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Carrier-Mediated Transport of Some Main Group Metal Ions across Various Organic Liquid Membranes

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Carrier-Mediated Transport of Some Main Group Metal Ions across Various Organic Liquid Membranes

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ABSTRACT

Extraction and facilitated transport of Na^+, K^+, Mg^{2+}, and Ca^{2+} ions have been studied using TDA-1 as carrier through BLMs using chloroform, dichloroethane and carbon tetrachloride liquid membranes. (See Symbols section for definitions.) Pic^-, Dnp^-, Onp^-, and SCN^- have been used as anions. K^+ and Ca^{2+} ions are selectively extracted into organic phase whereas no extraction of Na^+ and Mg^{2+} ions has been observed using single metal ion species. Higher extraction values are observed for Ca^{2+} ion than for Mg^{2+} ion, whereas selectivity for K^+ ion was retained using coexisting cations in the source phase. Na^+ and Ca^{2+} ions are transported to a greater extent than K^+ and Mg^{2+} ions. Poorer extraction and transport values are observed in carbon tetrachloride than in chloroform and dichloroethane. The ionophore shows higher extraction and transport efficiency for alkaline earth metal ions than for alkali metal ions.

Key Words. Extraction; Carrier; Transport; Liquid membrane

INTRODUCTION

Recently there has been considerable interest in possible uses of artificial membranes in specific separation procedures of industrial and academic importance (1). Cation transport across various liquid membrane configurations, viz., BLMs, SLMs, and ELMs, which combine the extraction, diffusion, and

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stripping processes, are particularly drawing maximum attention (2) since they constitute the cheapest separation techniques because of their relatively small inventory and low capital cost. Energy consumption is quite low and energy losses are negligible under proper conditions. Izatt et al. (3) critically evaluated the advantages, disadvantages, and novel features of LMs.

Various types of crowns (4), cryptands (5), and podands (6) have been investigated as host molecules which have the capability to extract guest ions selectively from aqueous solution into a hydrophobic membrane phase and transport ions across various liquid membrane systems. Vögtle and coworkers (7) showed that the polypodands and particularly acyclic cryptands form complexes with alkali and alkaline earth metal salts. In order to carry out solid–liquid phase-transfer catalysis and the recovery of metals, Soula (8) described the synthesis and properties of tris-(polyoxyalkyl amine) and selected TDA-1 as the phase transfer catalyst which represents the best efficiency/toxicity compromise.

In view of the above considerations, we report here the liquid–liquid extraction and carrier facilitated transport of Na^+, K^+, Mg^{2+}, and Ca^{2+} picrates, dinitrophenolates, orthronitrophenolates, and thiocyanates by TDA-1 (Fig. 1) through chloroform, dichloroethane, and carbon tetrachloride BLMs. The objective of this work is to provide information that could be helpful in the design of carriers that exhibit selectivity into membrane systems.

EXPERIMENTAL

TDA-1 was obtained from Fluka, Analytical grade chemicals and solvents were used for all experiments. Metal picrates, dinitrophenolates, and orthonitrophenolates were prepared as reported earlier (9).

Liquid–Liquid Extraction Studies

For extraction (10), 10 mL of 1.0×10^{-3} M aqueous metal salt solution was vigorously stirred with 10 mL of 1.0×10^{-3} M ionophore solution in an or-

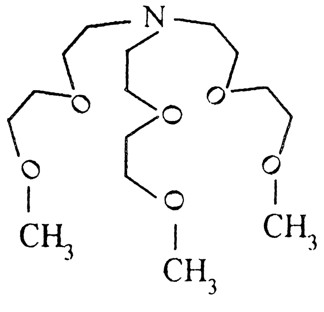

FIG. 1 Ionophore used in the present studies.

ganic solvent in a small beaker using a magnetic stirrer (100 rpm). The beaker was covered and kept in a thermostated incubator (25 ± 1°C). The amount of cation in the aqueous phase was initially determined. After 4 hours of stirring, the mixture was allowed to stand for 5 minutes for the separation of the two phases. The depleted aqueous phase was removed and analyzed for its metal content using a Philips 7700 double beam atomic absorption spectrophotometer. The amount of cation extracted by the ionophore was found by determining its difference in the aqueous phase before and after extraction. Values of the distribution ratio were calculated as follows (11):

$$D_{\mathrm{M}} = \frac{\text{total concentration of metal ion in organic phase}}{\text{total concentration of metal ion in aqueous phase}}$$

Transport Studies

The transport measurements were performed in a U-tube glass cell (12) placed in a thermostated incubator (25 ± 1°C). The 1.0×10^{-3} M carrier in 25 mL of organic solvent was placed in the bottom of the U-tube to serve as the membrane. Ten milliliters of 1.0×10^{-3} M aqueous metal salt solution was placed in one limb of the U-tube to serve as the source phase (S.P.) and 10 mL of double distilled water was placed in another limb of the U-tube to serve as the receiving phase (R.P). The two aqueous phases, i.e., the source and receiving phases, floated on the organic membrane phase in the two limbs of the U-tube. The membrane phase was constantly stirred using a magnetic stirrer (100 rpm). The samples were withdrawn from the receiving phase after 24 hours and analyzed for cation transported by using an atomic absorption spectrophotometer.

Cation flux (J_{M}) values were calculated using the relation (13):

$$J_{\mathrm{M}} = \frac{C_{(\text{receiving})} V}{At}$$

where $C_{(\text{receiving})}$ is the concentration of metal ion in the receiving phase, mol/dm^3; V is the volume of the receiving phase, dm^3; A is the effective area of the membrane, m^2; and t is the time, seconds.

RESULTS AND DISCUSSION

Liquid–Liquid Extraction

Literature values for selected physical properties of the solvents used are listed in Table 1. Results of extraction studies using single metal ion species are listed in Table 2. It is observed that ionophore extracts only K^+ and Ca^{2+}; no extraction of Na^+ and Mg^{2+} was observed. This is expected because the TDA-1 complexes of K^+ and Ca^{2+} are more stable than those of Na^+ and

TABLE 1

Values of Selected Physical Properties of the Solvents Used in the Present Studies

Solvent	Density (g-cm^3)	Surface tension (dyn-cm^{22})	Viscosity (cP)	Solubility in H_2O, 20°C (% by wt)	Dielectric constant	Dipole moment (debye)
$C_2H_4Cl_2$	1.2521	32.20	0.887	0.81	10.36	1.20
$CHCl_3$	1.4891	26.70	0.596	0.81	4.81	1.01
CCl_4	1.5939	26.40	0.965	0.08	2.24	0.00

Mg^{2+} due to the formation of pseudocyclic structures (14) which are suitable for the larger size of K^+ (1.33 Å) and Ca^{2+} (0.99 Å) ions. All seven donor centers, including three OCH_3 groups, participated in the coordination of the metal ion which is located at the center of the pseudocavity (15). It is presumed that all three OCH_3 groups of the smaller Na^+ and Mg^{2+} ions collide with each other to prevent adoption of a conformation suitable for these metal ions.

TABLE 2

Amount of Cation Extracted into an Organic Phase after 4 hours of Using Alkali and Alkaline Earth Metal Salts with TDA-1 in Chloroform, 1,2-Dichloroethane, and Carbon Tetrachloride (source phase: metal salt 10 mL, 1.0×10^{-3} M. organic phase: ionophore 10 mL, 1.0×10^{-3} M)

		$CHCl_3$		$C_2H_4Cl_2$		CCl_4	
No.	Metal salt	Cation extracted (ppm)	D_M	Cation extracted (ppm)	D_M	Cation extracted (ppm)	D_M
1	NaPic	0	0.0	0	0.0	0	0.0
2	NaDnp	0	0.0	0	0.0	0	0.0
3	NaOnp	0	0.0	0	0.0	0	0.0
4	NaSCN	0	0.0	0	0.0	0	0.0
5	KPic	0	0.0	5	0.12	5	0.25
6	KDnp	0	0.0	10	0.18	10	0.28
7	KOnp	0	0.0	0	0.0	0	0.0
8	KSCN	0	0.0	10	0.4	10	0.20
9	$Mg(Pic)_2$	0	0.0	0	0.0	0	0.0
10	$Mg(Dnp)_2$	0	0.0	0	0.0	0	0.0
11	$Mg(Onp)_2$	0	0.0	1	0.005	2	0.1
12	$Ca(Pic)_2$	26	0.22	43	0.43	0	0.0
13	$Ca(Dnp)_2$	18	0.16	31	0.31	0	0.0
14	$Ca(Onp)_2$	4	0.06	19	0.40	0	0.0

TABLE 3

Amount of Cation Extracted into an Organic Phase after 4 hours Using a Mixture of Alkali and Alkaline Earth Metal Salts (NaX + KX, $MgX_2 + CaX_2$, X = Pic^-, Dnp^-, Onp^-, SCN^-) with TDA-1 in Chloroform, 1,2-Dichloroethane, and Carbon Tetrachloride (source phase: 10 mL, 1.0×10^{-3} M mixture of NaX + KX, mixture of $MgX_2 + CaX_2$. organic phase: ionophore 10 mL, 1.0×10^{-3} M)

		$CHCl_3$		$C_2H_4Cl_2$		CCl_4	
No.	Metal salt	Cation extracted (ppm)	D_M	Cation extracted (ppm)	D_M	Cation extracted (ppm)	D_M
1	NaPic	0	0.0	0	0.0	0	0.0
2	NaDnp	0	0.0	0	0.0	0	0.0
3	NaOnp	0	0.0	0	0.0	0	0.0
4	NaSCN	0	0.0	0	0.0	0	0.0
5	KPic	0	0.0	15	0.1	15	0.1
6	KDnp	5	0.25	10	0.66	0	0.0
7	KOnp	0	0.0	0	0.0	0	0.0
8	KSCN	0	0.0	15	0.75	10	0.40
9	$Mg(Pic)_2$	0	0.0	5	0.12	2	0.04
10	$Mg(Dnp)_2$	5	0.13	7	0.13	5	0.13
11	$Mg(Onp)_2$	1	0.02	4	0.10	5	0.13
12	$Ca(Pic)_2$	17	0.10	28	0.17	5	0.02
13	$Ca(Dnp)_2$	17	0.10	13	0.07	12	0.07
14	$Ca(Onp)_2$	12	0.07	10	0.06	6	0.03

The results of the competitive extraction of alkali metal ions (Na^+ and K^+) and alkaline earth metal ions (Mg^{2+} and Ca^{2+}) are listed in Table 3. It is observed that the ionophore also exhibits selectivity toward K^+ ion when Na^+ and K^+ ions exist together. Higher extraction values were observed for Ca^{2+} ion than for Mg^{2+} ion when Mg^{2+} and Ca^{2+} ions exists together. No definite trend in the amount of cations extracted was observed when cations coexist in the source phase.

Transport Studies

The results of transport studies using single metal ion species are listed in Table 4, and the relative amount of cations transported in chloroform, 1,2-dichloroethane, and carbon tetrachloride are shown in Figs. 2, 3, and 4, respectively. It is observed that TDA-1 is a better carrier for the transport of Na^+ than of K^+, and of Ca^{2+} than of Mg^{2+}. This is because the amount of cation transported is dependent on the amount released rather than on the amount of uptake (16). The release of Na^+ and Ca^{2+} ions into the receiving phase take place much more rapidly than the uptake into the organic phase. In the case of

TABLE 4

Amount of Cation Transported after 24 hours Using Alkali and Alkaline Earth Metal Salts by TDA-1 through Chloroform, 1,2-Dichloroethane, and Carbon Tetrachloride (source phase: 10 mL, 1.0×10^{-3} M metal salt in aqueous phase. membrane: 1.0×10^{-3} M ionophore in 25 mL organic solvent. receiving phase: 10 mL distilled water)

		$CHCl_3$		$C_2H_4Cl_2$		CCl_4	
No.	Metal salt	Cation transported (ppm)	J_M [$\times 10^{-8}$] (mol/m^2/s)	Cation transported (ppm)	J_M [$\times 10^{-8}$] (mol/m^2/s)	Cation transported (ppm)	J_M [$\times 10^{-8}$] (mol/m^2/s)
1	NaPic	1.5	3.32	2	4.43	0.5	1.10
2	NaDnp	1	2.21	2	4.43	0.5	1.10
3	NaOnp	1	2.21	1.5	3.32	1	2.21
4	NaSCN	1	2.21	3	6.64	3	6.64
5	KPic	1.95	2.54	0.2	0.26	0	0
6	KDnp	0.30	0.39	0.3	0.39	0.1	0.13
7	KOnp	0.35	0.45	0.4	0.52	0.1	0.13
8	KSCN	0.7	0.91	0.25	0.32	0	0
9	$Mg(Pic)_2$	4	5.49	10	21.2	2	4.24
10	$Mg(Dnp)_2$	5	10.6	6	12.7	2	4.24
11	$Mg(Onp)_2$	5	10.6	10	21.2	7	14.8
12	$Ca(Pic)_2$	8	10.1	14	17.8	6	7.64
13	$Ca(Dnp)_2$	10	12.7	20	25.4	0	0.0
14	$Ca(Onp)_2$	20	25.4	18	22.9	3	3.82

K^+ and Mg^{2+} ions, release takes place slowly than uptake, allowing a much higher accumulation of K^+ and Mg^{2+} ions in the organic phase as a complex compared with that of Na^+ and Ca^{2+} ions, resulting in higher transport of Na^+ and Ca^{2+} ions into the receiving phase.

The results of the competitive transport of alkali metal ions (Na^+ and Ca^{2+}) and alkaline earth metal ions (Mg^{2+} and Ca^{2+}) are listed in Table 5. In general, there is decrease in the amount of Na^+, K^+, and Mg^{2+} ions transported whereas an increase is observed for the transport of Ca^{2+} ion when cations coexist in the source phase.

We found that carbon tetrachloride does not provide a smooth flow of cations across membrane and produces a barrier to the flow of cations compared to chloroform and dichloroethane (17). The observed order of solvents for the extraction and transport of cations is 1,2-dichloroethane $>$ chloroform $>$ carbon tetrachloride. The density and viscosity of solvents increase with an increase in chlorination whereas the dielectric constants, the dipole moments, and the mutual water–solvent solubilities of the solvents decrease with an increase in chlorination. The decrease of mutual water–solvent solubilities suggests that the interfacial boundary will be less distinct for chloroform and

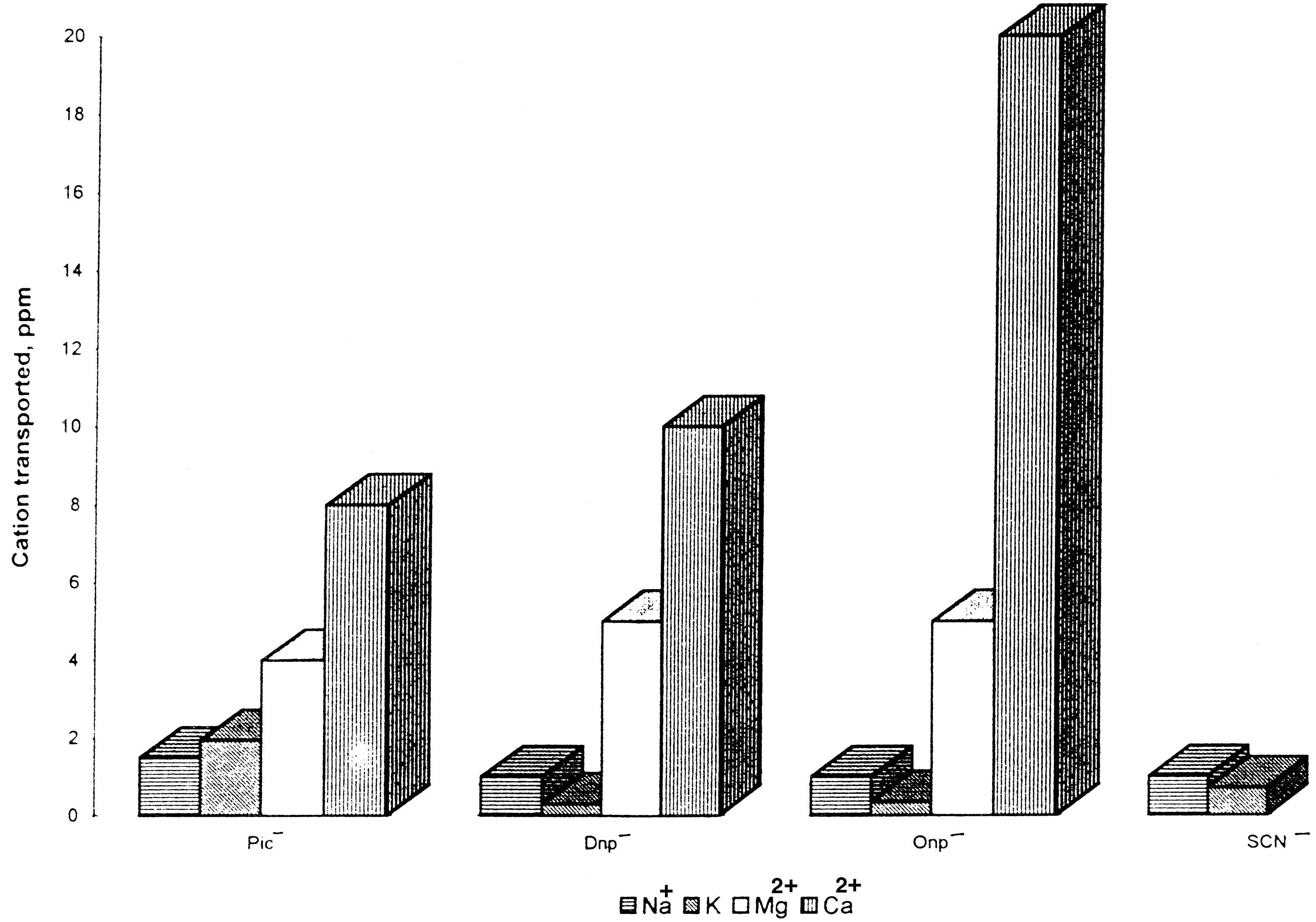

FIG. 2 Transport of alkali and alkaline earth metal ions using TDA-1 in chloroform liquid membrane.

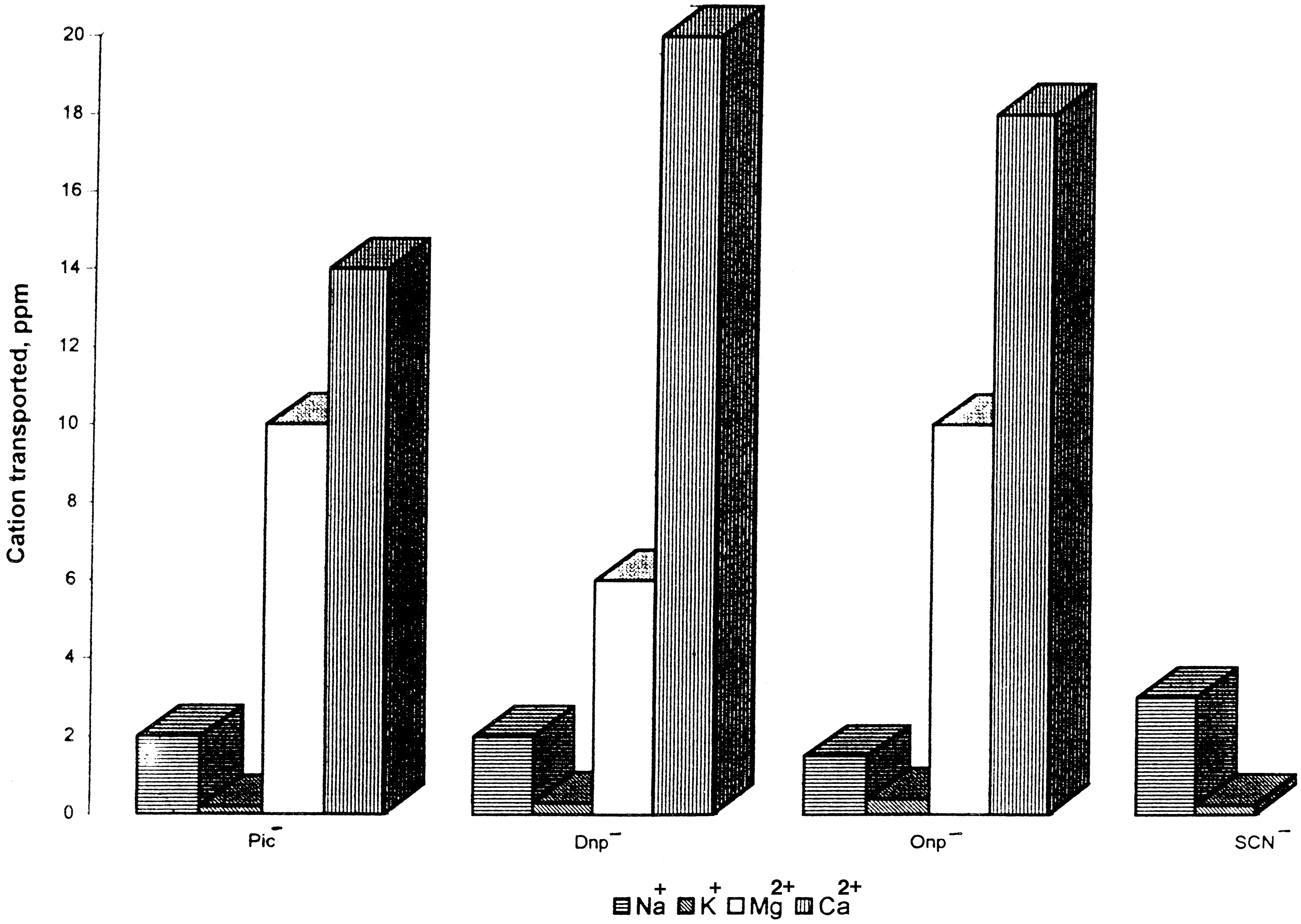

FIG. 3 Transport of alkali and alkaline earth metal ions using TDA-1 in 1,2-dichloroethane liquid membrane.

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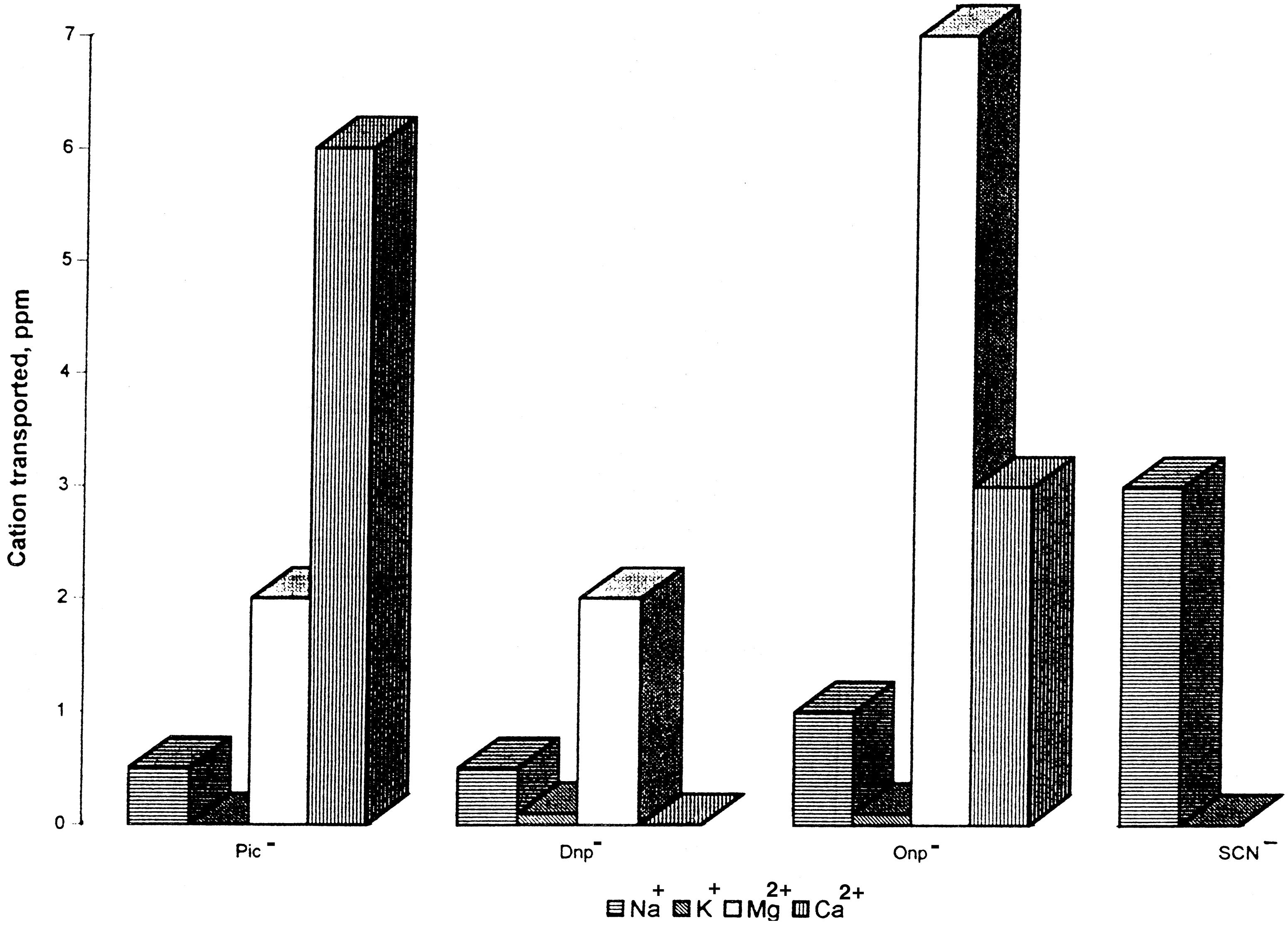

FIG. 4 Transport of alkali and alkaline earth metal ions using TDA-1 in carbon tetrachloride liquid membrane.

TABLE 5

Amount of Cation Transported after 24 hours Using a Mixture of Alkali and Alkaline Earth Metal Salts ($NaX + KX$, $MgX_2 + CaX_2$, $X = Pic^-$, Dnp^-, Onp^-, SCN^-) with TDA-1 in Chloroform, 1,2-Dichloroethane, and Carbon Tetrachloride (source phase: 10 mL, 1.0×10^{-3} M mixture of $NaX + KX$, mixture of $MgX_2 + CaX_2$. membrane: 1.0×10^{-3} M carrier in 25 mL organic solvent. receiving phase: 10 mL distilled water)

		$CHCl_3$		$C_2H_4Cl_2$		CCl_4	
No.	Metal salt	Cation transported (ppm)	J_M [$\times 10^{-8}$] (mol/m^2/s)	Cation transported (ppm)	J_M [$\times 10^{-8}$] (mol/m^2/s)	Cation transported (ppm)	J_M [$\times 10^{-8}$] (mol/m^2/s)
1	NaPic	0.2	4.4	0.8	1.7	0.8	1.7
2	NaDnp	0.8	1.7	1.6	3.5	0.4	0.8
3	NaOnp	0.8	1.7	1.6	3.5	0	0.0
4	NaSCN	2	4.4	0.8	1.7	0.4	0.8
5	KPic	0.2	0.2	0.1	0.1	0.1	0.1
6	KDnp	0.1	0.1	0.1	0.1	0	0.0
7	KOnp	0.25	0.3	0.1	1.3	0.1	0.1
8	KSCN	0.15	0.1	0.1	0.1	0	0.0
9	$Mg(Pic)_2$	4	8.4	4	8.4	4	8.4
10	$Mg(Dnp)_2$	5	10.6	4	8.4	4	8.4
11	$Mg(Onp)_2$	5	10.6	6	12.7	4	8.4
12	$Ca(Pic)_2$	44	56	52	66.2	32	40.7
13	$Ca(Dnp)_2$	43	54.7	46	58.6	43	54.7
14	$Ca(Onp)_2$	49	62.4	58	73.9	43	54.7

dichloroethane but very distinct for carbon tetrachloride. The transfer of hydrated ions from the aqueous into the organic phase is apparently facilitated in membrane systems with less distinct interfacial regions. The solvent with the highest dipole moment will best solvate the ions transferred to the organic phase, so it is expected that chloroform and dichloroethane will be better extractants of cations into the membrane complex. Carbon tetrachloride will have relatively thick water-free boundary layers that resist the flux of both ions and ligand. Further, the amount of ligand available in carbon tetrachloride for complexation will be relatively low and the ions will not solvate easily. Therefore, larger extraction and transport of cations through chloroform and dichloroethane and smaller through carbon tetrachloride can be predicted.

Higher extraction and transport values are observed for alkaline earth metal ions than for alkali metal ions. The major difference between monovalent and divalent cations is not only the cation diameter but also the charge density. Divalent cations possess both a smaller size and a higher charge density than monovalent cations, and this promises a stronger interaction with the donor oxygen atoms of the ligand. These results also suggest that the three-dimensional topologies of the ligands would allow complete inclusion and effective shielding of hydrophilic alkaline earth metal ions as in cryptand complexes.

CONCLUSIONS

In conclusion, this selectivity and specificity of TDA-1 for K^+ and Ca^{2+} ions during extraction and Na^+ and Ca^{2+} ions during transport after variations and modifications can lead to effective separation techniques (18). This type of ligand has found potential application for the design of ion-selective electrodes (19). Besides commercial uses, the selectivity observed among these biologically important ion pairs may also be of much importance as models for cation transport across biomembranes. They are expected to be helpful in understanding the more complex behavior encountered in biochemical transport processes. Further investigation of this noncyclic polyether which exhibits cation selectivity is in progress.

SYMBOLS

LMs	liquid membrane system
BLMs	bulk liquid membrane system
SLMs	supported liquid membrane system
ELMs	emulsion liquid membrane system
TDA-1	tris[2-(2-methoxy ethoxy)-ethyl]amine
Pic^-	picrate
Dnp^-	1,2-dinitrophenolate
Onp^-	orthonitrophenolate
SCN^-	thiocyanate

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