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Articles

Carboxylic Ionophore (Lasalocid A and A23187) Mediated Lanthanide Ion Transport across Phospholipid Vesicles†

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ABSTRACT: The transport kinetics of three lanthanide ions (viz., Pr^{3+}, Nd^{3+}, and Eu^{3+}) across dimyristoylphosphatidylcholine and dipalmitoylphosphatidylcholine unilamellar vesicles mediated by the two carboxylic ionophores lasalocid A and A23187 have been studied by proton nuclear magnetic resonance spectroscopy. Time-dependent changes in the chemical shifts of head group choline signals have been measured to calculate apparent rate constants of transport. These experiments have been done at different ionophore concentrations to determine the stoichiometry of the transporting species. The rates of transport have been found to be faster in the absence of intravesicular La^{3+} compared to those observed in its presence. The stoichiometry of the transporting species has been found to be 2:1 (ionophore:cation) for both lasalocid A and A23187 in dimyristoylphosphatidylcholine vesicles. However, stoichiometries of greater than 2 have been obtained for lasalocid A mediated lanthanide ion transport across dipalmitoylphosphatidylcholine vesicles. Possible reasons for the observations of such noninteger stoichiometries are discussed. Our results also indicated that A23187 is a more efficient carrier ionophore than lasalocid A.

Ever since the discovery that paramagnetic lanthanide ions (Pr^{3+} and Eu^{3+}) can distinguish between the nuclear magnetic resonance (NMR)[1] signals of choline protons from the internal and external surfaces of egg yolk lecithin (EYL) liposomes (Bystrov et al., 1971), their use to study the kinetics of mediated cation transport across model membranes has been steadily growing (Ting et al., 1981). A variety of both natural and synthetic ionophores have been shown by NMR (Fernandez et al., 1973; Hunt, 1975; Hunt et al., 1978; Degani et al., 1981; Donis et al., 1981; Grandjean & Laszlo, 1982, 1984) to transport paramagnetic cations (Pr^{3+}, Eu^{3+}, and Mn^{2+}) across unilamellar vesicles (ULVs) prepared by sonication of aqueous dispersions of synthetic lipids. It has also been suggested that this method can distinguish between the diffusive carrier and the pore mechanisms (Ting et al., 1981).

Extensive conformational studies in solution and in solid state have been carried out to demonstrate the diverse capabilities of the carboxylic polyether antibiotic ionophores (lasalocid A and A23187) to complex with physiologically important mono- and divalent cations and their abilities to form both the equimolar 1:1 (ionophore:cation) and the "ion sandwich" 2:1 complexes (Johnson et al., 1970; Reed & Lardy, 1972; Alpha & Brady, 1973; Degani et al., 1973; Degani & Friedman, 1974, 1975; Haynes & Pressman, 1974; Pfeiffer et al., 1974; Schmidt et al., 1974; Puskin & Gunter, 1975; Anteunis, 1976; Patel & Shen, 1976; Pfeiffer & Lardy, 1976; Shen & Patel, 1976; Chiang & Paul, 1977; Young & Gomperts, 1977; Chen & Springer, 1978; Vishwanath & Easwaran, 1983, 1985; Shastri & Easwaran, 1984). Our studies on the interaction of lanthanide ions with the carboxylic ionophore lasalocid A in acetonitrile and methanol have shown that it forms both 1:1 and 2:1 complexes with lanthanides and that their binding constants depend upon the size of the cation and the solvent polarity (Shastri et al., 1987). In spite of the observation of such nonequimolar complexes (both "ion sandwich" and "ionophore sandwich") for many ionophores in solution (Devarajan & Easwaran, 1981; Vishwanath & Easwaran, 1982, 1983, 1985; Shastri & Easwaran, 1984; Sankaram & Easwaran, 1985; Easwaran, 1985), experimental studies on their relevance to cation transport are limited

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[1] Abbreviations: DMPC, dimyristoylphosphatidylcholine; DPPC, dipalmitoylphosphatidylcholine; EYL, egg yolk lecithin; NMR, nuclear magnetic resonance; ULVs, unilamellar vesicles; MLVs, multilamellar vesicles.

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(Fernandez et al., 1973; Degani et al., 1981; Grandjean & Laszlo, 1982, 1984).

We have studied the transport kinetics of three lanthanide ions (namely, Pr^{3+}, Nd^{3+}, and Eu^{3+}) across dimyristoylphosphatidylcholine (DMPC) and dipalmitoylphosphatidylcholine (DPPC) ULVs in the liquid crystalline phase mediated by two carboxylic ionophores viz., lasalocid A and A23187, using ^1H NMR with the aim to correlate the cation complexing abilities of these ionophores with their transport characteristics. In most of the transport kinetics studies involving these ionophores, so far reported in the literature, the extravesicular medium alone contained the paramagnetic lanthanide ion (Pr^{3+} or Eu^{3+}), imposing an ionic gradient across the bilayer. In this study, experiments have been carried out both in the presence and in the absence of the intravesicular isomorphous diamagnetic lanthanide ion, La^{3+}, to examine the effect of such ionic gradients.

Materials and Methods

Sodium salt of lasalocid A, A23187, L-α-dimyristoylphosphatidylcholine, and L-α-dipalmitoylphosphatidylcholine were obtained from Sigma Chemical Co. Methanol-d_4 and D_2O were from Stohler Isotopes, and the lanthanide oxides were from Alpha Inorganics. Lanthanide nitrates were prepared from their corresponding oxides by treatment with concentrated nitric acid and recrystallization several times from double-distilled water.

Preparation of Unilamellar Vesicles. ULVs were prepared from multilamellar vesicles (MLVs) by sonication. MLVs were prepared as follows. A known amount of lipid (~50 mg) was dissolved in chloroform, and the solvent was completely removed by flushing with nitrogen gas to form a thin layer in a round-bottom flask and by drying overnight under vacuum. The lipid film was then dispersed in 2 mL of 10 mM $La(NO_3)_3$ solution in D_2O and was shaken thoroughly on a vortex mixer during which the sample temperature was maintained about 10 °C above the gel to liquid crystalline phase transition temperature of the lipid. The MLVs so formed were subjected to sonication on a Branson B-12 sonicator with a microtip at power level of 60% for 10 min with 10-s pulses. To this vesicle solution was added 2 mL of 10 mM $Ln(NO_3)_3$ (Ln represents Pr, Eu, or Nd) solution to equalize the ionic strength on both sides of the bilayer. In one set of experiments lanthanide ions were present only in the extravesicular medium. In all the experiments, ionophores were added as methanol (deuteriated) solutions after sonication to obtain the desired lipid:ionophore ratios.

^1H NMR spectra were recorded on a Varian FT-80A NMR spectrometer equipped with a variable-temperature accessory unit. The size of the vesicles was determined by measuring the ratio of the intensities of the outer and inner choline proton signals. The integrity of the lipid structure was confirmed by thin-layer chromotgraphy with 6.9:7.5:5.0 $CHCl_3$–CH_3OH–7 M NH_4OH as the eluent before and after the experiments.

Analysis of Kinetic Data. When the paramagnetic lanthanide ions are added to the vesicle solution, the signal from the outer head group choline of the lipid bilayer shifts either downfield (e.g., Pr^{3+} and Nd^{3+}) or upfield (e.g., Eu^{3+}). The chemical shift of the outer signal is linearly dependent on the concentration of the Ln^{3+} ion (Hunt et al., 1978; Bergelson, 1978) under our experimental conditions. As the ionophore-mediated transport goes on, the Ln^{3+} ions are exchanged with the isomorphous diamagnetic La^{3+} ions in the intravesicular space. This results in a shift of the inner choline signal toward the outer signal, which is also linearly dependent on the concentration of the Ln^{3+} ion (Ting et al., 1981). The apparent

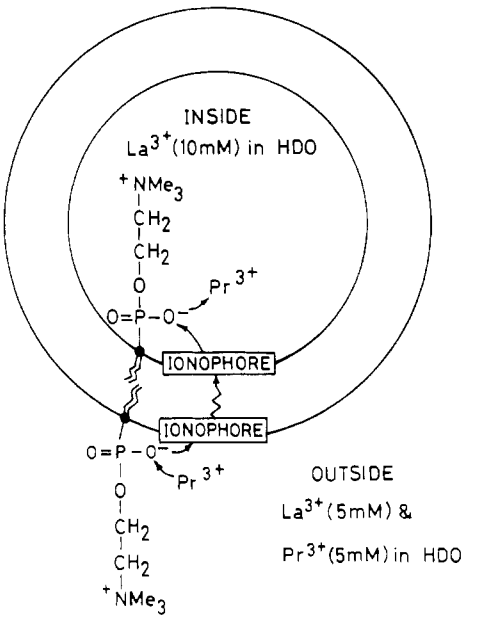

FIGURE 1: Schematic representation of the NMR kinetics experiment.

rate constant for transport, when the change in the inner choline chemical shift ($\Delta\delta$) changes linearly with time, is given by (Lee & Chan, 1977)

$$d(\Delta\delta)/dt = k'(\Delta\delta)$$

i.e., the slope of the straight line obtained by plotting ln $(\Delta\delta_0/\Delta\delta_t)$ vs. time, where the subscripts 0 and t refer to zero time and at time t, respectively. The stoichiometry of the transporting species can be determined from the rate constants for transport at various concentrations of the ionophore. If the stoichiometry is n, then for the reaction

$$nS + M_o \underset{}{\overset{k}{\rightleftharpoons}} nS + M_i$$

where M_o and M_i are the concentrations of Ln^{3+} ion outside and inside the vesicle, respectively, and S is the ionophore

$$k = [S]^n k'$$

or

$$\log k' = \log k - n \log [S]$$

Since k is constant, the slope of the straight line obtained by plotting log k' vs. log [S] gives the stoichiometry of the transporting species, n.

Results

Studies on A23187. The experimental strategy used to follow the transport kinetics by NMR is schematically shown in Figure 1. The transport kinetics of Pr^{3+}, Nd^{3+}, and Eu^{3+} ions across DPPC ULVs containing 10 mM $La(NO_3)_3$ in the intravesicular medium and 5 mM $Ln(NO_3)_3$ plus 5 mM $La(NO_3)_3$ in the extra vesicular medium at different concentrations of A23187 (in the range of 3000:1 to 500:1) have been followed by ^1H NMR at 60 °C. The kinetics of transport are followed by recording the spectra at regular intervals immediately after addition of the ionophore. As the paramagnetic lanthanide ion is transported inside with time, the inner choline proton signal shifted toward the outer choline proton signal with concomitant reduction in intensity and increase in line width. The transport is considered to be over when the inner choline signal merged with the outer signal and could no longer be identified. The spectra of control samples (i.e., without the ionophore) have also been periodically recorded, and no

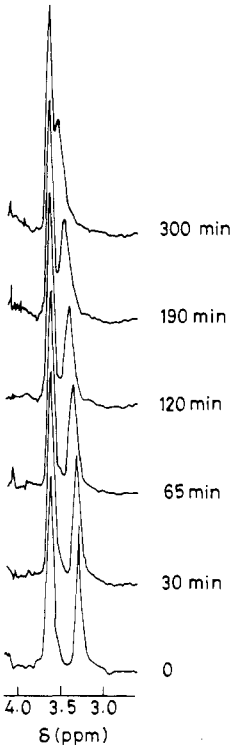

FIGURE 2: Time-dependent changes in the choline proton region for DPPC–A23187–Pr^{3+} system at 60 °C (lipid:ionophore = 1000:1).

Table I: Rate Constants for A23187-Mediated Ln^{3+} Transport across DPPC ULVs at 60 °C ([DPPC] = 18 mM; with Intravesicular La^{3+})

cation	[A23187] (μM)	lipid: ionophore	rate constant, k ($\times 10^3$ min^{-1})	slope of the double log plot
Pr^{3+}	17.28	1000:1	7.08	2.01 (±0.15)
	20.16	900:1	9.33	
	23.04	800:1	11.48	
	29.95	700:1	15.85	
Nd^{3+}	5.76	3000:1	0.63	2.10 (±0.05)
	11.52	1500:1	2.77	
	14.40	1250:1	5.84	
	17.28	1000:1	6.67	
	23.04	800:1	12.85	
Eu^{3+}	5.76	3000:1	1.67	2.17 (±0.08)
	8.64	2000:1	3.50	
	11.52	1500:1	7.24	
	17.28	1000:1	16.66	

changes have been observed in the inner choline proton signal during the time course of the kinetics. The time-dependent changes in the choline proton region during the Pr^{3+} transport mediated by A23187 at a lipid:ionophore ratio of 1000:1 across DPPC vesicles at 60 °C are shown in Figure 2.

The initial slopes of the lines obtained by plotting ln $(\Delta\delta_0/\Delta\delta_t)$ vs. time yield the apparent rate constants (k') at different concentrations of the ionophore. A double logarithmic plot of the concentration of the ionophore against the rate constants is used to calculate the stoichiometry of the transporting species. The values so obtained are given in Table I, and these values suggest that 2:1 is the stoichiometry of the transporting species in the case of all the three cations. Figure 3 shows ln $(\Delta\delta_0/\Delta\delta_t)$ vs. time plots at various concentrations of the ionophore A23187 mediated Nd^{3+} transport across DPPC ULVs with a double logarithmic plot shown in the inset.

The above set of experiments have been repeated with DPPC vesicles containing no intravesicular La^{3+} ions, and the data have been processed as before. The rates of transport at a given concentration of the ionophore are found to be much

Table II: Rate Constants for A23187-Mediated Ln^{3+} Transport across DPPC ULVs at 60 °C ([DPPC] = 18 mM; without Intravesicular La^{3+})

cation	[A23187] (μM)	lipid: ionophore	rate constant, k ($\times 10^3$ min^{-1})	slope of the double log plot
Pr^{3+}	6.00	3000:1	4.16	2.04 (±0.03)
	8.40	2000:1	8.51	
	12.00	1500:1	15.80	
	18.00	1000:1	43.30	
	21.60	833:1	53.70	
Nd^{3+}	6.00	3000:1	6.43	2.25 (±0.05)
	8.40	2000:1	12.99	
	12.00	1500:1	18.10	
	18.00	1000:1	28.80	
	21.60	833:1	48.80	
Eu^{3+}	6.00	3000:1	9.55	1.99 (±0.10)
	8.40	2000:1	20.00	
	12.00	1500:1	43.30	
	18.00	1000:1	60.00	
	21.60	833:1	89.10	

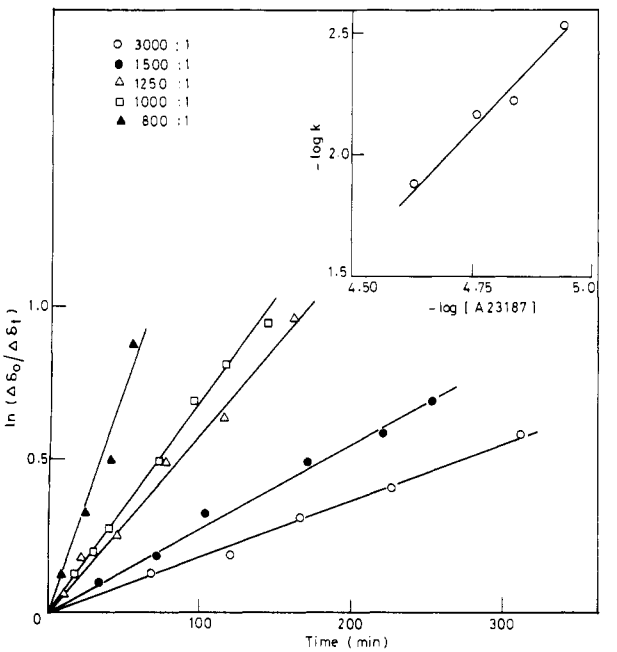

FIGURE 3: ln $(\Delta\delta_0/\Delta\delta_t)$ vs. time plots for DPPC–A23187–Nd^{3+} system. (Inset) log k vs. log [A23187].

faster in the absence of intravesicular La^{3+} compared to those observed in the presence of intravesicular La^{3+}. The stoichiometry of the transporting species was found to be 2:1 for all the three lanthanides as before.

The transport kinetics of lanthanides by A23187 across DMPC vesicles containing intravesicular La^{3+} have been studies at 40 °C. The spectral changes observed in the choline signal for Nd^{3+} transport at a lipid:ionophore ratio of 1000:1 are shown in Figure 4. The rate constants of transport are found to be smaller compared to those at the same concentration with DPPC ULVs (see Table III), and the stoichiometry of the transporting species is found to be 2:1 in this case as well.

Studies on Lasalocid A. Lasalocid A mediated lanthanide ion transport across DMPC and DPPC ULVs with intravesicular La^{3+} has been followed at 40 and 60 °C, respectively, at various concentrations of the ionophore (in the range 500:1 and 75:1). The spectral changes observed in the choline proton region for Eu^{3+} transport across DMPC ULVs at a lipid: ionophore ratio of 100:1 are shown in Figure 5. The data are treated in the same fashion as before to obtain the apparent rate constants and the stoichiometry of the transporting species.

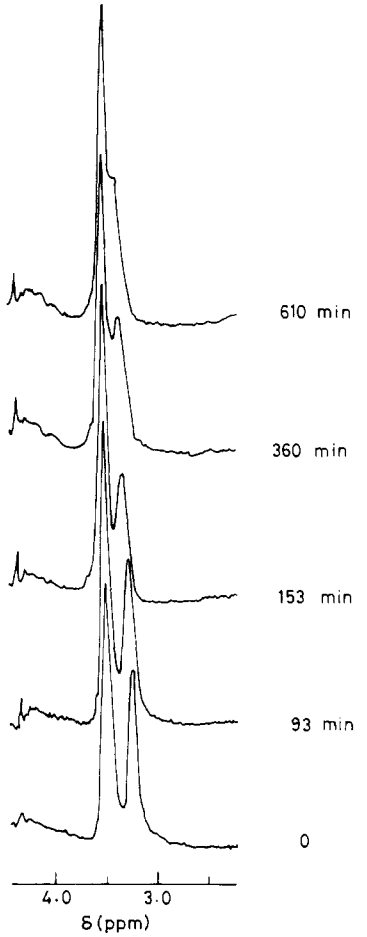

FIGURE 4: Time-dependent changes in the choline proton region for DMPC–A23187–Nd^{3+} system at 40 °C (lipid:ionophore = 1000:1).

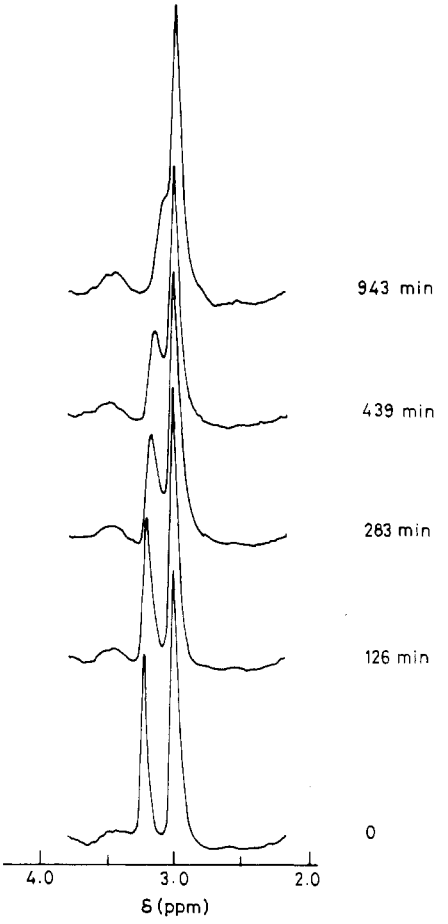

FIGURE 5: Time-dependent changes in the choline proton region for DMPC–lasalocid A–Eu^{3+} system at 40 °C (lipid:ionophore = 100:1).

Table III: Rate Constants for A23187-Mediated Ln^{3+} Transport across DMPC ULVs at 40 °C ([DMPC] = 18 mM; with Intravesicular La^{3+})

cation	[A23187] (mM)	lipid: ionophore	rate constant, k ($\times 10^3$ min^{-1})	slope of the double log plot
Pr^{3+}	0.012	1500:1	0.85	1.85 (±0.14)
	0.018	1000:1	1.65	
	0.022	833:1	2.04	
	0.029	625:1	3.53	
	0.036	500:1	5.75	
Nd^{3+}	0.012	1500:1	0.57	2.25 (±0.12)
	0.018	1000:1	1.56	
	0.022	833:1	2.54	
	0.027	666:1	3.86	
	0.036	500:1	7.87	
Eu^{3+}	0.012	1500:1	0.63	2.04 (±0.08)
	0.018	1000:1	1.27	
	0.022	833:1	2.16	
	0.027	666:1	3.32	
	0.036	500:1	4.62	

Table IV: Rate Constants for Lasalocid A Mediated Ln^{3+} Transport across DPPC ULVs at 60 °C ([DPPC] = 18 mM; with Intravesicular La^{3+})

cation	[LS] (mM)[a]	lipid: ionophore	rate constant, k ($\times 10^3$ min^{-1})	slope of the double log plot
Pr^{3+}	0.036	500:1	0.061	2.56 (±0.20)
	0.045	400:1	0.487	
	0.060	300:1	1.850	
	0.090	200:1	3.445	
	0.180	100:1	8.300	
Nd^{3+}	0.045	400:1	0.087	2.55 (±0.18)
	0.060	300:1	0.250	
	0.090	200:1	0.680	
	0.180	100:1	3.160	
Eu^{3+}	0.045	400:1	0.170	2.58 (±0.15)
	0.060	300:1	0.390	
	0.090	200:1	0.990	
	0.180	100:1	1.350	

[a] LS stands for lasalocid A.

The rate constants for transport mediated by lasalocid A are much smaller for DPPC ULVs compared to the case of A23187, and they are further reduced in the experiments with DMPC ULVs (see Tables IV and V). In the case of DMPC ULVs the stoichiometry of the transporting species has been found to be 2:1 whereas values larger than 2:1 have been obtained with DPPC ULVs.

Discussion

The results of the kinetic experiments show that both A23187 and lasalocid A permit the passage of Pr^{3+}, Nd^{3+}, and Eu^{3+} ions across both DMPC and DPPC vesicles. In all the cases, the chemical shift and the line width of the inner choline proton signals change with time in a manner typical of "slow mediator exchange" (Ting et al., 1981). Such spectral changes are consistent with a model in which the transmembrane cationic motions are slow on the NMR time scale. A plausible mechanism, therefore, for carboxylic ionophore induced enhancement of cation transport would be a carrier mechanism.

Analysis of the ionophore concentration-dependent rate constants suggests that an "ion sandwich" (2:1) complex is the transporting species for Ln^{3+} transport across DMPC and DPPC vesicles mediated by A23187 (see Tables I–III). The solution conformation studies of ion sandwich complexes of A23187 (Deber & Pfeiffer, 1976; Pfeiffer et al., 1974) with

Table V: Rate Constants for Lasalocid A Mediated Ln^{3+} Transport across DMPC ULVs at 40 °C ([DMPC] = 18 mM; with Intravesicular La^{3+})

cation	[LS] (mM)[a]	lipid: ionophore	rate constant, k ($\times 10^3$ min^{-1})	slope of the double log plot
Pr^{3+}	0.030	500:1	0.022	2.27 (±0.20)
	0.045	400:1	0.116	
	0.060	300:1	0.239	
	0.090	200:1	0.648	
	0.180	100:1	2.728	
Nd^{3+}	0.047	380:1	0.098	2.09 (±0.18)
	0.063	285:1	0.148	
	0.094	190:1	0.173	
	0.189	95:1	0.503	
	0.283	60:1	7.002	
Eu^{3+}	0.041	435:1	0.016	2.01 (±0.08)
	0.052	350:1	0.019	
	0.069	260:1	0.023	
	0.103	175:1	0.052	
	0.207	90:1	0.155	
	0.310	60:1	1.242	

[a] LS stands for lasalocid A.

divalent cations are in accordance with this observation, especially when one bears in mind that the cation is best shielded when wrapped by two apposing ionophore molecules. The formation of a 2:1 complex as the transporting species is suggestive of a relay carrier mechanism (Ivanov et al., 1975). The cation transporting species, whether 1:1 or 2:1 complexes, are electroneutral and hence are probably ion paired with the nitrate anions for charge neutralization.

Presence of intravesicular La^{3+} has a dramatic effect on the observed rate constants of Ln^{3+} transport. The apparent rate constants calculated at a given ionophore:lipid ratio, when the La^{3+} is absent in the inner pools of DPPC vesicles, are 5–10 orders of magnitude larger than when it is present (e.g., compare Tables I and II). The process monitored here with intravesicular La^{3p} is one that maintains electroneutrality, which is brought about by a $Ln^{3+}_{out} \rightleftharpoons Ln^{3+}_{in}$ exchange. When La^{3+} is absent inside, a 2:1 complex transports inside and comes back as the free monomer. The molecular weight of the free monomer is about 2.4 times less than that of the 2:1 complex, and hence, the free monomer diffuses back faster. This factor probably brings the enhancement in the rate constants when La^{3+} is not present in the intravesicular space. Indeed, it has been shown that the rate constant for transport of the free acid (28 s^{-1}) is much greater than that for the 2:1 Ca^{2+}–A23187 complex (0.1–0.3 s^{-1}) (Kolber & Haynes, 1981).

Lasalocid A behaves in a similar fashion. It transports the Ln^{3+} ions via a 2:1 complex across the DMPC ULVs. Interestingly, exceptions to the general observation of a 2:1 complex as the transporting entity are found for this ionophore in DPPC vesicles where noninteger stoichiometries larger than 2 (see Table IV) have been obtained. Possible explanations for these abnormalities within the framework of a diffusive carrier mechanism are as follows. The apparent rate constants obtained would be directly proportional to the rates of transport only when that step is the rate-limiting one. When the rates of cation complexation/decomplexation (both by ionophore and lipid) are comparable in their magnitudes to the diffusion rates, this would be no longer true (Grell et al., 1974). This competition between these rates contributes to the experimentally determined rate constants and probably results in noninteger stoichiometries for the transporting species (Hladky, 1979). A cotransport of the cation via both a 2:1 and 3:1 complex could possibly result in noninteger stoichiometries greater than 2. Although we found no evidence for the formation of 3:1 LS–Ln^{3+} complexes (Shastri et al., 1987), Chen and Springer (1978) have observed a LS_3Pr complex formation in methanol. Formation of a LS–DPPC–Ln^{3+} ternary complex more stable than the carrier–cation complex might also cause such abnormalities, although there is no evidence in favor of such ternary complexes.

In conclusion, the present studies have shown that (i) A23187 is a more efficient carrier compared to lasalocid A, (ii) the rates of transport are dependent on the presence or absence of the intravesicular La^{3+}, and (iii) the stoichiometry of the transporting species is a nonequimolar 2:1 complex for both A23187 and lasalocid A. Since the paramagnetic lanthanide ions are considered to be good substituents for the physiologically important divalent cations (Evans, 1983), the carboxylic ionophores might bring about the divalent cation transport via a nonequimolar 2:1 complex in biological membranes as well.

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Registry No. DMPC, 18194-24-6; DPPC, 63-89-8; A23187, 52665-69-7; Pr, 7440-10-0; Nd, 7440-00-8; Eu, 7440-53-1; lasalocid A, 25999-31-9.

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Influence of Solvent and of Cation Size on the Conformations of Lasalocid A–Lanthanide(III) Ion Complexes: Circular Dichroism and Fluorescence Studies†

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ABSTRACT: The interaction of lanthanide(III) nitrates (La^{3+} to Lu^{3+}) with the carboxylic ionophore lasalocid A (LS) has been studied by circular dichroism (CD) and fluorescence spectroscopic techniques in acetonitrile and in methanol. Analysis of the CD data in acetonitrile has revealed the coexistence of both 1:1 (ionophore:cation) and 2:1 complexes in solution. For 1.22 Å > ionic radius > 1.13 Å, 1:1 complexes are preferred, and for 1.13 Å > ionic radius > 1.03 Å, 2:1 complexes are preferred. Induced CD bands for Ln^{3+} ions have been observed upon binding to LS in acetonitrile. The LS–Ln^{3+} complexes are less stable in methanol than in acetonitrile. CD spectral changes showed that the conformations of the complexes in methanol are different from those in acetonitrile. The complexes have rather open conformations in methanol compared to those in acetonitrile. The results underscore the importance of ionic radius, solvent environment, and ionization state of LS in determining the conformations of the ionophore–cation complexes.

Among the carrier ionophores, a carboxylic polyether antibiotic, lasalocid A (LS)[1] (Figure 1), has been the subject of extensive studies because of its diverse cation binding abilities with physiologically important monovalent and divalent cations and its transporting properties (Alpha & Brady, 1973; Degani et al., 1973; Degani & Friedman, 1974; Haynes & Pressman, 1974; Shen & Patel, 1976; Patel & Shen, 1976). By use of nuclear magnetic resonance (NMR) spectroscopy, it has been shown to transport Pr^{3+} ions across egg yolk lecithin (EYL) model membranes as a diffusive carrier with the transporting species forming a nonequimolar 2:1 complex (Fernandez et al., 1973). The conformation of the LS–Pr^{3+} complex in methanol has been studied with the aid of circular dichroism (CD), fluorescence, and NMR spectroscopic methods (Chen & Springer, 1978). These studies have shown that Pr^{3+} ion binds mainly to the salicylic acid moiety of the ionophore molecule forming a tris complex (LS_3Pr). However, Richardson and Dasgupta (1981) have, from their ultraviolet (UV) fluorescence, and circular polarization of luminiscence (CPL) studies on the interaction of Pr^{3+}, Nd^{3+}, Eu^{3+}, Tb^{3+}, and Gd^{3+} ions with LS anion in methanol, arrived at the conclusion that LS–Ln^{3+} complexes are of 1:1 stoichiometry and the coordination to the cation is provided by the carbonyl group, the tetrahydrofuran, the tetrahydropyran, and the two hydroxyl group oxygens besides the carboxylate anion. In view of the recent observations that the conformations of the LS–cation complexes are solvent polarity dependent (Vishwanath & Easwaran, 1983, 1985; Shastri & Easwaran, 1984), it is of interest to investigate the stoichiometries and conformations of LS–cation complexes in different solvents of varying polarity. The lanthanide series offers the unique advantage of controlling the size of the cation in steps of about 0.2 Å without any changes in the charge, which is another important factor that governs the conformations of the LS–cation complexes (Alpha & Brady, 1973; Shastri, 1985). In this paper, we present the results of our CD and fluorescence studies on the interaction of lanthanide nitrates with LS in acetonitrile and methanol.

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[1] Abbreviations: CD, circular dichroism; CPL, circular polarization of luminescence; EYL, egg yolk lecithin; LS, lasalocid A (free acid); NMR, nuclear magnetic resonance; UV, ultraviolet.

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