IONOPHORIC PROPERTIES OF ORGANOMETALLIC TRIPODS OF THE TYPE $[C_5H_5\ Co\ \{P(O)(OR)_2\}_3]^-$ (L_{OR-}, R = Me, Et, iPr). A STUDY OF LITHIUM-PROTON COUPLED COUNTERTRANSPORT IN A BULK LIQUID MEMBRANE

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Résumé : L'extraction liquide-liquide du lithium par les ligands orgonométalliques $Na^+[C_5H_5Co\{P(O)(OR)_2\}_3]^-$ (L_{OR-}, R = Et, iPr) s'effectue par échange ionique quantitatif.

Le spectre de masse de la phase organique montre que les espèces extraites sont des dimères $Li_2(L_{OR})_2$. L'échange quantitatif Na^+/H^+ est aussi observé.

Les spectres de masse et d'électrospray de la phase organique montrent l'existence du dimère $H_2(L_{OR})_2$ dans cette phase. L'existence du complexe mixte LiH ($L_{OR})_2$ est aussi rapportée. Le transport du lithium à travers la membrane liquide contenant le tripode $Na^+[C_5H_5Co\{P(O)(OR)_2\}_3]^-$ se passe par le biais d'un contre transport couplé du proton. Ce transport est caractérisé, par la formation du complexe mixte $LiH(L_{OR})_2$ dans la membrane liquide.

Key words : organometallic tripods, liquid-liquid extraction, lithium-proton countertransport.

I - INTRODUCTION

Several crown ethers, cryptands, spherands and calixarenes neutral and ionizable derivatives are known to exhibit remarquable carriers properties towards alkali ions [1,2,3,4]. Among alkali metal ions, lithium is one of the most attractive and important ion for application [5]. For example, there is a possibility that large amounts of lithium are required

for the production of tritium, which is used as a reactant in the nuclear fusion reaction. The tripodal organometallic ligand [$(C_5H_5$ Co $\{P(O)(OR)_2\}_3$]$^-$ with R = Me, Et, iPr (noticed L_{OR}^-) (figure 1) has already been shown to be a selective lithium carrier in phosphotidyl-choline vesicles[6]. In order to get more information on the transport mechanism and on the nature of the chemical species involved in the transport process, we have investigated the transport through a water-dichloroethane-water bulk liquid membrane as well as the correspon-ding liquid-liquid equilibria.

FIGURE 1 : *Compound used as extractant*
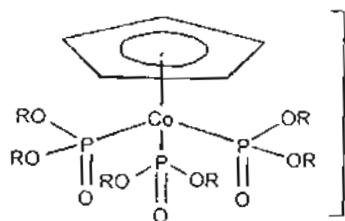
Materials and experimental Section :

Reagents : NaLOMe, NaLOEt, NaLOiPr were synthetized according to reference [7]. The dichloroethane (SDS) was purified by pre-equili-bration with water (removal of the stabilizer). The alkali ions solutions were prepared using distilled water. The lithium chloride (99.3 %) was from Roth. The lithium nitrate (99 %) was from Janssen Chimika. HCl (37 %) and HNO_3 (65 %) were from Merk.

Solvent Extraction Experiments : Extraction experiments were carried out with a water / dichloroethane systems. The curves (figures 2, 3, 4,) were obtained from equilibration of 10 ml aliquots of aqueous phase (LiX = 0,1 M with X = Cl, NO_3) With equal volume of organic phase (dichloroethane containing NaLOiPr in variable concentration) and vigorously stirred (20 mn) in stoppered tubes immersed in a thermostated bath (25 ± 0.2 °C). Salting in and salting out effects are deduced merely by visual observations.

Liquid Membrane Experiments : Liquid membrane experiments were performed with a U shaped glass tube. A membrane solution (dichloroethane containing a carrier (NaLOEt, NaLOiPr)), a source phase (aqueous solution of lithium salt 0.1 M) and a receving phase (aqueous solution of HCl 0,01 M) were stirred simultaneous at 100 rpm. The whole apparatus were placed in a thermostat controlled at 25 ±.0.2 °C. The exchanges in the concentrations of lithium in the receiving phase and organic phase (figure 5) were followed by using a Perkin Elmer (2380) Atomic Emission Spectrophotometer with air-acetylene flame. Extraction experiments performed with pure dichloroethane showed no detectable presence of lithium in the organic phase.

Mass Spectra : The mass spectra of the organic phases were obtained using fast-atom (Xenon) bombardment excitation source (FAB+ mass spectra) on a ZAB HF VG Analytical. The samples were dissolved in m-nitrobenzyl alkohol as matrix and subjected to impingement by atoms accelerated at 8 kV. Fragments having a mass to charge ratio up to 1400 were detected. The Electrospray (ES mass spectra) of the organic phases were obtained on a VG BioQ triple quadrupole with a mass to charge (m / z) The electrospray interface was heated to 50 °C. The sampling cone voltage varies from 10 to 50 V.

Results and discussion :

Liquid liquid extraction :

The transport through a liquid membrane can formally be considered as the resultant of an extraction between the feed phase and the membrane phase and a back extraction (stripping) between the membrane and the receiving phase; hence data on the two phase equilibria can provide useful information on the understanding of the liquid membrane transfert[8,9].

Salting in -salting out :

If NaLOR salt(R = Me, Et, iPr) in dichloroethane is brought into contact with a CX water solution (C^+ = H^+, Li^+, Na^+, K^+, Rb^+, Cs^+., X^- = Cl^-) two different features are observed at the equilibrium namely either a salting in (L_{OR^-} is almost quantitatively in the aqueous phase) or a salting out (L_{OR^-} is almost quantitatively in the organic phase) (table I). It is observed that the lipophilicity of R greatly favors the solubility of L_{OR^-} in the organic phase. Whatever the nature of the co-cation, salting out of L_{OR^-} is observed if R = isopropyl and where as salting in is observed when R = methyl. When R = ethyl, a clear disruption in the partition behavior is observed passing from lithium to sodium. It is interesting to correlate this behavior with the kwown crystal structures of the corresponding complexes[10]. With sodium the crystal structure is trimeric of formula $(NaL_{OEt})_3,2H_2O$, where the water molecules participate to the complexation of the sodium ion. In addition they can be in direct contact with the surrounding solvent molecules. This feature contributes to increase the hydrophilicity of the complex solute. With lithium and even in the presence of water, an anhydrous dimer $Li_2(L_{OEt})_2$ is formed. In this structure the Li cation which is naturally hydrophilic, is encapsulated in a tetrahedral environment constituted by four phosphoryl groups. As a result, on the basis of the complexe structures the lithium complex should be considered as much more lipophilic than the sodium one.

TABLE 1 : *Different features observed if NaLOR (R = Me, Et, iPr) in dichloroethane is brought into contact with a CX water solution ($C^+ = H^+$, Li^+, Na^+, K^+, Rb^+, Cs^+., $X^- = Cl^-$).*

	H^+	Li^+	Na^+	K^+	Rb^+	Cs^+
Methyl	S I	S I	S I	S I	S I	S I
Ethyl	S O	S O	S I	S I	S I	S I
Isopropyl	S O	S O	S O	S O	S O	S O

Formation of a Li - L complex in the organic phase :

Quantitative analysis of the Li^+ (LiX in the aqueous phase) Na^+ (NaL_{OiPr} in the organique phase) (figure 2) confirm that a Li -L_{OiPr} complex of 1 : 1 stoechiometry is quantitatively formed in the organic phase. The similar complex is formed for R = Et). It is also observed that the exchange does not involve any transfer of inorganic anion into the organic medium. FAB^+ mass spectra show the presence of the dimer in both cases ($HLi_2(L_{OEt})_2^+$: m/e = 1 079.3 ; $HLi_2(L_{OiPr})_2^+$: m/e = 1247.4).
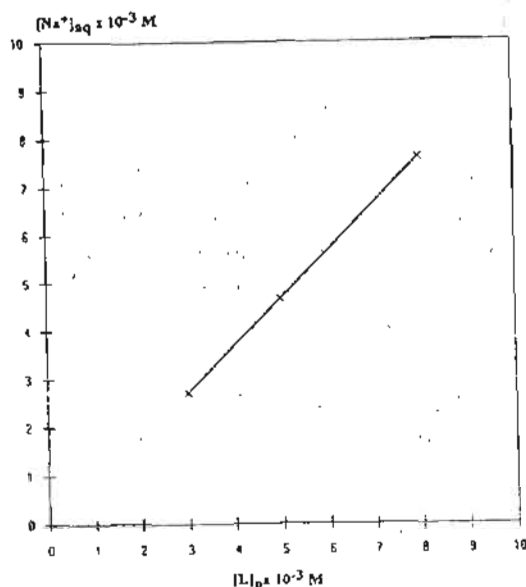
FIGURE 2 : *Exchange between Li+ (LiCl in the aqueous phase) and Na+ (NaL$_{OiPr}$ in the organique phase)*
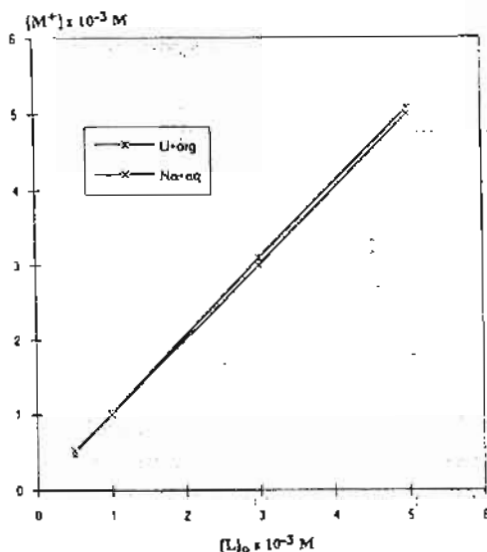
Formation of a H - L complex in the organic phase :

HL$_{OR}$ (R = Et, iPr) complexes in the organic phase are also quanti-tatively formed from H - Na exchanges in similar conditions (figure 3). In order to get additional information on the HL$_{OR}$ complex, several mass spectra investigations are carried out on HL$_{OiPr}$ organic systems. Most of the experiments show the existence of ions which can be originated by HL$_{OiPr}$ (FAB$^+$: H$_2$L$^+$ m/e = 620.9, FAB$^-$, ES$^-$: L$^-$ m/e = 619.2). However it should be noted that ES$^+$ spectra indica-te the existence of both H$_3$L$_2$$^+$ (m/e =1241.77) and H$_2$L$^+$; moreover the intensity of the corresponding signals evolve differently when the voltage increases: an increase of H$_2$L$^+$ accompanied by a decrease of H$_3$L$_2$$^+$ with an increasing voltage, indicates that H$_2$L$^+$ might be a fragmentation of H$_3$L$_2$$^+$. This behavior supports the existence of the dimer H$_2$L$_2$ in the organic phase.

FIGURE 3 : *Exchange between H^+ (HCl in the aqueous phase) and Na^+ (NaL$_{OiPr}$ in the organique phase).*

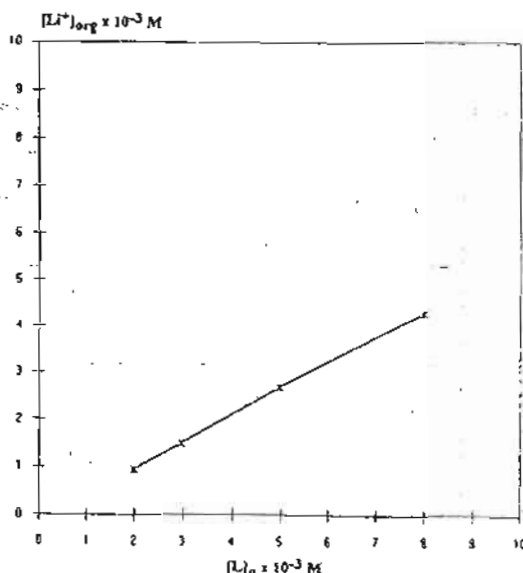|	[L]$_0$ (x 10^{-4} M)	[Li]$_{org}$ (x 10^{-4} M)	V$_{Li}$ (x 10^{-4} M/L.h)
Exp 1 L = NaL$_{OiPr}$	15.0	3.3	1.45
Exp 2 L = NaL$_{OiPr}$	30.0	7.2	3.1
Exp 3 L = LiL$_{OiPr}$	15.0	3.5	1.5

Formation of a $HLiL_2$ complex in the organic phase :

If a NaL_{OiPr} organic solution is brought into contact with an aqueous mixture of HCl (10^{-3} M) and $LiNO_3$ (1M) an ion exchange process takes place characterized by the presence of lithium in the organic phase according to a concentration ratio $[Li^+]org / [L]o = 0,5$ (figure 4). This suggest the existence and the quantitative formation of a species L : Li having 2 : 1 stoechiometry. The existence of this species is confirmed by mass spectra carried out on organic solutions originated by HL_{OiPr} in contact with $LiNO_3$ aqueous solution. Indeed the FAB^+ mass spectra as well as the ES^+ mass spectra of such solutions show the existence of species H_2LiL_2+ (m/e = 1247.3).

FIGURE 4 : *Exchange between H^+ and Li^+ mixter (LiCl / HCl in the aqueous phase) and Na^+ (NaL_{OiPr} in the organique phase)*
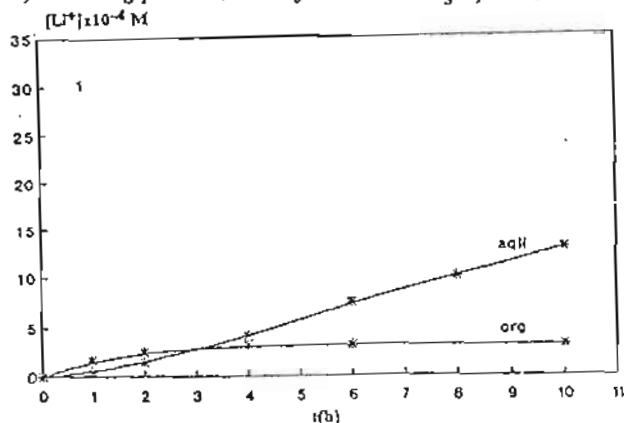
H-Li coupled counter transport :

The occurence of two phase exchange processes suggests that it is possible to transport lithium via a pH pump (figure 5 (experiment 1), figure 6 (experiment 2) figure 7 (experiment 3)). The transport kinetic is studied by following the concentration versus time in the membrane phase and in the receiving phase. Experiments are carried out with L_{OR^-} (R = iPr) . The main features of the transport are characterized by the following observations (table 2) :

TABLE 2 : *Transport of lithium through dichloroethane liquid membranes containing NaL_{OiPr} (exp1, 2) or LiL_{OiPr} (Exp 3).*

	$[L]_0$ (x 10^{-4} M)	$[Li]_{org}$ (x 10^{-4} M)	V_{Li} (x 10^{-4} M/L.h)
Exp 1 $L = NaL_{OiPr}$	15.0	3.3	1.45
Exp 2 $L = NaL_{OiPr}$	30.0	7.2	3.1
Exp 3 $L = LiL_{OiPr}$	15.0	3.5	1.5

FIGURE 5 : *Transport of lithium through dichloroethane liquid membrane containing 1,5 10^{-3} M NaL$_{OiPr}$. Source phase : 90 ml of 0.1 M LiCl aqueous solution, receiving phase : 90 ml of 0.01 M HNO$_3$ aqueous solution.*

FIGURE 6 : *Transport of lithium through dichloroethane liquid membrane containing 3. 10-3 M NaLOiPr. Source phase : 90 ml of 0.1 M LiCl aqueous solution, receiving phase : 90 ml of 0.01 M HNO$_3$ aqueous solution.*
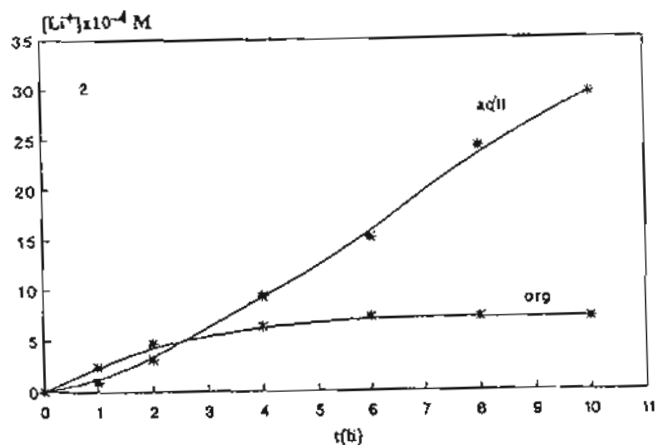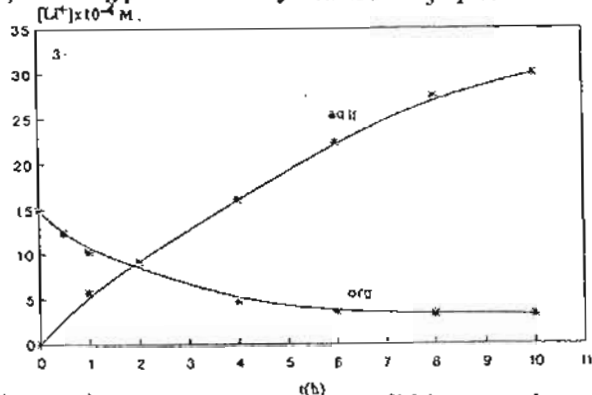
FIGURE 7 : *Transport of lithium through dichloroethane liquid membrane containing 1,5 10-3 M LiL$_{OiPr}$ Source phase : 90 ml of 0.1 M LiCl aqueous solution, receiving phase : 90 ml of 0.01 M HNO$_3$ aqueous solution.*

1) The steady state rate as well as the lithium membrane concentration are proportional to the total carrier concentration. (figure 5 and 6).

2) The lithium transport from phase I to phase II is accompanied by the counter transport of the proton characterized by the decrease of the pH in the aqueous phase I.

3) The nature of the original salt (Li or Na salt) used as carrier in equal concentration (figure 5 and figure 7) leads to an identical steady state (equal rate and equal lithium concentration in the membrane phase).

4) Mass spectra (FAB$^+$, ES$^+$) confirms the presence of HLi(L$_{OR}$)$_2$ already characterized in the two phase exchange.

5) At the steady state regime the concentration of lithium in the membrane is 1/4 of the L$_{OR}$- analytical concentration (Lo in table 2). This is consistent with the quantitative formation of HLi(L$_{OR}$)$_2$ and the quantitative decomposition of this complex at the second interface. All these observations are in agreement with the proton / lithium counter transport process which takes place via an exchange reaction which can be written :

$$H_2L_2 \; org + Li^+aq \longrightarrow HLiL_2 \; org + H^+aq$$

The schematic mechanism for the carrier mediated counter transport of the lithium and the proton is described in figure (8).

- at the interface of aqueous phase I / membrane guest salt is complexed with carrier
- the resulting lipophilic complexe diffuses across the membrane
- the release of guest salt occurs at the interface of membrane / aqueous phase II
- the free carrier diffuses back across the membrane.

<u>FIGURE 8</u> : *A schematic mechanism for the carrier mediated countertransport of a lithium and a proton*
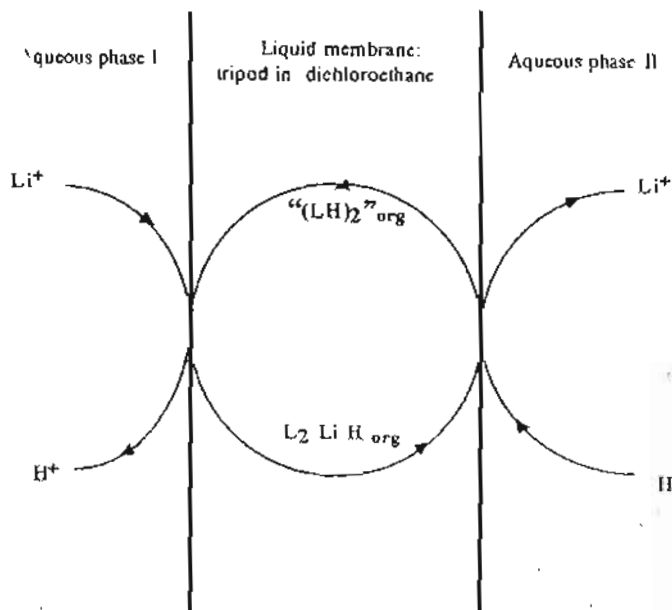
CONCLUSION

- The acidic form "LH" and the lithium salt of the tripod can be formed in the organic phase via a cation exchange process. Mass spectra measurements seem to indicate that the acidic form is dimeric.

- It is shown that the transport of Lithium takes place via a counter transport process based on a cation exchange. In a proton-lithium counter transport process it is shown that the transporting species is a dimer of formula $HLiL_2$. This species is also characterized in liquid-liquid exchange processes.

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