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Complex Formation between 2,9-Dihydroxy-1,10-diphenoxy-4,7-dithiadecane and La^{3+}, UO_2^{2+}, Ce^{3+}, and Y^{3+}Cations in Acetonitrile–Ethyl Acetate Binary Media as Studied by Conductometry[1]

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Abstract—Complexation between the 2,9-dihydroxy-1,10-diphenoxy-4,7-dithiadecane (DHDPDTD) ligand and La^{3+}, UO_2^{2+}, Ce^{3+}, and Y^{3+} cations has been studied by means of conductometry in acetonitrile–ethyl acetate binary mixtures over a range of temperature. Formation of the 1 : 1 complexes has been confirmed, and the complexes stability constants have been determined taking advantage of GENPLOT software. The complexes stability is affected by the metal ion nature and the solvent composition. The ligand selectivity towards metal ions depends on the solvent composition. In detail, the complexes stability decreases in the $Ce^{3+} \approx UO_2^{2+} > Y^{3+} > La^{3+}$ series in pure acetonitrile at 15°C, whereas the stability series in pure ethyl acetate at the same temperature is as follows: $UO_2^{2+} > La^{3+} \approx Y^{3+} > Ce^{3+}$. Standard thermodynamic parameters of the complexation reaction ($\Delta_c H^0$ and $\Delta_c S^0$) have been determined and found to be affected by the metal ion nature and the binary solvent composition.

Keywords: conductometry, acetonitrile, ethyl acetate, binary solvent, complex formation

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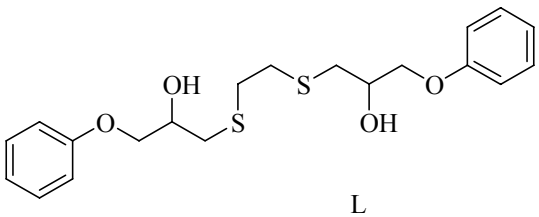
Open-chain and macrocyclic ethers containing several different heteroatoms (nitrogen, oxygen, and sulfur) form an important class of ligands capable of efficient complex formation with heavy metal ions [1, 2]. In view of requirements of environmental monitoring, determination of heavy metal cations using such complex formation reactions has recently attracted emerging attention [3, 4]. 2,9-Dihydroxy-1,10-diphenoxy-4,7-dithiadecane (hereafter designated as L) has been demonstrated to efficiently coordinate to transition and heavy metal cations [5]. Numerous experimental studies have been devoted to complexation between macrocyclic ligands and various metal cations in pure and binary solvents using (for example, [6–9]); however, to our knowledge, there has been no data on complexation between 2,9-dihydroxy-1,10-diphenoxy-4,7-dithiadecane and metal cations (Scheme 1).

A number of physico-chemical techniques have been applied to study metal ions complexation [10–18]; conductometry has been recognized as a sensitive, simple, and cheap method to elucidate stoichiometry, stability, selectivity and thermodynamics of the complexes formation in solution. The mentioned parameters are often affected by nature and composition of the solvent [19–21]. In the present paper, we report on experimental study of complexation between 2,9-dihydroxy-1,10-diphenoxy-4,7-dithiadecane (L) and La^{3+}, UO_2^{2+}, Y^{3+}, and Ce^{3+} $[M]^{n+}$ cations in acetonitrile–ethyl acetate binary mixtures over a range of temperature taking advantage of conductometry method.

Scheme 1.



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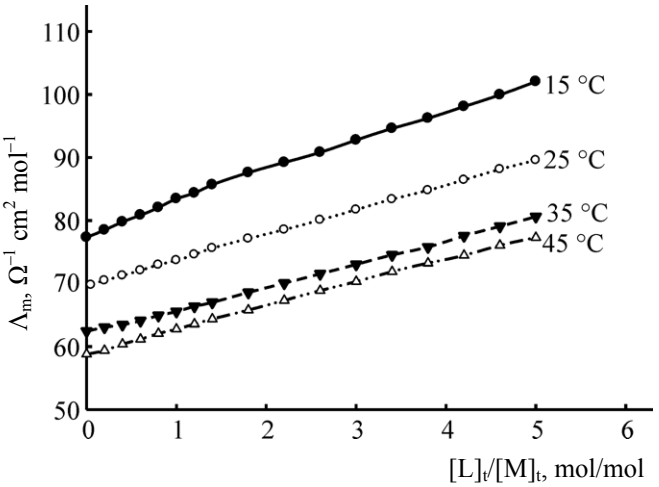

Fig. 1. Molar conductance of the system as function of the [L]/[La^{3+}] plot at 50 mol % of MeCN in the solvent and at different temperatures.

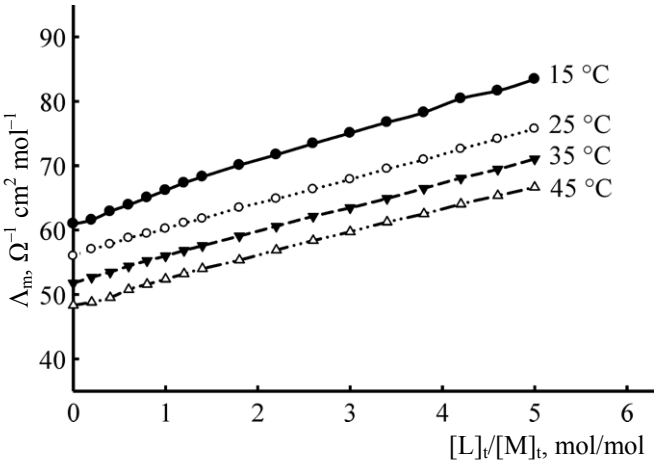

Fig. 2. Molar conductance of the system as function of the [L]/[UO_2^{2+}] plot at 50 mol % of MeCN in the solvent and at different temperatures.

EXPERIMENTAL

$UO_2(NO_3)_2 \cdot 6H_2O$, $La(NO_3)_3 \cdot 6H_2O$, $Y(NO_3)_3 \cdot 6H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, acetonitrile MeCN, and ethyl acetate AcOEt (all from Merck Company) of the highest purity available were used without purification.

2,9-Dihydroxy-1,10-diphenoxy-4,7-dithiadecane (L). 1,2-Dithioethane (13.5 mL, 160 mmol) and ethylene oxide (300 mmol) were added to a solution of potassium carbonate (50 g, 350 mmol) in 65 mL of water. The mixture was refluxed in an oil bath upon continuous stirring. The reaction course was monitored via TLC (silica gel 60 F254, benzene–ethyl acetate 1 : 1). After the reaction was complete, the mixture was cooled down; the precipitated product was filtered off, washed with water (3 × 50 mL), and dried in an oven at 50–55°C during 4 h to obtain white solid substance; mp 79°C (from carbon tetrachloride). ^{1}H NMR spec-trum, δ_H, ppm: 2.39 br (2H, O<u>H</u>), 2.71 d.d (2H, *J* 7.2 and 15.5 Hz, CH_2S), 2.79 d.d (2H, *J* 4.2 and 17.8 Hz, CH_2S), 2.85 s (4H, SCH_2CH_2S), 4.04 d.d (2H, *J* 6.2 and 15.8 Hz, CH_2O), 4.12 m (2H, CH), 4.15 d.d (2H, *J* 4.1 and 13.7 Hz, CH_2O), 6.84–7.38 m (10H, Ph). ^{13}C NMR spectrum, δ_C, ppm: 33.10, 35.80, 69.91, 70.92, 114.90, 121.09, 120.74, 159.2. Mass spectrum (EI), *m*/*z* (rel. intensity): 394 [M^+], 287 (85%) $C_{13}H_{19}O_3S_2$ 243 (86%) $C_{11}H_{15}O_2S_2$, 211 (90%) $C_{11}H_{15}O_2S$, 75 (100%) C_6H_5. Found, %: C 61.13; H 6.72; S 16.07. $C_{20}H_{26}O_4S_2$. Calculated, %: C 60.88; H 6.64; S 16.25. Other details are to be found in [22].

Conductance was measured using a Jenway 4510 digital conductometer at 1 kHz. Constant temperature (±0.1°C) was maintained with a connected circulating water bath (LAUDA). The tested solution was placed in a double-glass water jacket cell and was continuously stirred with a magnetic bar. The conductance measuring cell consisted of two platinum electrodes; the cell constant was of 0.98 cm^{-1}.

The $(ML)^{n+}$ complexes formation and stability was studied via conductometric titration of 20 mL of the metal salt solution (1×10^{-4} mol/L) with a ligand solution (2×10^{-3} mol/L; the solvent and temperature being consistent with those of the metal ion solution) to about five-fold excess of the ligand with respect to the metal ion.

RESULTS AND DISCUSSION

Complexation between 2,9-dihydroxy-1,10-diphenoxy-4,7-dithiadecane (L) with La^{3+}, UO_2^{2+}, Y^{3+}, and Ce^{3+} cations $[M]^{n+}$ in acetonitrile–ethyl acetate (MeCN–AcOEt) binary solvents was investigated by plotting the molar conductance (Λ_m) as function of ratio of total molar concentrations of the ligand and the cation ($[L]_t/[M]_t$). The data demonstrated that the 1 : 1 complexes were formed in the cases of all the studied systems. As representative examples, the data for complexation with La^{3+} and UO_2^{2+} at 50 mol % MeCN in the solvent are shown in Figs. 1 and 2, respectively. The data for the other metal ions studied in this work were similar and are omitted for clarity.

As seen in Figs. 1 and 2, the molar conductivity gradually increased upon addition of the ligand to the salt solution. That was an indication that the ions in the

Table 1. Formation constants of the studied $[ML]^{n+}$ complexes log K_f as functions of temperature and the solvent composition

Cation and solvent nature (molar ratio in the cases of binary solvents)	log K_f ± SD			
	15°C	25°C	35°C	45°C
		UO_2^{2+}		
MeCN	3.02±0.20	2.72±0.19	fitting failed	2.83±0.11
MeCN–AcOEt (3 : 1)	3.05±0.10	2.74±0.11	2.72±0.17	2.82±0.09
MeCN–AcOEt (1 : 1)	2.65±0.08	2.72±0.12	2.78±0.10	2.82±0.08
MeCN–AcOEt (1 : 3)	2.81±0.08	2.80±0.08	2.76±0.10	2.73±0.11
EtOAc	2.93±0.10	2.75±0.12	3.04±0.11	2.77±0.10
		Ce^{3+}		
MeCN	3.13±0.12	fitting failed	2.80±0.14	2.78±0.11
MeCN–AcOEt (3 : 1)	2.80±0.10	2.83±0.08	fitting failed	2.79±0.10
MeCN–AcOEt (1 : 1)	2.60±0.06	2.76±0.10	2.71±0.12	2.72±0.11
MeCN–AcOEt (1 : 3)	2.78±0.10	2.82±0.23	2.70±0.13	2.81±0.08
EtOAc	2.71±0.07	2.72±0.13	2.79±0.10	2.77±0.10
		Y^{3+}		
MeCN	2.91±0.10	2.70±0.17	2.74±0.17	2.75±0.21
MeCN–AcOEt (3 : 1)	2.73±0.12	2.75±0.11	2.77±0.09	2.76±0.11
MeCN–AcOEt (1 : 1)	2.78±0.08	2.72±0.13	2.81±0.08	2.81±0.07
MeCN–AcOEt (1 : 3)	2.63±0.11	2.70±0.14	2.78±0.09	2.71±0.13
EtOAc	2.80±0.12	2.84±0.10	2.74±0.09	2.80±0.10
		La^{3+}		
MeCN	2.82±0.11	2.62 ±0.11	2.83 ±0.11	2.75±0.14
MeCN–AcOEt (3 : 1)	2.80 ±0.09	2.75±0.12	2.78±0.11	2.70±0.13
MeCN–AcOEt (1 : 1)	2.65 ±0.10	2.74 ±0.11	2.51±0.21	2.79±0.08
MeCN–AcOEt (1 : 3)	2.80±0.08	2.77 ±0.09	2.79±0.09	2.74±0.11
EtOAc	2.85 ±0.07	2.70 ±0.13	2.81 ±0.09	2.67±0.09

complex were more mobile than the free solvated cations, probably due to the strong solvation of the cations with the MeCN–AcOEt binary solvents. The complexation between the ligand and the metal cation in the presence of the solvent S can then be described by the following equilibrium of the competitive binding of the solvent and the ligand with the cation:

$$[M^{n+}]S_x + [L]S_y \leftrightarrow [ML]^{n+}S_z + (x + y - z)S.$$

If the cation solvation number x was sufficiently high, the solvent replacement from the solvation sheath with the ligand produced less bulky and more mobile cation as compared with the solvated one, thus increasing the solution conductance. Another reason for such conductance behavior could be that in the absence of the ligand the small anions were strongly bound to the cation forming relatively immobile ion pairs or associates. The cation complexation with the ligand disrupted the ion pairs and released the free solvated anions, thus increasing the conductance.

The slope of the plots in Figs. 1 and 2 did not show any significant change upon addition of the ligand, evidencing about formation of relatively weak ML complexes with the studied cations. The 1 : 1 complexation stoichiometry was confirmed by fitting

the experimental curves with the corresponding theoretically derived functions. For example, Fig. 3 illustrates the fitting of the data from Fig. 2, showing excellent agreement; the data for other studied systems were fairly well fitted with the 1 : 1 complexation model as well.

Stability constants of the studied 1 : 1 complexes were determined over the range of temperature and the solvent composition via processing of the molar conductivity data taking advantage of the non-linear least squares optimization routine implemented in GENPLOT software [23]. Mathematical aspects of the procedure have been discussed in [24]. It should be noted that in the algorithm neglected association between M^{n+} and its counter-anion during calculation of the complexes formation constants, since the studied solutions were highly dilute. Furthermore, as the ligand concentration was always below 2×10^{-3} mol/L, the solution viscosity changes were neglected as well. The so derived stability constants of the studied $[ML]^{n+}$ complexes are listed in Table 1.

Selectivity and kinetics of the complexes formation reflecting their relative stability as well as stoichiometry may be strongly influenced by the solvent properties including its ordering, polarity, polarizability, donor-acceptor ability, etc. [25]. Such behavior may result from the changes in solvent–solvent interaction with their binary mixture composition. The intermolecular interactions in certain binary solvents have been studied in [26]. For example, the dipolar structure of the pure solvents is broken upon mixing of DMF with MeCN due to the strong intermolecular dipole–dipole interactions [27]. Hydrogen bonding interaction between MeCN and MeOH molecules (K_{as} =1.23) has been revealed in their binary mixtures [28]. Since dielectric constant of AcOEt (ε = 6.02) is much lower than that of MeCN (ε = 36), we expected that stability of the complexes studied in this work should be increased with more of AcOEt in the binary solvents.

However, from the data collected in Table 1 it is to be seen that, contrary to our expectations, stability constants of the studied complexes was only marginally dependent on the solvent composition. Furthermore, in most of the cases the effects of temperature and the cation nature did not fall outside the confidence limits of the stability constant determination.

Even though the observed effects were not substantial, certain influence of the solvent composition could be revealed when analyzing the stability

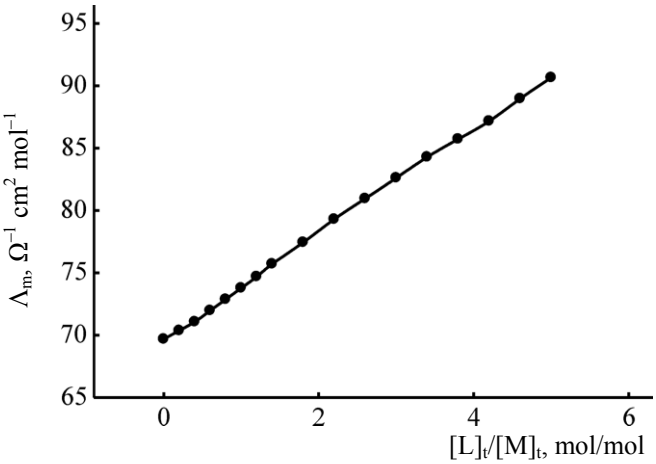

Fig. 3. Fitting (line) of the experimental data (markers) from Fig. 2 (T = 25°C) with the 1 : 1 complexation model.

constants obtained at 15°C. In particular, the complexes stability obeyed the following cations series: $Ce^{3+} \approx UO_2^{2+} > Y^{3+} > La^{3+}$ (in MeCN) and $UO_2^{2+} > La^{3+} \approx Y^{3+} > Ce^{3+}$ (in AcOEt). Hence, the selectivity of the ligand for the studied metal cations was somewhat affected by the nature of the solvent.

Overall, the UO_2^{2+} complex was more stable as compared to the other studied $[ML]^{3+}$ complexes. It has been commented that ligands containing oxygen donor atom(s) generally form stronger complexes with alkaline and alkaline-earth metal cations, whereas sulfur-containing ligands efficiently bind heavy metal cations [29]. The ligand studied in this work contained four oxygen and two sulfur sites, but the non-bonding electrons of the oxygen atoms involved in resonance with the aromatic rings interacted weakly with cations; therefore, the sulfur hetero atoms acting as soft base determined the stronger complex formation with soft UO_2^{2+} in most of the studied solvents.

The stability constants values shown in Table 1 were recalculated into the corresponding Gibb's free energy of the complexes formation, and analysis of its temperature behavior further gave standard enthalpy and entropy of the complexes formation assuming that the components C_p were constant over the considered temperature range. The calculated standard thermodynamic parameters are summarized in Table 2. In most cases the complex formation enthalpy was close to zero, and the studied complexation could be considered athermal. However, the complex formation entropy was positive, and the complexation was entropy-driven. The increase of the system entropy in

Table 2. Thermodynamic parameters of the studied $[ML]^{n+}$ complexes formation as functions of the solvent composition

Cation and solvent nature (molar ratio in the cases of binary solvents)	$\Delta_c G^0$, kJ/mol	$\Delta_c H^0$, kJ/mol	$\Delta_c S^0$, J mol^{-1} K^{-1}
		UO_2^{2+}	
MeCN	–15.52±1.10	~0	52.05±3.69
MeCN–AcOEt (3 : 1)	–15.64±0.63	~0	52.46±2.11
MeCN–AcOEt (1 : 1)	–15.52±0.71	9.54±0.68	84.05±0.68
MeCN–AcOEt (1 : 3)	–16.00±0.45	–5.05±0.92	36.73±2.69
EtOAc	–15.70±0.66	~0	52.66±2.21
		Ce^{3+}	
MeCN	poor fit	–21.99±5.79	poor fit
MeCN–AcOEt (3 : 1)	–16.14±0.46	~0	54.13±1.54
MeCN–AcOEt (1 : 1)	–15.77±0.56	~0	52.89±1.88
MeCN–AcOEt (1 : 3)	–16.08±1.31	~0	53.93±4.39
EtOAc	–15.52±0.70	~0	52.05±2.35
		Y^{3+}	
MeCN	–15.42±0.98	~0	51.72±3.29
MeCN–AcOEt (3 : 1)	–15.72±0.61	~0	52.73±2.05
MeCN–AcOEt (1 : 1)	–15.51±0.75	~0	52.02±2.52
MeCN–AcOEt (1 : 3)	–15.35±0.80	~0	51.48±2.68
EtOAc	–16.21±0.56	~0	54.37±1.88
		La^{3+}	
MeCN	–14.97±0.65	~0	50.21±2.18
MeCN–AcOEt (3 : 1)	–15.68±0.68	~0	52.59±2.28
MeCN–AcOEt (1 : 1)	–15.65±0.65	~0	52.49±2.18
MeCN–AcOEt (1 : 3)	–15.84±0.52	~0	53.13±1.74
EtOAc	–15.43±0.74	~0	51.75±2.48

the course of the complexes formation was well in line with the increase of the solutions molar conductance documented in Figs. 1–3 and discussed above.

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