}) and the time (t_{max}) are calculated. Values of kinetic constants explain that the highest maximum flux and the best MB transport is obtained in chloroform environment at 150 rpm stirring speed and at a temperature of 25℃, whereas the lowest maximum flux and the worst MB transport is obtained in CCl_4 environment. In addition, a "blank" experiment was performed in which the membrane contained no carrier. No movement of the MB across the membrane was detected in the blank experiment.

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