

Gelled Membrane Composed of Dioctyldithiocarbamate Substituted on Poly(Vinylchloride) and Di(2-Ethylhexyl)Dithiophosphoric Acid

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SYNOPSIS

Substitution of chlorine on poly(vinylchloride) (PVC) by dioctyldithiocarbamate (DODTC) groups results in a modified polymer (MP) with a glass transition temperature of between -43 and 84°C , depending on the degree of substitution. Formation of a gelled membrane composed of MP and di(2-ethylhexyl)dithiophosphoric acid (DTPA), as both an ion carrier and a solvent, was demonstrated. The gelled membrane can be formed with the weight ratio between (MP) : (DTPA) as low as 1 : 99 or higher. The membrane is capable of selective separation of metal ions. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Substitution of chlorine on PVC by functional groups, such as thiolate, xantate, dithiophosphate, and dithiocarbamate, was carried out either in aprotic solvents, such as dimethylformamide (DMF), or in water suspension using phase transfer catalyst.¹⁻⁴ The modified polymer can be cast to form a solid membrane and can be used, for example, to separate liquid in pervaporation experiments. Recently,⁵ PVC modified by 2-(2'-butoxyethoxy)ethyl thiolate mixed with zeolite NaA was cast as a membrane and was used in separation of water from ethanol at the azeotropic point. One promising application of such modification was to synthesize a polymeric material, which could form a gel membrane with an appropriate solvent, that could be used also as a selective ion complexing agent (membrane carrier). Separation of ions by PVC gelled membranes has been reported recently.⁶⁻⁸ In those cases, the carriers were dissolved in a mixture of polymer and plasticizer. Another way to prepare a gelled membrane was to use plasticized polymer in which the plasticizer is capable of selectively complexing certain ions. It was found that DTPA, when introduced into supported liquid membranes, can serve

as an excellent carrier for silver, mercury, and other ions.⁸⁻¹⁰ Therefore, DTPA was used as a carrier and solvent for gel membrane by matching it to a modified PVC as a polymer. A report of a gel membrane composed of PVC modified by dioctyldithiocarbamate (DODTC) and DTPA as a solvent and ion carrier is described below.

EXPERIMENTAL

Preparation of DODTC, Sodium Salt

The DODTC material was prepared reacting dioctylamine with carbon disulfide according to the general procedure.¹¹ The $^1\text{H-NMR}$ (80 MHz) of the salt taken in $\text{CD}_3\text{C}(\text{O})\text{CD}_3$ shows the expected integration ratio between the different protons. The methyl group is a triplet centered around 0.8 ppm. The absorption of the protons on the methylene chain is around 1.2 ppm. The methylene group, attached to the nitrogen, shows a quartet centered around 4.1 ppm. The ratio between the above protons is 3 : 12 : 4, respectively. The sulfur content of the salt was found to be 15.2 wt % as compared to 17.26 w/w % S content, calculated according to the molecular formula $\text{C}_{17}\text{H}_{34}\text{NO}_2\text{S}_2\text{Na}$. This difference might be due to the crystal water molecules that remained after drying, as in the case of diethyldithiocarbamate sodium salt, which included 3 molecules of water.

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These water molecules are evident from the ^1H -NMR spectrum.

Displacement of Chlorine on PVC by DODTC

The procedure of displacement of chlorine by thiolate group has been reported previously.^{3,4} The same procedure, with a slight variation, was adopted to the modification of PVC with the dioctyldithiocarbamate group. The modification was carried out as described below.

One mol of PVC (43 grade, Frutarom, Israel) was mixed with 750 cm³ of dried DMF until a clear solution was obtained. To this solution, 0.4 mol of DODTC sodium salt, dissolved in 200 cm³ of DMF, was added. The mixture was stirred while heating at 45°C under a stream of nitrogen. Samples were withdrawn intermittently from the reaction mixture and were precipitated in methanol. The polymer was washed with water to remove the unreacted DODTC and the remaining sodium salt, was washed again with methanol, and was dried under vacuum at room temperature.

The sulfur and chlorine content of each sample was measured by elemental sulfur and chlorine analysis¹²; DSC analysis was performed on a Mettler TA3000 System. These analyses are summarized in Table I.

NMR spectra were recorded at 80 or 400 MHz on a Bruker AC200 or on a Bruker AMX400 spectrometer, using CDCl_3 as a solvent.

A Nicolet 510 FTIR spectrometer was used to record all infrared spectra of the gels and the freshly prepared DTPA in the range of 4000–200 cm⁻¹, using NaCl cells.

Table I The Relation Between the Reaction Time and the Following Characteristics of MP: Sulfur W/W Content (%S), Chlorine W/W Content (%Cl), Glass Transition Temperature (T_g)

Sample	Time (min)	%S	%Cl	T_g (°C)
0	0	0.00	56.80	86
1	90	4.85	42.45	65
2	180	5.52	38.75	51
3	270	6.12	36.64	46
4	345	7.06	34.72	44
5	2 days	8.59	28.18	19
Completed substitution		18.65	0.00	-43 ^a

^a Calculated value.

Membrane Preparation and Permeability Measurements

Di(2-ethylhexyl)dithiophosphoric acid (DTPA) was synthesized and purified as described elsewhere.¹³ The mixtures of PVC, modified by DODTC (modified polymer, MP) and DTPA, were dissolved in tetrahydrofuran (THF, Bio-Lab. Ltd.), resulting in transparent solutions (impregnating liquids). Celgard 2400 (Celanese Plastics Co.), a poly(propylene) film of 25 μm thickness, a porosity of about 35%, and an effective pore size of 0.1 μm was used as a solid support. A known weight of the support was immersed in an open Petri dish containing the impregnating liquid and was kept there for 24–48 h. The impregnated membranes were dried by keeping them in a closed box containing silica gel.

After impregnating and drying, the excess of the gelled MP was mechanically removed from the membranes' surface. The gelled supported liquid membranes (GSLM) were obtained as transparent films of 25 μm thick. The weight gain of the dried GSLM was 50–60%. The contents of MP and DTPA ($[\text{MP}]_m$ and $[\text{DTPA}]_m$) were calculated as ratios between the weight of MP or DTPA and the total weight of the gel in the membrane pores.

In separate experiments, the relaxation of the gels composed of MP and DTPA was investigated. The gels of known weights were placed in a closed box containing silica gel. Periodically, the gels were cleaned by thorough wiping of the gels' surfaces with a filter paper and were weighed.

The permeability measurements were carried out at 20°C and were performed in a membrane cell with receiver and feed chambers of 20 cm³ each. The feed chamber contained a water solution of metal salts. The membrane working area was 5 cm². The solutions in both chambers were stirred by magnetic bars. The metal ions' concentrations in the receiver chamber were analyzed periodically using a Perkin-Elmer Model 5100 PC atomic absorption spectrophotometer. The pH values in the solutions were monitored with a Corning Model 240 pH-meter. The rates of ion transfer through the membrane, J , mol/cm²s, were evaluated from the steady-state slopes of F vs. time plots, where F is the total amount (mol) of metal ion in the receiver chamber at a given time.

RESULTS AND DISCUSSION

Characterization of the Modified Polymer

The theoretical relation between the wt % of sulfur S and chlorine Cl on the substituted polymer can be expressed as follows:

$$[\text{Cl}] + 3.04[\text{S}] = 56.80 \quad (1)$$

The experimental points (Table I) correspond to the theoretical relation well. Thus, we conclude that each DODTC group displaces one chlorine atom from the polymer. Other reactions, such as dehydrochlorination if it exists, are minor.

The progress of the reaction can be followed by measuring the percent of sulfur in the modified polymer as a function of the reaction time. The kinetics of the substitution fits a second order kinetics (carried out to about 70% conversion), which can be described by the following equation:

$$dx/dt = k_2(a_0 - x)(b_0 - x) \quad (2)$$

where

$$k_2 t = A^{-1} \ln \left(\frac{[2x - (a_0 + b_0) - A]}{[2x - (a_0 + b_0) + A]} \right) \quad (3)$$

Here a_0 is the initial concentration of PVC (0.976 M), b_0 is the initial concentration of DODTC sodium salt (0.4605 M), x is the concentration of the substituted PVC, k_2 is the second order rate constant, and $A = [(a_0 + b_0)^2 - 4a_0b_0]^{1/2}$

The plot of eq. (3) is given in Figure 1. The second order rate constant was calculated to be $9.4 \cdot 10^{-5} \text{ M}^{-1} \text{ sec}^{-1}$.

The glass transition temperature of the MP was investigated. Assuming that the modified polymer behaves like a random copolymer, the following relation should hold:

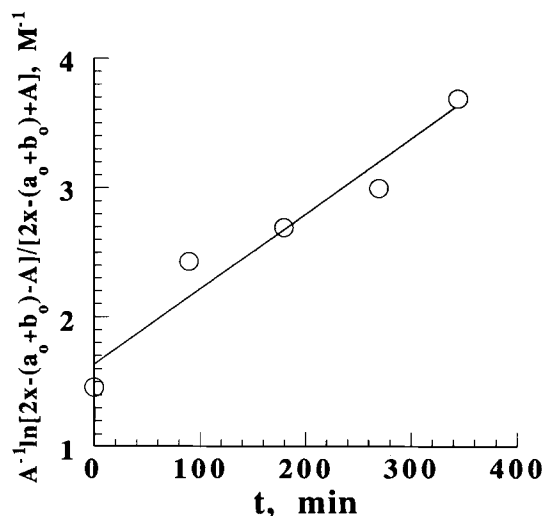


Figure 1 Kinetics of the modification of PVC. See explanations in the text.

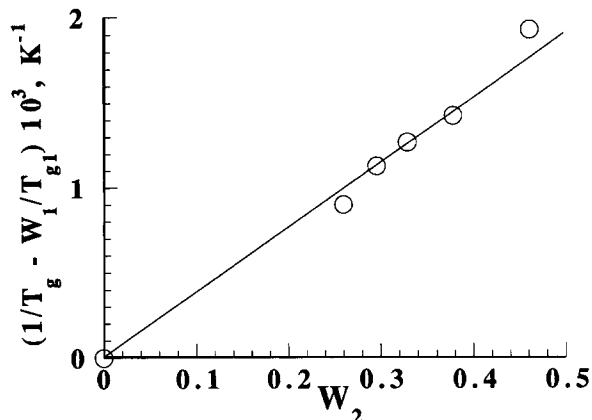


Figure 2 Plot related to eq. (4). See explanations in the text.

$$1/T_g = [(W_1/T_{g1}) + (BW_2/T_{g2})] / (W_1 + BW_2) \quad (4)$$

where T_g , T_{g1} , and T_{g2} are the glass transition temperatures of MP, PVC, and of the fully modified polymer, respectively, W_1 and W_2 are weight fractions of the unmodified and modified parts of the polymer, and constant B is equal to about 1 for the random copolymer.¹⁴

The plot, related to eq. (4), is shown in Figure 2, from which the glass transition temperature of the totally modified polymer was calculated to be about 230°K.

¹NMR (400 MHz) of the last withdrawn sample ($S = 8.59\%$, $\text{Cl} = 28.18\%$) of the modified polymer in CDCl_3 shows the expected spectrum (Fig. 3). The spectrum reveals two broad absorption peaks centered at 4.5 ppm and 2.2 ppm corresponding to $\text{H}-\text{C}-\text{Cl}$ and $\text{H}-\text{C}-\text{H}$, respectively. This absorption belongs to the hydrogen attached to the main chain. The $\text{H}-\text{C}-\text{S}$ absorption can be seen at 1.65 ppm. Four more absorption peaks, which are due to the dioctyl groups attached to the dithiocarbamate group, are also observed in the spectrum. They are as follows: a triplet due to the methyl group centered at 0.89 ppm, a multiplet centered around 1.31 ppm due to the methylene chain, and two peaks due to the methylene groups attached to the nitrogen, centered around 3.6 and 3.9 ppm. The existence of two methylene absorption peaks is an indication that the free rotation at the $\text{C}-\text{N}$ bond is restricted. The ratios between the peaks of the different proton-containing groups on the octyl chain are: 3.0 : 11.0 : 2.1, which is in agreement with the calculated ratio of 3.0 : 12.0 : 2.0. The ratio between the $\text{H}-\text{C}-\text{Cl}$ protons and the protons of the methyl

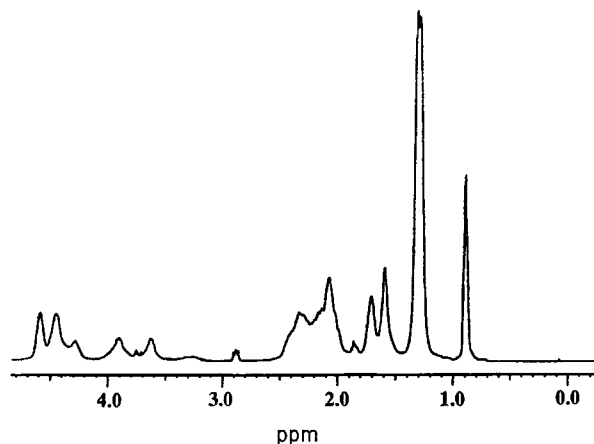


Figure 3 $^1\text{H-NMR}$ spectrum of the last withdrawn sample of MP.

group on the octyl chain centered at 0.89 ppm is 0.86. Using the wt % of S and Cl, obtained by elemental analysis, the above ratio is calculated to be 0.98, which is in agreement with the ratio obtained by NMR analysis.

Properties of Gelled Supported Liquid Membranes (GSLMs)

The freshly prepared GSLMs, containing more than 7 w/w % of MP, are characterized by high permeability towards metal ions and protons. The transfer rate of a "virgin" GSLM contained 10 w/w % of MP towards silver (J_{Ag}) and protons was measured to be 2×10^{-10} mol/cm²s. In these experiments, the feed and receiver stripping phases consisted of 3.6 mM AgNO₃ in deionized water and 0.8 M thiourea in 1M H₂SO₄, respectively, in accordance with the optimal conditions described recently.¹⁰ In separate experiments, the weight of the freshly prepared GSLMs before and after their contact with aqueous solutions was measured. It was found that the membranes lost about 20% of their weight after contact with water, due to the losses of THF remaining in the membranes after their preparation. The loss of THF can increase the microviscosity of the gel, causing the profound decrease of permeability. Thus, one can suggest that the membranes undergo profound changes in morphology during the time. This is supported by the experiments with the gels composed of MP and DTPA (Fig. 4). It can be seen that the specific amount of DTPA removed from the gels ($\Delta W/W_0$) is dependent on time and on the initial gel composition. After 3 days, the gels reached equilibria. This fact can be explained by the time-dependent specific interactions of DTPA with MP.

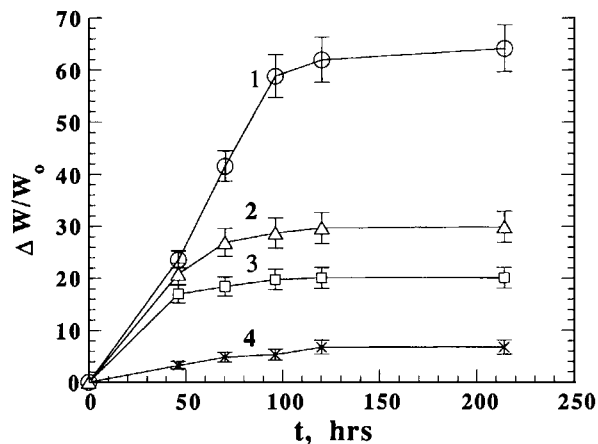


Figure 4 Kinetics of the relative change of weights ($\Delta W/W_0$) of the gels. The gels were composed of DTPA and MP of the following concentrations: 1–4.5 w/w %; 2–10 w/w %; 3–30 w/w %; 4–50 w/w %.

Figure 5 represents the infrared spectra of pure DTPA and different compositions of gels recorded 2 days after the preparation. One can see that the band at 670 cm^{-1} , which corresponds to the P=S antisymmetric stretching¹³ in pure DTPA liquid,

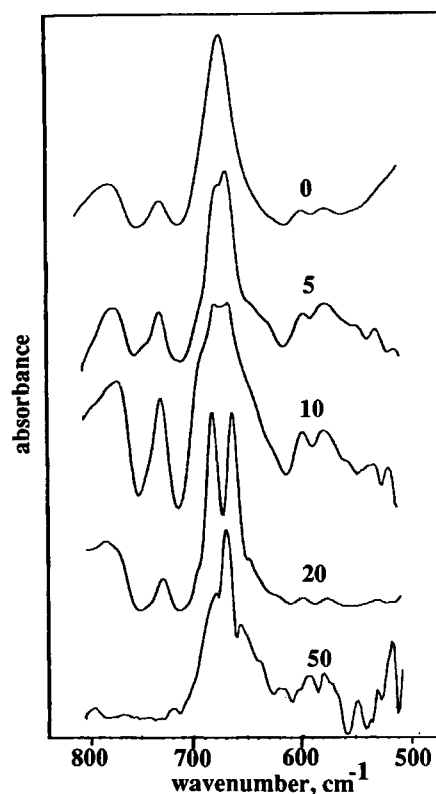


Figure 5 FTIR spectra of the gels composed of MP and DTPA. Wt % of MP in each sample is indicated.

splits in the spectra of the gels. The splitting is developed from the onset of the gel preparation and gradually becomes constant. Also, the splitting is more pronounced at a higher concentration of MP in the gel. The phenomenon of the dithiophosphoryl group interaction with the electron donor groups, such as C=S or CH—Cl, is well documented.¹⁵ Rearrangements of the hydrogen bonds between chlorine or sulfur atoms of MP and protons of DTPA lead to the change of P=S stretching vibrations and to the observed splitting in the IR spectra. A similar effect was shown to occur when DTPA was dissolved in chlorinated hydrocarbons. The above results give evidence of structure relaxation of the gel. According to the experiments shown in Figure 4, the total equilibrium was reached 3 days after the gel preparation. Thus, we investigated the transport properties of GSLMs kept in a closed box after this period had passed.

The results of typical kinetic experiments of silver transport are shown in Figure 6. The “equilibrated” GSLMs contained 7.1 (curve 1) and 20.7 (curve 2) wt % of MP. The silver transfer rates J_{Ag} were evaluated from the slopes of the stationary state fluxes, whereas the effective diffusion coefficients (D_e) were found using the following equation⁸:

$$D_e = l^2/6t_l \quad (5)$$

where l is the membrane thickness, and t_l is the lag time.

In the experiments shown in Figure 6, the J_{Ag} and D_e values were found to be 3.6×10^{-11} and 1.5×10^{-11} mol/cm²s and 4.8×10^{-10} and 1.4×10^{-10} cm²/s for the GSLMs that contained 7.1 and 20.7

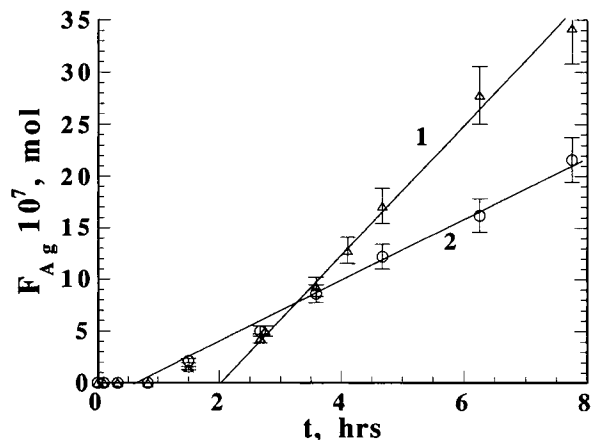


Figure 6 Kinetics of silver transport through GSLMs composed of DTPA and 7.1 w/w % (curve 1) and 20.7 w/w % (curve 2) of MP. Initial feed: 3.7 mM AgNO₃, pH 4.1. Initial receiver: 1 M H₂SO₄ saturated with thiourea.

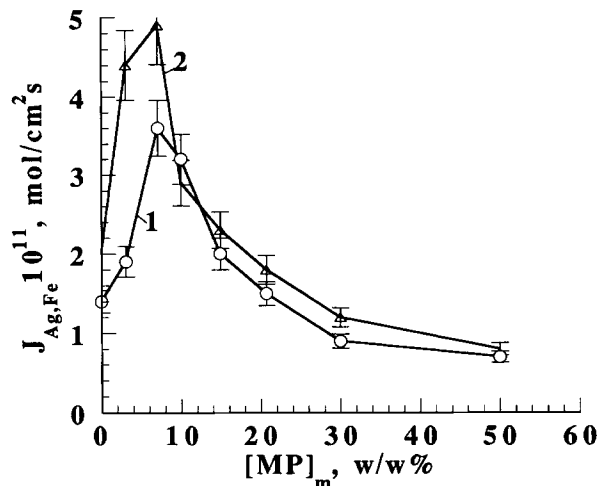


Figure 7 Dependencies of silver (curve 1) and iron (III) (curve 2) transfer rates on the content of the polymeric material, $[MP]_m$, in the membranes. For initial conditions, see Figure 6.

w/w % of MP, respectively. Note that the J_{Ag} and J_{Fe} values, obtained for the membrane impregnated with just DTPA, did not exceed 1.4×10^{-11} and 2×10^{-11} mol/cm²s, respectively. Such low permeability is caused by high viscosity of the concentrated DTPA, due to the processes of oligomerization and association.¹⁰

Figure 7 represents the dependencies of silver (curve 1) and iron(III) (curve 2) transfer rates on the concentration of the modified polymer in the membranes. The $J_{Ag,Fe}$ values increased with the rise of $[MP]_m$ from 0 to 7.1 w/w %, and at $[MP]_m > 7.1$ w/w % the transfer rates decreased. The dependencies shown in Figure 7 were obtained using GSLMs 2 days after their preparation. The same dependencies were obtained with the same GSLMs kept 60 days in air. This gives evidence of the GSLM's stabilization after 2–3 days. The higher J values at low concentrations of MP, as compared to the J values in pure DTPA, can be explained by the interruption of the regular hydrogen bonds, which exist in the pure DTPA, by the added modified polymeric molecules. The difference in J at $[MP] < 7.1\%$ cannot be attributed to the change of the pathlength due to the THF migration into water. The loss of THF may have caused only a 20% increase in permeability. At above 7.1 w/w % of MP in the gelled membrane, the transfer rates become lower due to the increase in the tortuosity of the gelled phase.

The dependencies of the effective diffusion coefficient of silver (curve 1) and iron(III) (curve 2) on the concentration of the polymeric material in

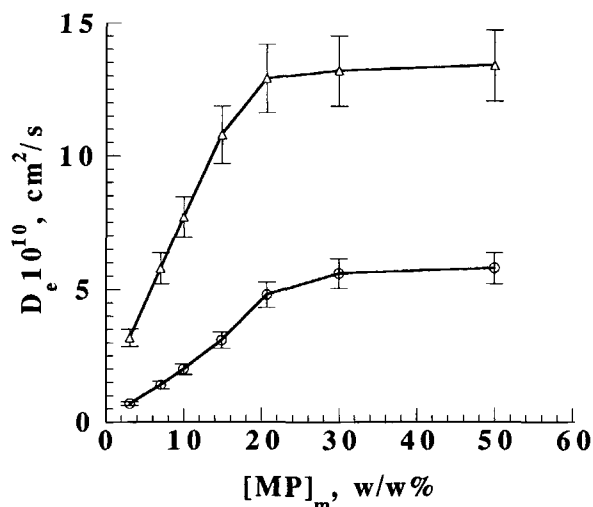


Figure 8 Dependencies of the effective diffusion coefficient, D_e , of silver (curve 1) and iron(III) (curve 2) on the concentration of the polymeric material in the membranes. In experiments with iron(III), a 1 M oxalic acid was used as a stripping agent.

the GSLM is shown in Figure 8. An effective diffusion coefficient was obtained using eq. (5). The D_e values increased with increasing polymer concentrations up to 20%. At $[MP]_m > 20\%$, the dependencies approached plateaus.

The results obtained with the GSLMs are similar to the ones shown in Figure 8 and they may be explained assuming that the metal diffused through the membrane is being bounded and unbounded to the carrier. At high $[MP]_m$ (or low $[DTPA]_m$) the D_e approaches the diffusion coefficient of the metal

salt unbounded to the carrier (D_u). At $[MP]_m \rightarrow 0$, or $[DTPA]_m \rightarrow 1$, D_e approaches the diffusion coefficient of the metal ion bounded to the carrier (D_b). Considering $D_u \gg D_b$, one can explain the results shown in Figure 8. Note that a similar effect was observed in our recent work,⁸ which dealt with the three-component GSLMs. The increase of D_e in this case was followed by the increase of the effective distribution coefficient of metal between GSLM and the aqueous phase due to the polymerization of the carrier (DTPA).

It was of interest to estimate the transport characteristics of GSLM towards different metal ions. We chose metals that are important for hydrometallurgy and wastewater treatment, such as silver, mercury, zinc, cadmium, nickel, and iron(III). The results of transport experiments, as well as the values of extraction constants of metal ions by DTPA and stability constants of the complexes formed in the stripping receivers, are collected in Table II. The GSLMs containing (7.1 ± 0.5) w/w % MP were aged 4 days after preparation. The content of the stripping and feed phases is listed in Table II.

It can be seen that the metal transfer rates are dependent mainly on the stripping reaction. The transport of iron(III) was negligible when the stripping phase containing sulfuric acid saturated by thiourea (TU) or concentrated HCl, because the binding of Fe^{3+} with DTPA was much stronger than the binding with Cl^- ions or TU. The transfer rates of iron were increased by the use of a strong stripping agent, such as oxalic acid. Thus, in the experiments with GSLM, one can regulate membrane selectivity by choosing a certain stripping agent.

Table II Ion Transport Characteristics of GSLM

Metal Ion	J , mol/cm ² s	Log K_{ex} ^{16,17}	Log B ¹⁸	Stripping Phase	Feed Phase
Cd ²⁺	5.2×10^{-11}	7.01	10.6	HCl 10 M	CdOAc ₂ , Fe(NO ₃) ₃ , ZnOAc ₂ 4 mM each
	2.4×10^{-11}		7.1	1 M H ₂ SO ₄ + 0.8 M TU	CdOAc ₂ 4 mM
Ag ⁺	3.1×10^{-11}	41.3	13.1	1 M H ₂ SO ₄ + 0.8 M TU	AgNO ₃ 4 mM
Hg ²⁺	3.8×10^{-11}	> 41	72.8	1 M H ₂ SO ₄ + 0.8 M TU	Hg(NO ₃) ₂ 4 mM
Fe ³⁺	$< 10^{-12}$	8.62	4.7	HCl 10 M	Fe(NO ₃) ₃ , ZnOAc ₂ , CdOAc ₂ 4 mM each
	4.4×10^{-11} $< 10^{-12}$		36.4	Oxalic Acid 1 M 1 M H ₂ SO ₄ + 0.8 M TU	Fe(NO ₃) ₃ 4 mM FeCl ₃ 4 mM
Zn ²⁺	$< 10^{-12}$	2.25	-0.6	HCl 10 M	ZnOAc ₂ , CdOAc ₂ , Fe(NO ₃) ₃ 4 mM each

CONCLUSIONS

The procedure of displacement of chlorine in PVC by the dioctyldithiocarbamate group has been reported. The obtained modified polymer (MP) was characterized by NMR, DSC, and elemental analysis. The discovered compatibility and interactions of di(2-ethylhexyl)dithiophosphoric acid (DTPA) with MP caused the formation of the gelled membranes. The formation is followed by the relaxation of a gel structure. The transport properties of the gelled supported liquid membranes (GSLMs) are dependent on the carrier (DTPA) concentration in the membranes. Effective diffusion coefficient was shown to increase with the rise of the concentration of the polymeric component in the gel. Prepared GSLMs are capable of selective separating of the metal ions. The effect of the stripping reaction on metal ion transport makes it possible to regulate membrane selectivity.

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NOMENCLATURE

A	$[(a_0 + b_0)^2 - 4a_0b_0]^{1/2}$, M
a_0	initial concentration of PVC in reacting solution (0.976 M)
b_0	initial concentration of DODTC, sodium salt, in reacting solution, (0.461 M)
Cl wt %	% of chlorine in polymer
D_b	diffusion coefficient of metal bounded to the carrier, cm^2/s
D_e	effective diffusion coefficient, cm^2/s
D_u	diffusion coefficient of metal unbounded to the carrier, cm^2/s
J	transfer rate of the corresponding ion, $\text{mol}/\text{cm}^2\text{s}$
k_2	second order rate constant, $\text{M}^{-1}\text{sec}^{-1}$
K_{ex}	extraction constant
l	membrane thickness, cm
S	wt % of sulfur in MP
T_g	measured glass transition temperature, $^{\circ}\text{K}$
T_{g1}	glass transition temperature of PVC, $^{\circ}\text{K}$
T_{g2}	glass transition temperature of the totally modified polymer, $^{\circ}\text{K}$
t_i	lag time, s

W_1	weight fraction of PVC sample
W_2	weight fraction of totally modified polymer
W_0	initial weight of the fresh gel composed of MP and DTPA, kg
ΔW	difference between the initial and current weights of the gel, kg $x = a_0 S/18.65$
B	stability constant of the complex

REFERENCES

1. T. Nakagawa, T. Taniguchi, and M. Okawara, *Koguo Kagaku Zasshi*, **70**, 2382 (1967).
2. M. Okawara, *Joint Conference ACS and JCS*, Hawaii, 1979, p. 39.
3. S. Marian and G. Levin, *J. Appl. Polym. Sci.*, **26**, 3295 (1981).
4. A. Nkanash and G. Levin, in *Modification of Polymers*, C. E. Carraher, Jr. and J. A. Moore, Eds., Plenum, New York, 1983, pp. 109–129.
5. M. Goldman, D. Fraenkel, and G. Levin, *J. Appl. Polym. Sci.*, **37**, 1791 (1989).
6. A. M. Neplenbroek, D. Bargeman, and C. A. Smolders, *Desalination*, **79**, 303 (1990).
7. L. Bromberg, G. Levin, J. Libman, and A. Shanzer, *J. Membr. Sci.*, **69**, 143 (1992).
8. L. Bromberg, G. Levin, and O. Kedem, *J. Membr. Sci.*, **71**, 41 (1992).
9. L. Bromberg, I. Lewin, and A. Warshawsky, *Hydro-metallurgy*, to appear.
10. L. Bromberg, I. Lewin, and A. Warshawsky, *J. Membr. Sci.*, **70**, 31 (1992).
11. D. Oktavec, J. Stefanec, B. Siles, V. Konecny, and J. Garaj, *Collection Czechoslov. Chem. Commun.*, **44**, 2487 (1979).
12. D. C. White, *Mikrochimica Acta*, **3**, 449 (1961).
13. L. Bromberg, I. Lewin, H. Gottlieb, and A. Warshawsky, *Inorg. Chim. Acta*, **197**, 95 (1992).
14. T. G. Fox, *Bull. Amer. Phys. Soc.*, **1**, 123 (1956).
15. R. A. Cherkasov, in *Structure and Reactivity of Organic Compounds*, B. A. Arbuzov, Ed., Nauka, Moscow, 1978, pp. 107–145.
16. I. S. Levin and V. V. Sergeeva, *Izv. Sib. Otd. Akad. Nauk SSSR Ser. Khim.*, **3**, 53 (1974).
17. Yu. M. Yukhin, N. E. Kozlova, L. A. Novoseltseva, and I. S. Levin, *Izv. Sib. Otd. Akad. Nauk SSSR Ser. Khim.*, **7**, 64 (1974).
18. K. B. Yatsimirskii and V. P. Vasil'ev, *Instability Constants of Complex Compounds*, Van Nostrand, New York, 1960, 214 pp.

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