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ORIGINAL PAPER

Application of 2-(octylsulphanyl)benzoic acid as Pb^{2+} selective ionophore in hybrid membrane system

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A solution of 2-(octylsulphanyl)benzoic acid in 1,2-dichloroethane was used as a liquid membrane for selective pertraction of Pb^{2+} cations. Transport processes were carried out in a multi-membrane hybrid system (MHS) consisting of two cation-exchange membranes (CEM) and a flowing liquid membrane (FLM) in the following order: CEM | FLM | CEM. The liquid membrane phase was dehydrated continuously using a pervaporation method (PV). The system was capable of transporting Pb^{2+} ions selectively from a multi-cation aqueous solution composed of Na^+, K^+, Ca^{2+}, Mg^{2+}, and Pb^{2+} nitrates. A comparative study of the carrier efficiency under various feed pH conditions was performed. It was found that the carrier exhibited sufficient selectivity and transport efficiency under a broad range of operational conditions, with a maximum transport rate of Pb^{2+} ions attaining the value of $(1.09 \pm 0.03) \times 10^{-10}$ mol cm^{-2} s^{-1} and the selectivity coefficient of up to 40.

Keywords: pertraction, lead, multi-membrane hybrid system, pervaporation, 2-(octylsulphanyl)benzoic acid

Introduction

The liquid membrane (LM) technique, when applied in its practical form, i.e. the multi-membrane hybrid system (MHS), is regarded as one of the most promising methods of aqueous feeds treatment (Kislik, 2010; Oberta et al., 2010). It has recently been demonstrated that the MHS system can exhibit improved properties in comparison with conventional liquid membranes (Kislik, 2010). In general, the application of cation-exchange membranes (CEM) in combination with a liquid membrane, as presented in Fig. 1, results in the pre-concentration of cations in the vicinity of a feed polymer and liquid membrane interface (Szczepańska, 2010), and prevents carrier elution from the liquid membrane solution. The process is based on effective cation-exchange sorption mediated by CEM in contact with an aqueous solution. However, the cation-exchange pre-concentration is usually not selective (Oberta et al., 2010) and the subsequent separation of particular cations occurs in the system as a result of the specific properties of the carrier dissolved in the liquid membrane solvent. The selective cation carriers commonly applied are strong organic acids (e.g. with a phosphate group) with alkyl chains providing good solubility in hydrophobic solvents. Conversely, carboxylic acids are not commonly used because of their relatively low acidity. However, the introduction of an electronegative atom, such as sulphur, into the vicinity of a carboxylic group may result in an increase in the acid dissociation constant (Pasto & Kent, 1965) and the overall liquid membrane transport capacity. Some of the compounds listed above have already been examined as the extractants or carriers of various cations, mainly Ag^+ (Barnes et al., 1971; Ford et al., 1972; Pettit & Sherrington, 1968; Saito et al., 1998; Siswanta et al., 1996), Cu^{2+} (Geary & Malcolm, 1970; Gholivand & Khorsandipoor, 2000), as

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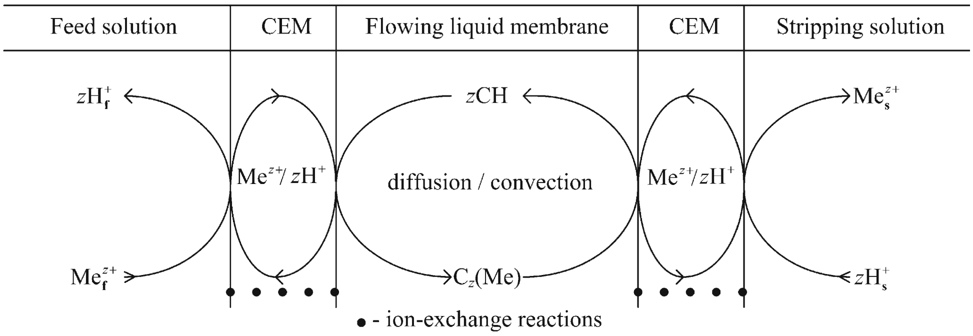

Fig. 1. Scheme of cations' counter-transport occurring in studied hybrid membrane system.

well as many others (Baba & Inoue, 1984; Bramlett et al., 2004; Doh et al., 1995; Irving & Fernelius, 1956; Stypinski-Mis & Anderegg, 2000) The complexation ability of these acids is associated with the presence of sulphur atoms, which can create stable but weak bonds with some cations (Irving & Fernelius, 1956).

To the best of the authors' knowledge, the transport properties of 2-(octylsulphanyl)benzoic acid (OSBA) as applied to a multi-membrane hybrid system are examined and described in this paper for the first time. The ionophore selectivity towards Pb^{2+} ions was tested with the model feed solution composed also of the competing Na^+, K^+, Mg^{2+}, and Ca^{2+} metal ions. The competing cations were chosen as the representatives of common mono- and bivalent cations present in the environment. In addition, the calculated values of the output fluxes and selectivity coefficients were compared with the results recently reported on various carriers and cations by other authors. The aim of the work was to prove that there was no need to use very sophisticated and expensive carriers to obtain reasonable ionic fluxes and selectivity.

Experimental

Lead, potassium, sodium, magnesium, and calcium nitrates, sodium and potassium hydroxides, as well as 65 % nitric acid (all of reagent grade, POCh, Gliwice, Poland) were used for preparation of the aqueous solutions. Extra pure 1,2-dichloroethane (Riedel-de Haën, Germany) was used as the liquid membrane solvent. All the chemicals were used as received, without further purification.

2-(octylsulphanyl)benzoic acid (OSBA) was synthesised according to the following procedure: a mixture of 30.8 g (0.2 mol) of thiosalicylic acid, 23.6 g (0.42 mol) potassium hydroxide, and 38.6 g (0.2 mol) 1-bromooctane (all of reagent grade, POCh, Gliwice, Poland) was refluxed in 500 cm^3 of absolute ethanol under nitrogen atmosphere for more than 5 h. The mixture was then cooled to room temperature, diluted with 500 cm^3 of water and acidified with hydrochloric acid. The white precipitate so formed was filtered, washed first with cold ethanol and several times with water, and air-dried. After crystallisation from aqueous ethanol, 39.6 g of the desired product (Fig. 2, 74.3 % yield) was obtained.

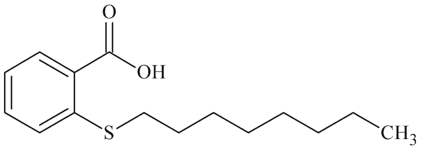

Fig. 2. The structure of 2-(octylsulphanyl)benzoic acid (OSBA).

The dissociation constant of the carrier (K_a) was determined using a titration method. A known portion of OSBA was dissolved in a 1 : 1 water–dioxane mixture (dioxane of reagent grade, POCh, Gliwice, Poland) with the ionic strength I maintained by the addition of potassium nitrate ($I = 0.1$ mol dm^{-3}). A 30 cm^3 sample of the solution was potentiometrically titrated with potassium hydroxide (8.19×10^{-3} mol dm^{-3}). The pK_a value was estimated as equal to the pH value in the middle point of the titration curve, i.e. at the mid-point between the beginning of the curve and the end-point of titration. The procedure of determination was repeated and the pK_a value was calculated as an arithmetic mean of three measurements.

All transport experiments were performed in the multi-membrane hybrid system (MHS) constructed as presented in Fig. 3. Two circular cation-exchange membranes (Nafion-117, Du Pont de Nemours, USA, each 28.26 cm^2, 0.20 mm thickness, ion-exchange capacity equal to 0.997 mol per kg of dry membrane in acidic form) were clamped in a triple-compartment cell containing the feed (f), flowing liquid membrane (FLM), and the stripping solution (s), respectively. In addition, two circular-shaped Nafion-117 membranes with a total area of 64.31 cm^2 were used in the pervaporation module for continuous liquid membrane dehydration. The Nafion-117 membranes were used in the PV module because of their high mechanical and chemical resistance as well as their good hydrophilic properties (Kujawski et al., 1991). The feed (Pb^{2+}, Ca^{2+}, Mg^{2+}, K^+, Na^+ nitrates, all 0.01 mol dm^{-3} in

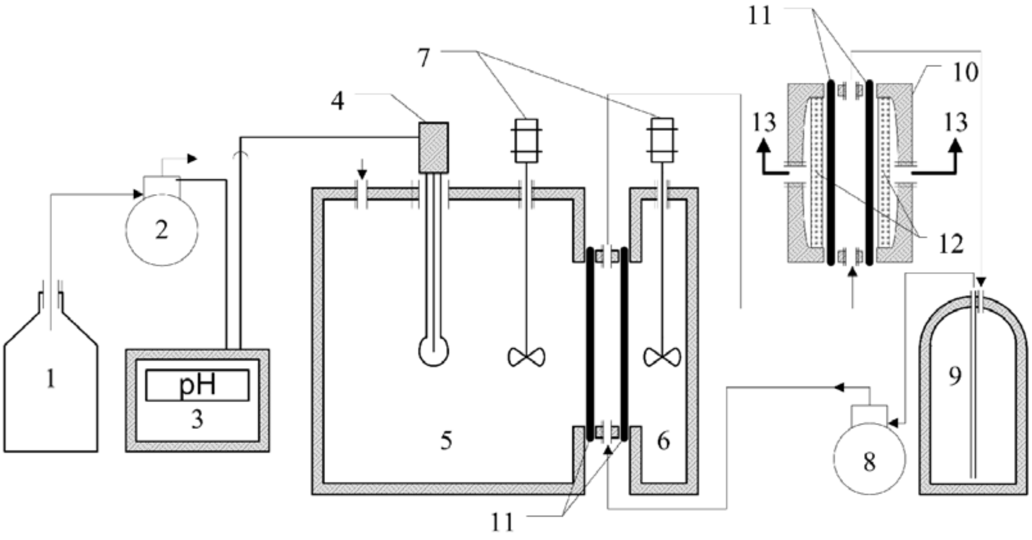

Fig. 3. Scheme of the multi-membrane hybrid system: sodium hydroxide reservoir (1), dosing pump (2), pH controller (3), combination electrode (4), feed solution (5), stripping solution (6), stirrers (7), piston pump (8), liquid membrane reservoir (9), pervaporation unit (10), cation-exchange membranes (11), stainless steel porous support (12), vacuum system (13).

double-distilled water, 500 cm^3) and the stripping solution (HNO_3 1 mol dm^{-3} in double-distilled water, 60 cm^3) were mechanically stirred (100 min^{-1}, distance from CEMs – 5 cm in feed, 0.5 cm in stripping solution) in order to homogenise the bulk solutions as well as to minimise the thickness of the diffusion layers adjacent to CEMs. The feed pH was measured in the course of the process using a combination of a glass electrode (HI 1131, Hanna Instruments, France) and a pH controller (W-252-pH-NL, Walchem, USA). In several experiments, the feed pH was maintained constant by a pH control system coupled with an electromagnetic piston pump (A752-95T, Milton Roy, USA) dosing sodium hydroxide solution (0.5 mol dm^{-3}). The liquid membrane (65 cm^3 of OSBA solution in 1,2-dichloroethane) was pumped with a Teflon piston pump (150 cm^3 min^{-1}, OSI, France) in a closed circuit composed of the reservoir, MHS cell, and the pervaporation unit. Prior to each transport experiment, all the CEMs were converted to their acidic form by several immersions in 1 mol dm^{-3} nitric acid and then in water in order to remove free electrolytes. The PV membranes were supported by stainless steel porous plates. The pervaporation module was connected to a glass vacuum system operating at a pressure of 0.5–1 MPa. Water removed from the system was frozen in one of two receivers using solid carbon dioxide as the cooling medium. The amount of permeated water was determined by weighing. The aqueous phases were sampled periodically and the concentrations of the respective cations in the feed and stripping solution were determined by the atomic absorption spectroscopy method (AAS, SpectrAA-20, Varian Inc.).

Transport of cations was represented quantitatively by $Q_{\text{s,Me}} = f(t)$ cumulation curves, i.e. the amount of moles transported through 1 cm^2 of the CEM-stripping solution interface in time t. The stripping rates (output fluxes) $J_{\text{s,Me}}/(\text{mol cm}^{-2}\ \text{s}^{-1})$ were estimated as the slope of the rectilinear fragment of appropriate $Q_{\text{s,Me}}/(\text{mol cm}^{-2})$ vs. t/s curves, corresponding to the pseudo-stationary state of a transport run according to the following equations

$$J_{\text{s,Me}} = \frac{\Delta Q_{\text{s,Me}}}{\Delta t} \tag{1}$$

$$\Delta Q_{\text{s,Me}} = \frac{\Delta[\text{Me}]_{\text{s},t} V_{\text{s}}}{1000 A_{\text{s}}} \tag{2}$$

In Eqs. (1) and (2), $[\text{Me}]_{\text{s},t}/(\text{mol dm}^{-3})$ denotes the concentration of Me^{z+} cation in the stripping phase in time t, $V_{\text{s}}/(\text{cm}^3)$ is the volume of the stripping solution and $A_{\text{s}}/(\text{cm}^2)$ is the area of the polymer membrane-stripping phase interface. The $J_{\text{s,Me}}$ values and their standard deviations were calculated using the least squares method. The total metal flux $J_{\text{s},\Sigma\text{Me}}/(\text{mol cm}^{-2}\ \text{s}^{-1})$ was calculated as the sum of all particular stripping fluxes – Eq. (3), and the fractional fluxes $N_{\text{s,Me}}/\%$ were calculated according to Eq. (4).

$$J_{\text{s},\Sigma\text{Me}} = \Sigma J_{\text{s,Me}} \tag{3}$$

$$N_{\text{s,Me}} = \frac{100 J_{\text{s,Me}}}{J_{\text{s},\Sigma\text{Me}}} \tag{4}$$

In order to evaluate the improvement in transport resulting from variation of the carrier concentration or the feed pH, the facilitation factors *FF* were calculated – Eq. (5).

$$FF = \frac{J_{\text{s},\Sigma\text{Me}}}{J^{\text{blank}}_{\text{s},\Sigma\text{Me}}} \tag{5}$$

In the above equation, $J_{\mathrm{s},\Sigma\mathrm{Me}}^{\mathrm{blank}}$/(mol cm^{-2} s^{-1}) is the overall metal flux observed in the blank experiment, i.e. without carrier in FLM and with non-constant feed pH. To evaluate the separation ability of the system studied, the time-independent selectivity coefficients were calculated as ratios of the pseudo-stationary stripping rates of Pb^{2+} and the other respective cations, as given in Eq. (6).

$$\beta_{\mathrm{Me}}^{\mathrm{Pb}} = \frac{J_{\mathrm{s,Pb}}}{\sum J_{\mathrm{s,Me}\neq\mathrm{Pb}}} \tag{6}$$

Results and discussion

In a general assumption, the efficiency of the pertraction process is usually highly dependent on its mechanism. Two significant steps of the overall transport across the liquid membrane phase involved can be recognised. The first step is the cation-exchange reaction occurring on the feed–FLM interface which leads to the formation of a hydrophobic complex which is able to penetrate the non-aqueous medium. The opposite reaction occurs on the second interface where the transported cations are released into the stripping CEM due to the reverse cation-exchange reaction. The second key step is diffusion through the bulk volume of the membrane. The influence of the diffusion process can, however, be minimised by vigorous stirring or efficient pumping of the membrane solution in order to minimise the thickness of the diffusion layers adjacent to CEMs in the case of an agitated bulk liquid membrane or flowing liquid membrane, respectively. Nevertheless, it is more difficult to overcome the transport limitations resulting from the rate of processes occurring at the liquid membrane interfaces. For this purpose, the reaction mechanism should be determined, i.e. whether the co-transport or counter-transport constitutes the pertraction of cations in the liquid membrane. As described previously (Oberta et al., 2010), the ionisable carrier operates according to a counter-transport mechanism and the process is limited by the reactions occurring at the CEM–FLM phase boundaries. Considering the pK_{a} value of OSBA calculated as equal to 4.39 ± 0.02, the overall transport process mediated by this reagent is regarded as being strongly influenced by the pH in the boundary layer where the complexation process occurs. As described earlier, at the beginning of every experiment, the CEMs were always in their acidic form, and thus, at the zero time of the transport run, the FLM was contacted from both sides with the Nafion membrane polyelectrolyte material of low pH. Thus, it was concluded that the pH of the feed CEM–FLM phase boundary is substantially lower than the value measured in the bulk volume of the feed. It was observed that in the course of the transport the feed pH decreased from ≈ 5.0 to ≈ 2.3 within the first hour of a transport run as a result of the ion-exchange reactions of the CEM membrane; the lower value should be taken into consideration when analysing the processes running under casual pH conditions (without pH adjustment). The typical cumulation curves calculated against the results of the experiments running under casual and constant pH conditions are presented in Figs. 4 and 5, respectively.

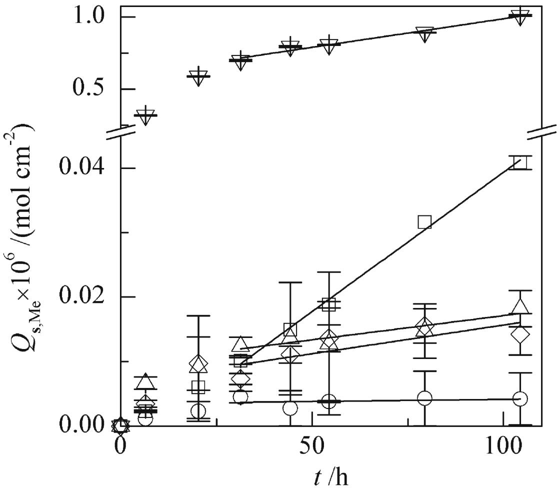

Fig. 4. The cations' cumulation in the experiment performed under casual pH conditions ([OSBA] = 0.15 mol dm^{-3}). The feed pH varied from 4.80 down to 2.84. Na^{+}(△), K^{+} (□), Mg^{2+} (○), Ca^{2+} (◇), Pb^{2+} (▽).

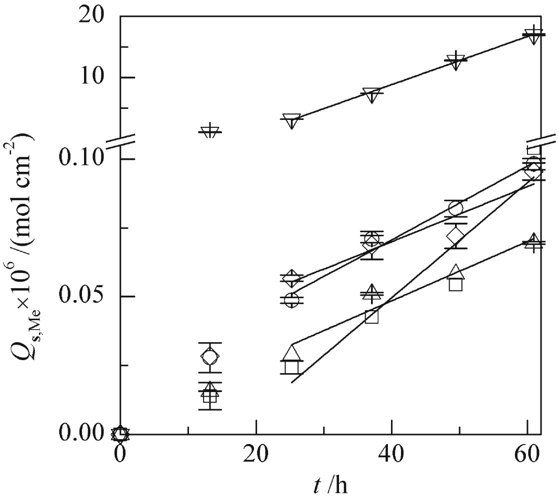

Fig. 5. The cations' cumulation in the experiment performed under constant pH conditions. The constant feed pH was equal to 5.00 ± 0.02 ([OSBA] = 0.15 mol dm^{-3}). Na^{+} (△), K^{+} (□), Mg^{2+} (○), Ca^{2+} (◇), Pb^{2+} (▽).

The curves corresponding to the experiments performed at the constant feed pH exhibit higher maximum $Q_{\mathrm{s,Me}}$ values than the curves observed when the casual conditions were applied. The output fluxes $J_{\mathrm{s,Me}}$ and selectivity coefficients $\beta_{\mathrm{Me}}^{\mathrm{Pb}}$ calculated from the results of experiments carried out under various conditions are summarised in Tables 1 and 2. The re-

Table 1. Results of series of experiments performed with various carrier concentrations

Parameter	Carrier concentration/(mol dm^{-3})			
	0 (blank)	0.05	0.1	0.15
$J_{\mathrm{s,\Sigma Me}}$/(mol cm^{-2} s^{-1})	(0.24 ± 0.01) × 10^{-12}	(0.29 ± 0.1) × 10^{-12}	(0.48 ± 0.01) × 10^{-12}	(1.1 ± 0.1) × 10^{-12}
FF	1	1.2	2	5.6
$J_{\mathrm{s,Pb}}$/(mol cm^{-2} s^{-1})	(0.09 ± 0.02) × 10^{-12}	(0.275 ± 0.05) × 10^{-12}	(0.45 ±0.03) × 10^{-12}	(0.9 ± 0.1) × 10^{-12}
$J_{\mathrm{s,K}}$/(mol cm^{-2} s^{-1})	(0.017 ± 0.003) × 10^{-12}	(0.02 ± 0.01) × 10^{-12}	(0.04 ± 0.01) × 10^{-12}	(0.115 ± 0.05) × 10^{-12}
$J_{\mathrm{s,Na}}$/(mol cm^{-2} s^{-1})	(0.024 ± 0.003) × 10^{-12}	–^{a}	(0.02 ± 0.01) × 10^{-12}	(0.02 ± 0.01) × 10^{-12}
$J_{\mathrm{s,Ca}}$/(mol cm^{-2} s^{-1})	(0.055 ± 0.005) × 10^{-12}	–	–	(0.02 ± 0.01) × 10^{-12}
$J_{\mathrm{s,Mg}}$/(mol cm^{-2} s^{-1})	(0.054 ± 0.005) × 10^{-12}	–	–	–
$N_{\mathrm{s,Pb}}$/%	38.5	93.6	86.8	85.7
$N_{\mathrm{s,K}}$/%	7.3	6.4	8.4	10.3
$N_{\mathrm{s,Na}}$/%	10.0	0	4.7	1.8
$N_{\mathrm{s,Ca}}$/%	22.5	0	0	1.9
$N_{\mathrm{s,Mg}}$/%	21.7	0	0	0
$\beta^{\mathrm{Pb}}_{\mathrm{\Sigma Me}}$	0.625	13.8	6.43	6.07
$J_{\mathrm{H_2O}}$/(g cm^{-2} h^{-1})	(34 ± 1) × 10^{-4}	(40.4 ± 0.3) × 10^{-4}	(40.4 ± 0.6) × 10^{-4}	(17.8 ± 0.1) × 10^{-4}

a) Only trace values with no significant trend found.

Table 2. Results of series of experiments performed with various pH values of the feeding phase; carrier concentration in membrane phase was always equal to 0.15 mol dm^{-3}

Parameter	pH of the feeding phase		
	3.2	4.0	5.0
$J_{\mathrm{s,\Sigma Me}}$/(mol cm^{-2} s^{-1})	(13 ± 1) × 10^{-12}	(52 ± 4) × 10^{-12}	(111 ± 3) × 10^{-12}
FF	57	215	460
$J_{\mathrm{s,Pb}}$/(mol cm^{-2} s^{-1})	(13 ± 1) × 10^{-12}	(51 ± 4) × 10^{-12}	(109 ± 3) × 10^{-12}
$J_{\mathrm{s,K}}$/(mol cm^{-2} s^{-1})	(0.11 ± 0.01) × 10^{-12}	(0.5 ± 0.1) × 10^{-12}	(0.6 ± 0.1) × 10^{-12}
$J_{\mathrm{s,Na}}$/(mol cm^{-2} s^{-1})	–^{a}	(0.05 ± 0.01) × 10^{-12}	(0.3 ± 0.1) × 10^{-12}
$J_{\mathrm{s,Ca}}$/(mol cm^{-2} s^{-1})	(0.10 ± 0.04) × 10^{-12}	(0.06 ±0.01)×10^{-12}	(0.3 ± 0.1) × 10^{-12}
$J_{\mathrm{s,Mg}}$/(mol cm^{-2} s^{-1})	–	(0.05 ± 0.03) × 10^{-12}	(0.35 ± 0.03) × 10^{-12}
$N_{\mathrm{s,Pb}}$/%	98.5	98.6	98.6
$N_{\mathrm{s,K}}$/%	0.8	1.1	0.5
$N_{\mathrm{s,Na}}$/%	0.0	0.1	0.3
$N_{\mathrm{s,Ca}}$/%	0.7	0.1	0.3
$N_{\mathrm{s,Mg}}$/%	0.0	0.1	0.3
$\beta^{\mathrm{Pb}}_{\mathrm{\Sigma Me}}$	64.3	70.8	70.3
$J_{\mathrm{H_2O}}$/(g cm^{-2} h^{-1})	(75.4 ±0.5) × 10^{-4}	(56.9 ± 0.8) × 10^{-4}	(91.2 ± 0.8) × 10^{-4}

a) Only trace values with no significant trend found.

sults indicate that the MHS with the OSBA carrier exhibits marked selectivity towards Pb^{2+} in comparison with other cations under all the conditions applied in the experiments. Moreover, it was noticed that an increase in the carrier concentration improved the Pb^{2+} flux across the membranes. This observation is in agreement with the theory of the carrier-facilitated transport mechanism. The OSBA application results in the fractional flux of Pb^{2+} reaching ≈ 90 %. Moreover, it was observed that an increase in the carrier concentration in FLM impaired the total system selectivity with $\beta^{\mathrm{Pb}}_{\mathrm{Me}}$ varying from 13.8 to 6.1 in the series of experiments run under casual pH conditions.

The ionic fluxes observed in the system are comparable with those reported previously after the study of the MHS with octylsulphanylacetic acid (OSAA) (Oberta et al., 2010) as the selective Pb^{2+} ion carrier. Moreover, similar values were reported after the investigations on 1,2-dichloroethane (DCE) solutions of polymeric carriers, i.e. poly(ethylene glycols) or the poly(oxyethylene) phosphates for pertraction of Cu^{2+}, Zn^{2+}, Mn^{2+}, Co^{2+}, and Ni^{2+} ions in the MHS system (Wódzki et al., 2001, 2002). Similar results, related to the aqueous hybrid liquid membrane, were reported (Eyal & Kislik, 1999; Kislik & Eyal, 2000) and for the pertraction of Zn^{2+}, Cu^{2+}, and Co^{2+} from model solutions as well as from industrial waste waters. The ionic fluxes were improved in one or two orders of magnitude in comparison with these calculated for OSBA when the commercially available carriers, i.e. mono- and di-(2-ethylhexyl) phosphorous acids (M2EHPA and D2EHPA respectively) were applied (Kislik, 2010). These values were confirmed by Gega et al. (2001) who examined D2EHPA, Cyanex-272, Cyanex-301, and Cyanex-302 for the selective transport of Co^{2+} over Ni^{2+} ions under constant pH conditions. In general, all the compounds referred to exhibited satisfactory selectivity coefficients with maximum values reaching up to 40. This value is comparable with those observed in this study.

With regard to Pb^{2+} ion transports achieved in systems other than MHS, the fluxes should not be compared directly with those presented here, because of the substantial differences in the construction of the pertractor. However, it is possible to compare the selectivity coefficients presented here with the results reported for various ionophores; for example acyclic polyether carboxylic acids (Hiratani et al., 1994; Kim et al., 1999). In comparison with these acids, OSBA exhibits similar or higher $\beta_{\mathrm{Me}}^{\mathrm{Pb}}$ values. Moreover, OSBA selectivity was much higher than lasalocid A, one of the natural metal ligands whose selectivity coefficient towards Pb^{2+} over the other ions investigated only achieved a value of up to 2.37 (Canet et al., 2002). It was concluded that the presence of an atom of sulphur in the vicinity of the carboxylic group may enhance the carrier selectivity because of the high affinity of a weak Lewis base (S) towards weak Lewis acid (Pb^{2+}).

No significant influence of the varied system parameters on the pervaporated water fluxes was found. However, when the system operated under constant pH conditions, the water uptake was slightly higher. This phenomenon probably results from the higher amount of water transported as the solvation shell of ions permeating the CEMs.

Conclusions

To conclude, 2-(octylsulphanyl)benzoic acid (OSBA) can be applied as an ionophore- mediating pertraction in the multi-membrane hybrid system. This compound exhibits satisfactory selectivity towards Pb^{2+} transported from feeds containing cations such as Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}. The selectivity coefficients presented in this study were comparable or higher than the data recently reported by various authors. Irrespective of operational conditions such as the feed pH as well as OSBA concentration in the non-aqueous medium, the carrier exhibits adequate transport properties. The stripping rates are comparable with those reported for ionisable polyethers and some macromolecular carriers but lower than those reported for some commercially available organophosphorous acids, e.g. di-(2-ethylhexyl)phosphorous acid. The stripping rates are highly dependent on the feed pH because of the relatively low dissociation constant of the carrier investigated. Thus, the system appears not to be applicable to the treatment of low pH industrial effluents such as acidic electroplating rinse solutions. However, it can be used as an auxiliary laboratory device for the pre-concentration of Pb^{2+} ions above the detection limit of traditional and instrumental analytical methods. Furthermore, it appears to be applicable to the decontamination of natural water of slightly acidic pH.

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