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Modified Fe_3O_4 colloidal dispersed magnetic particles as carrier in liquid membranes

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In this paper we present the results related to magnetic particles synthesis (obtained by a variant of Massart method, which consists in ferric ions co-precipitation into a potassium hydroxide solution) and their stabilization with SAP 230 (consisting of a mixture of two modified polyisobutene derivatives in mineral base oil). The obtained stabilized magnetic particles were functionalized with a crown ether derivative (aminobenzo-18-crown ether) and used for liquid membranes preparation in dioxan. The colloidal magnetic particles were characterized by FT-IR spectroscopy, thermal analysis and Scanning Electron Microscopy and Na^+ and K^+ from different inorganic salts were separated in order to test and evaluate the liquid membrane performances.

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1. Introduction

In the last 20 years the membrane materials studies are continuously increasing with new polymer types, composite materials and nanosystems or ultra micro dispersed systems. Recognized selectivity of the liquid membranes is insufficient explored due to operating difficulties such as: phases mixing, contact surface, membrane stability. An important step was the preparation of magnetic liquids as membrane phases, but the performances of these materials are limited from base solvent nature and from magnetic particles type [1-3].

The synthesis and investigation of magnetic properties of nanostructured magnetic materials present interest from both fundamental and technological point of view [4]. Nanoparticles have received considerable attention in the past two decades due to the interesting properties related to their size [5]. Ferrofluids represent a special category of smart and membrane nanomaterials, consisting of stable dispersion of magnetic nanoparticles in different liquid carriers [6]. Ferrofluids are widely used in industrial applications, but are also important as a model system for dipolar fluids. In scientific research, magnetite (Fe_3O_4) particles have been investigated extensively, because their synthesis is convenient and well known [7].

Pathmamanoharan et al. [8] published preliminary results on the synthesis and characterization of iron particles stabilized with modified polyisobutene (PIB) and oleic acid in decalin. They found that the size of particles grafted with polyisobutene could be controlled well, whereas this was not possible for oleic-acid-coated particles [9]. K. Butter et al [9] presented an extensive study on iron dispersions, synthesized by thermal decomposition of ironcarbonyl, in which they systematically varied the radius of particles and studied the effect of size on the physical behavior of magnetic fluids in a broad size range. To stabilize the particles they used two different surfactants, i.e., PIB or oleic acid [10, 11].

In this paper we present the results related to magnetic nanoparticles synthesis based on ferric oxides and their stabilization with SAP 230 (consisting of a mixture of two modified polyisobutene derivatives in mineral base oil). The obtained stabilized magnetic particles were functionalized with a crown ether derivative (aminobenzo-18-crown ether) and used for liquid magnetic membranes preparation. The colloidal magnetic particles and synthesis intermediates were characterized by FT-IR spectroscopy, NMR spectrometry and Scanning Electron Microscopy and Na^+ and K^+ from different inorganic salts were separated in order to test and evaluate the liquid membrane performances.

2. Experimental

2.1 Materials

For magnetic particles preparation, Mohr salt ($Fe_2(NH_4)_3 \bullet (NH_4)_2SO_4$) and ferri sulfuric alum salt ($FeSO_4 \bullet (NH_4)_2SO_4$) from Merk were used. Potassium hydroxide (KOH) was purchased from Fluka. As solvents, dioxan, acetone, and deionized water from Merk were used. For liquid membrane test performances, natrium chloride (NaCl), potassium chloride (KCl), potassium perchlorate ($KClO_4$), potassium phenoxide ($C_6H_5O^-K^+$), potassium 1, 3, 5-trinitro phenoxide ($C_6H_2(NO_2)_3O^-K^+$), sodium perchlorate ($NaClO_4$), sodium phenoxide ($C_6H_5O^-Na^+$) and sodium 1, 3, 5-trinitro phenoxide ($C_6H_2(NO_2)_3O^-Na^+$) from Merk were used. In experiments aminobenzo-15-crown ether (Fluka) and cyanuric chloride (Merck) were also used.

2.2. Methods

Colloidal dispersed magnetic particles preparation. Magnetic nanoparticles are obtained by a variant of Massart method [4], which consists in ferric ions co-precipitation into a potassium hydroxide solution. 250 cm^3 of Mohr salt solution 0,1 M and 250 cm^3 of ferri-ammonium sulfuricum (ferri alum) are mixed under stirring. 1,5 L of potassium hydroxide 1M are added in three portions. After 4 hours, the black suspension is separated in magnetic field. The entire quantity of suspension is dialyzed until pH≈9 value is achieved. The magnetic particles are washed with methanol, ethanol and then with acetone. After magnetic separation the particles are covered and engraftment.

The synthesized magnetic particles were stabilized using SAP 230 (consisting of a mixture of two modified polyisobutene derivatives in mineral base oil) with structural formula presented in Fig. 1. The process was performed in dioxan, by mixing a quantity of 5 g of magnetic particles and 2 mL of SAP 230 in 10 mL of solvent.

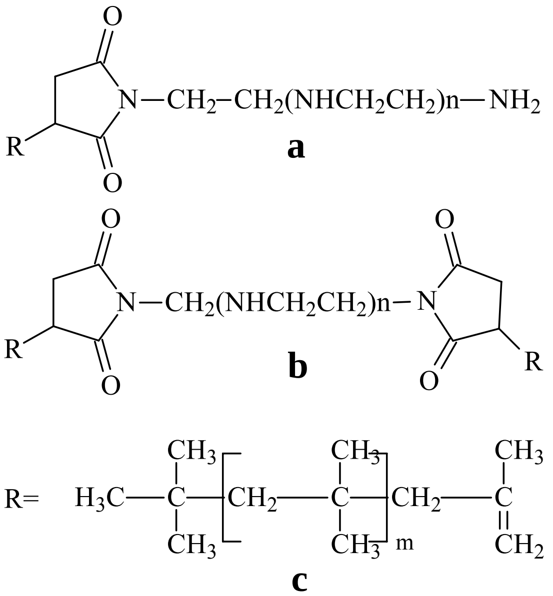


Fig. 1. Structural formula of modified PIB – SAP 230, m=17, n=4.

Amino benzo-18-crown ether functionalization with cyanuric chloride. The functionalization of crown ethers with cyanuric chloride is performed in dioxan, under stirring at 40°C, in dioxan. The reaction product is isolated by solvent evaporation at 80 °C. The reaction is presented in Fig. 2.

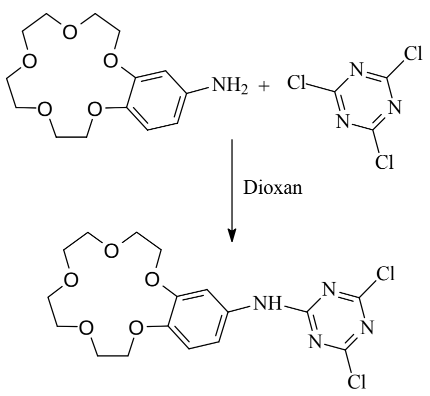


Fig. 2. Functionalization reaction of Amino benzo 18 crown 6 ether functionalization with cyanuric chloride.

Amino benzo-18-crown ether grafting on colloidal magnetic particles. The lighted colored dispersion is reintroduced in the ceramic tank of the mill with 3g cyanuric chloride and is mixed for 3 hours and after this the aminobenzo-18-crown ether and is mixed for another 3 hours. Finally, the brown dispersion is washed with three portions of deionised water.

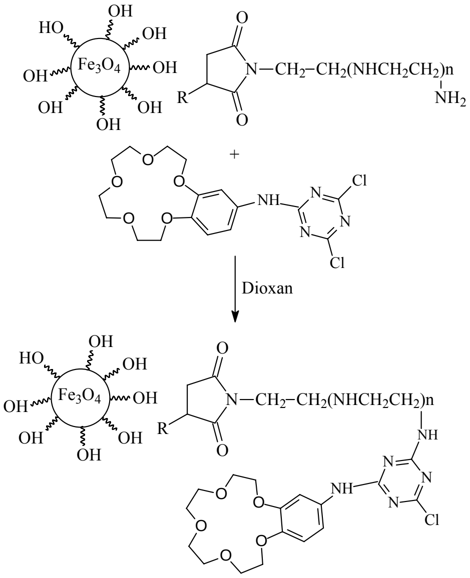
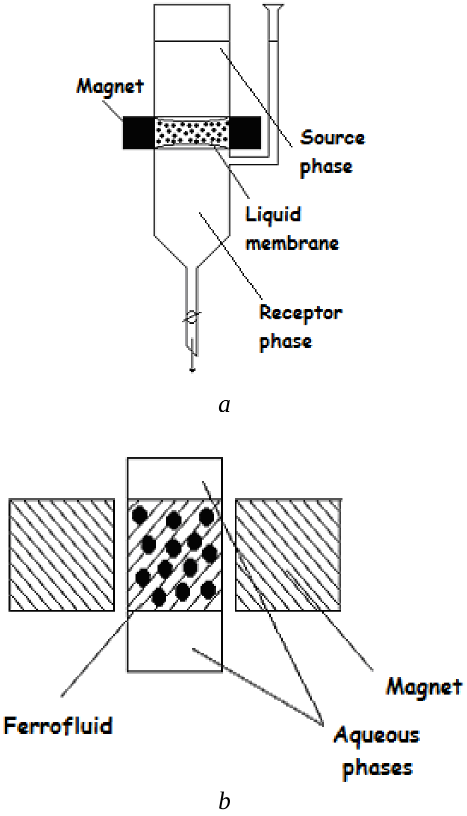


Fig. 3. Reaction scheme for magnetic nanoparticles functionalisation.

The transport of Na^+ and K^+ ions through dioxan-functionalized magnetic particles liquid membrane. Into a liquid membrane system schematically represented in Fig. 1 the following solutions are introduced: a) source phase-potassium or sodium salts 10^{-5}M, pH≈4,8 realized with $CH_3COO^-Li^+$/ CH_3COOH; b) liquid membrane based on functionalized Fe_3O_4 magnetic particles in dioxan and c) receptor phase-alkaline solution, pH=8-10 realized with LiOH 10^{-6}-10^{-4}M. The membrane system is represented in Fig. 4 with illustrated transport mechanism for Na^+. For comparison, a liquid membrane with crown ethers dissolved in ferrophase was synthesized without a covalent interaction between magnetic particles and crown ethers. Na^+ and K^+ were analyzed by flamphotometry using Phlapho 4 Carl Zeiss Jena Photometer. The experiments were performed at $25^{O}C$.



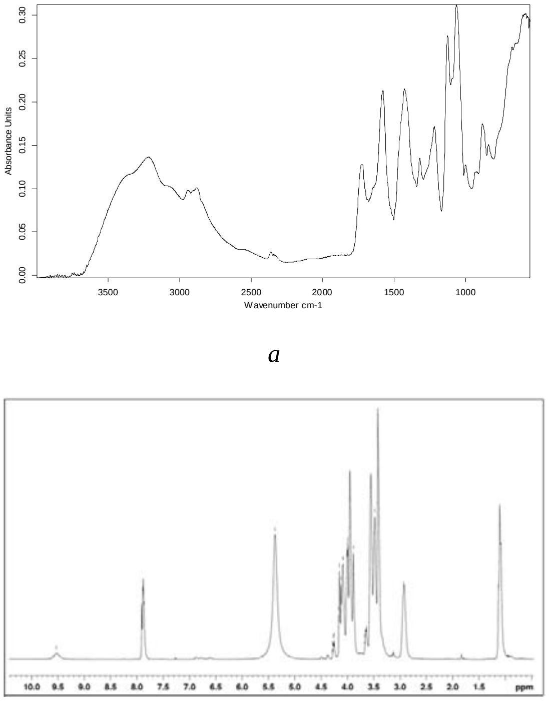
a

b

Fig. 4 Magnetic liquid membrane device: Schematic representation of permeation cell (a); Disperse magnetic membrane detail (b).

3. Results and discussion

In this paper we propose a simple and accessible bonding method between amino-benzo-crown ether and magnetic nanoparticle for magnetic liquid membranes. Chemical coprecipitation was selected as the method to synthesize nanoparticles for this study. This method produces nanoparticles in large quantities (order of grams) in a relatively short amount of time and utilizes inexpensive and readily available chemicals as precursors. These two advantages are important in the fabrication of nanocomposites whose potential applications will require a specimen mass of tens of grams. A sample with filler loading of approximately 5% volume requires a few grams of nanoparticles. Since samples with higher volume fractions were desired, the demand for nanoparticles increased very quickly [12]. The first characterized compound was the intermediate resulted in reaction between crown ether derivative and cyanuric chloride. The main advantage of using cyanuric chloride as spacer is given by the aromatic characteristic of the ring. After the first reaction of a chloride atom at $40^{o}C$, the aromatic ring is deactivated and the formation of dimmers is less probable. The reaction at a second chloride atom must be performed at more then $60^{o}C$. The synthesized compound was characterized by FT-IR spectroscopy (Bruker Tensor 27 with diamond ATR annex) and ^1H-NMR spectrometry (Bruker NMR AM 300, 300 MHz, in $CDCl_3$) and the spectrum are presented in Fig. 5. In FT-IR spectrum the absorption peaks from 880 cm^{-1} and 1650 cm^{-1} are attributed to =C- respectively =N- bonds in the aromatic ring plane. The 1580 cm^{-1} absorption band is attributed to –NH– formation bond after the intermediate synthesis. The absorption band at 1270 cm^{-1} is specific for –O– bond from crown ether molecule. The NMR spectrometry was performed in $CDCl_3$ and the data are: H NMR ($CDCl_3$ – d_6) δ_H: 1.13 (1H, s), 2.93 (1H, s), 7,89 (1H, q, J=4.35) with chemical shift for –NH– bond formation at $\delta_H \approx 2.93$ ppm.



a

b

Fig. 5. FT-IR spectrum (a) and NMR spectrum (b) of amino benzo crown-18-etherfunctionalized with cyanuric chloride.

After the covering of magnetic particles, respectively the functionalization with crown ether derivative the obtained colloidal dispersed magnetic particles (Fe_3O_4-SAP-CE) were characterized by FT-IR spectroscopy (Fig. 6) and SEM microscopy (FESEM Hitachi S 4900) (Fig. 7).

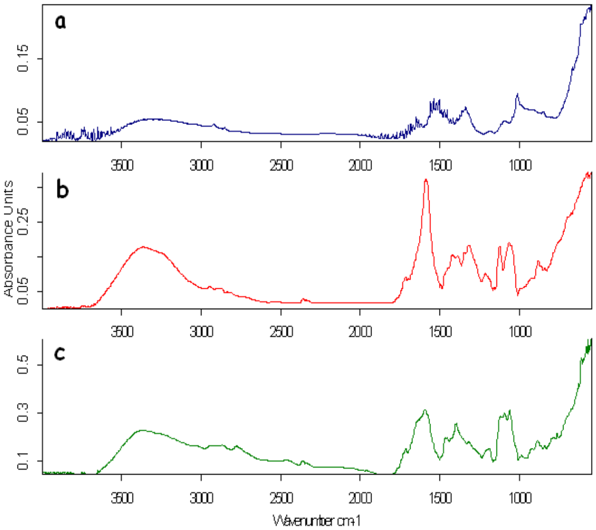


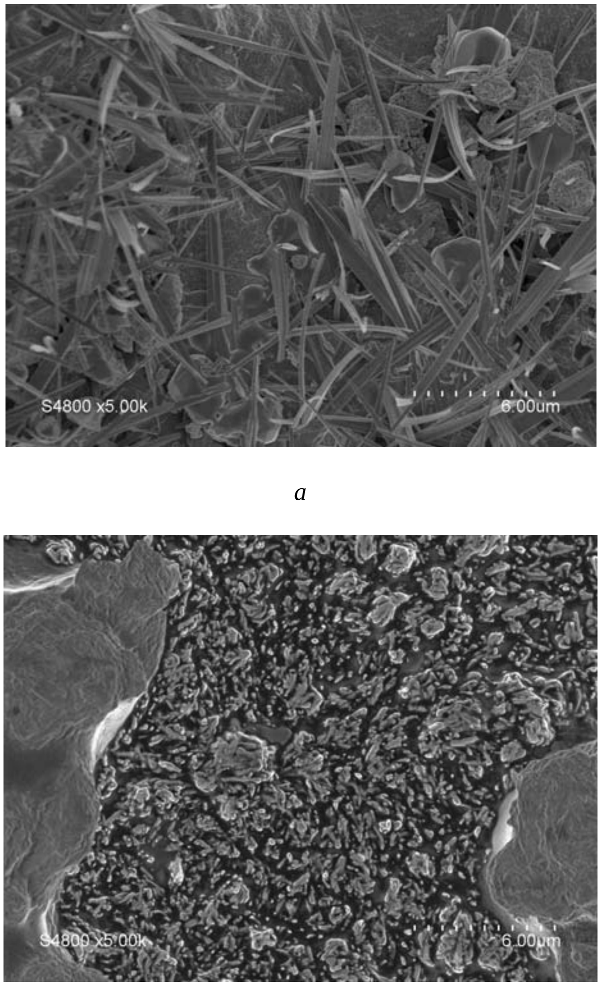
Fig. 6. FT-IR spectrum of magnetite particles (a), magnetite particles covered with SAP (b) and crown ethers functionalized magnetite particles covered with SAP (c).

Absorption characteristic bands for Fe-O bond from Fe_3O_4 are situated in range 375-570 cm^{-1}, but these two bands are shifted higher values respectively 440 cm^{-1} and 600 cm^{-1} (Fig. 3a). After the coating of magnetic particles with SAP specific absorption bands for $–NH_2$ group at 3300-3600 cm^{-1}, C=O at 1650 cm^{-1} and C-C at 720 cm^{-1} can be observed (Fig. 3b). The functionalization reaction is demonstrated by the specific absorption band for –C–NH– at 1568 cm^{-1} shifted with 12 cm^{-1} in comparison with the same group from intermediate crown ether derivative due to the electronic effect of the aliphatic carbon chain.

Magnetic nanoparticles preparation by modified Massart method [2] starting from Mohr salt and alum direct to a system with their characteristics presented in Scheme I. FT-IR spectroscopy indicates that nanoparticles are covered with a hydroxyl coating (3000-3600 cm^{-1}). The thermal analysis indicates the dehydration (mass lost efect TG and endothermic effect DTA at 107 ^oC) and TEM images (x100000) show that nanoparticles are quasi-nano-dispersed with medium dimension about 20 nm.

In comparison with crude magnetic particles aggregated in acicular formations, the covered ones are well dispersed and apparently are not aggregated which is a good proof of their cover.

Magnetic liquid preparation was performed by mixing the chosen solvent (dioxan) with obtained composite magnetic particles (Fe_3O_4-SAP-CE) for four hours in the Retsch colloidal mill. The stabilized magnetic liquid dispersion was placed into the well known liquid membrane system [3], schematically presented in Fig. 5.



a

b

Fig. 7. SEM images of Fe_3O_4 magnetic particles (a) and SAP covered Fe_3O_4 magnetic particles (b).

Into this vertical system source phase was continuously recycled and the receiving phase was maintained under stirring at the top part of the system. For diffusion transport and concentration reasons the source phase and the receiving phase were added in 10:1 volume reports. The data for Na^+ and K^+ ions transport results through liquid membrane are presented in Table 1. Cation transport was coupled with hydronium cation as driving force (Fig. 5). The functionalized Fe_3O_4-SAP-CE magnetic particles used as carriers presents better results for sodium and less transport properties for potassium because the sodium ionic radius is more compatible with the chosen crown ether. On the other hand, the dissolved carriers without a covalent interaction between magnetic particle and crown ether (in similar membrane concentration) present lower results in comparison with composite particles used as carrier (Table 1).

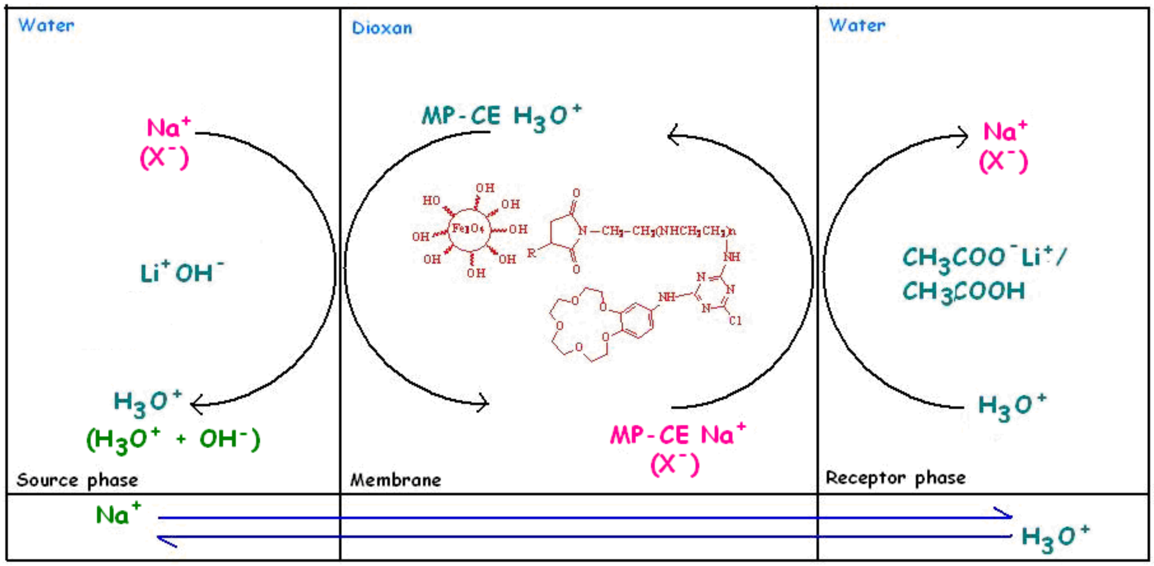


Fig. 8. Representation of a liquid membrane system; PM-CE represent the functionalized magnetic particles, PM-CE Na$^+$, the complex between crown ether functionalized Fe$_3$O$_4$ magnetic particle and sodium ion and X$^-$ the counter ion (chloride, perchlorate, phenoxide or 1, 3, 5-trinitro phenoxide).

Table 1. Na$^+$ and K$^+$ ions transport through liquid membrane.

Source Phase	J (J × 10^6 mol /cm^2 × h)	
pH=12, 10^{-3}M	With crown ether dissolved in ferrophase	With crown ether grafted on nanoparticles
NaCl	2.7	3.2
NaClO$_4$	4.8	4.5
$C_6H_5O^-Na^+$	5.5	6.1
$C_6H_5(NO_2)_3O^-Na^+$	5.8	7.3
KCl	1.0	1.2
KClO$_4$	1.8	2.3
$C_6H_5O^-K^+$	3.6	4.3
$C_6H_5(NO_2)_3O^-K^+$	3.6	4.5

The Brownian transport of particles amplifies the diffusion coefficient with a convective component according to Eq. 1.

$$D^t = D^{Fick} \cdot D^{conv} \tag{1}$$

D^t represents the diffusion coefficient into the liquid membrane, D^{Fick} represents the Fick diffusion coefficient and D^{conv} the contribution of convection. This observation is necessarily in both transport cases (Na$^+$ and K$^+$) and the value is about 21±3% from Fick value.

4. Conclusions

The prepared composite Fe$_3$O$_4$-SAP-CE magnetic particles by reaction between stabilized magnetic particles (using SAP 230) with a crown ether derivative (aminobenzo-15-crown ether), is an interesting carrier for magnetic liquid membranes. The Na$^+$ and K$^+$ transport using prepared magnetic liquid membranes offer the following results:

- Na$^+$ transport is favoured by the crown ether type (aminobenzo-15-crown ether).
- The anion lipophilicity amplify the cation transport in order: $Cl^- < ClO_4^- < C_6H_5O^- < C_6H_5(NO_2)_3O^-$.
- Using crown ethers grafted on magnetic particles presents better results in comparison with dissolved crown ethers used as carriers. The diffusion coefficient enhanced with convective value D^{conv} = 21±3% D^{Fick}.

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