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Solvent Influence upon Complex Formation between Different 1,8-Dioxo-octahydroxanthene Derivatives and Yttrium(III) Cation in Some Non-Aqueous Solvents Using Conductometric Method¹

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Abstract—The complexation reactions between the yttrium(III) cation and (4-chlorophenyl, phenyl, 4-nitrophenyl, 4-methylphenyl) 9-substituted 1,8-dioxo-octahydroxanthene were studied in acetonitrile (AN) and methanol (MeOH) at different temperatures using the electrical conductivity measurements. The conductance data show that the stoichiometry of all formed complexes between the Y^{3+} cation and the studied ligands is 1 : 1 [ML]. The order of stability of the complexes formed between the organic ligands and Y^{3+} cation in pure MeOH at 45°C was found to be: (3,6,6-Tetramethyl-9-(4-chlorophenyl)-1,8-dioxo-octahydroxanthene· Y^{3+}) > (3,6,6-Tetramethyl-9-(4-methoxyphenyl)-1,8-dioxo-octahydroxanthene· Y^{3+}) > (3,6,6-Tetramethyl-9-(4-methylphenyl)-1,8-dioxo-octahydroxanthene· $Y^$

octahydroxanthene Y^{3+}). The values of the standard thermodynamic parameters (ΔH_c° , ΔS_c°) for formation of the complexes were obtained from temperature dependence of the formation constants of the complexes using the van't Hoff plots. The experimental results show that the thermodynamics of the complexation reactions is influenced by the nature of solvent system and in most cases, the complexes are entropy stabilized.

Keywords: Y³⁺ cation, 1,8-dioxo-octahydroxanthene derivatives, acetonitrile, methanol conductometery **DOI:** 10.1134/S0036023616020029

Xanthene and its derivatives are an important class of heterocyclic compounds. These compounds have aroused a great interest due to the variety of biological and therapeutic properties such as: anti-bacterials, antioxidant, antifungal, antiviral, anti-inflammatory, anti-depressants, anti-malarial, photodynamic therapy and antagonists for the paralyzing action of zoxazolamine [1-7]. Furthermore, these compounds are utilized in material science as leuco-dye [8], in laser technology [9], as pH sensitive fluorescent materials for the visualization of biomolecular assemblies [10] and as rigid carbon skeletons for the construction of chiral bidentate phosphine ligands in catalytic processes [11]. Because of the vital role of the heavy metal cations in biological systems and also in industrial, the study of the complexes of these metal cations with such organic ligands is important [12]. Numerous thermodynamic studies have been carried out upon complexation processes between the macromolecule organic ligands and various metal cations using different experimental techniques [13], but to the best of our knowledge, there is no experimental data for the complexation reactions between xanthene's derivatives and the metal cations in solutions.

The complex formation between the macromolecule ligands and the metal cations has been studied by various physico-chemical techniques such as: spectrophotometry [14], NMR spectrometry [15], polarography [16, 17], potentiometry [18] and conductometry [19]. Among these methods, the conductometry has been considered as a sensitive and inexpensive method with a simple experimental arrangement. In addition, the measurements can be carried out at low solution concentrations, where the interactions between the cations and anions are known to be small [20]. Studies of different complexes in various aqueous and nonaqueous solvents show that the thermodynamic and kinetic parameters for complexation processes and even the stoichiometry of the complexes are affected by the nature and composition of the solvent system [21, 22].

In the present work, we studied the complex formation between five different derivatives of xanthenes: 3,3,6,6-Tetramethyl-9-(phenyl)-1,8-dioxo-octahydrox-

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anthene ($C_{23}H_{26}O_3$) (Scheme 1), 3,3,6,6-Tetramethyl-9-(4-methoxyphenyl)-1,8-dioxo-octahydroxanthene ($C_{24}H_{28}O_4$) (Scheme 2), 3,3,6,6-tetramethyl-9-(4chlorophenyl)-1,8-dioxo-octahydroxanthene ($C_{23}H_{25}ClO_3$) (Scheme 3), 3,3,6,6-Tetramethyl-9-(4-nitrophenyl)-1,8-dioxo-octahydroxanthene ($C_{23}H_{25}NO_5$) (Scheme 4) and 3,3,6,6-Tetramethyl-9-(4-methylphenyl)-1,8dioxo-octahydroxanthene ($C_{24}H_{28}O_3$) (Scheme 5) and Y³⁺ metal cation at different temperatures in pure AN and MeOH solvents using theconductometric method.



Scheme 1. Structure of $C_{23}H_{26}O_3$.



Scheme 2. Structure of $C_{24}H_{28}O_4$.



Scheme 3. Structure of $C_{23}H_{25}ClO_3$.



Scheme 4. Structure of $C_{23}H_{25}NO_5$.



Scheme 5. Structure of $C_{24}H_{28}O_3$.

EXPERIMENTAL

Materials

 $Y(NO_3)_3 \cdot 6H_2O$ was purchased from Merck chemical company and was used without purification. Acetonitrile and methanol both from Merck company were used with the highest purity and the organic ligands were synthesized.

General Experimental Procedure for Synthesis of the Ligands

The aldehyde (2.0 mmole), 5,5-dimethyl-1,3cyclohexanedione (4.0 mmole) and diacetoxyiodobenzene (5 mol %) were mixed in water (10 mL) at room temperature. The mixture was refluxed for the times which are given in Table 1. Completion of the reaction was monitored by TLC (Hexane : EtOAc 8 : 2). After completion of the reaction, the mixture was

Table 1. Synthesis of 9-aryl substituted 1,8-dioxo-octahydroxanthenes in aqueous media

C	Ar	O L	
\checkmark			

Entry	Ar	Product ^a	Time, min	Yield, %	mp, °C
1	C ₆ H ₅ -	3a	30	94	196—198
2	4-MeOC ₆ H ₄ -	3b	60	90	150-152
3	$4-ClC_6H_4-$	3c	60	89	210-212
4	$4-NO_2-C_6H_4$	3d	180	94	222
5	4-MeC ₆ H ₄	3e	210	91	217-218

^a All the products were well characterized by ¹H NMR and IR spectral data.

cooled to room temperature and the solid product was filtered off and dried. The purity of the ligands was checked by TLC and all these organic compounds gave satisfactory spectroscopic data.

3,3,6,6-Tetramethyl-9-phenyl-1,8-dioxo-octahydroxanthene (3a). White solid, mp: 196–198°C, IR (KBr) (ν_{max}): 3350, 2980, 1795, 1725, 1699, 1640, 1520, 1360, 1345, 1260, 1233, 1201, 1195, 850, 843 cm⁻¹.

¹H NMR (CDCl₃): $\delta_{\rm H}$ 300 MHz 1.09 (s, 6H), 1.23 (s, 6H), 2.27–2.49 (m, 8H), 5.54 (s, 1H), 7.08–7.28 (m, 5H) (Scheme 1).

3,3,6,6-Tetramethyl-9-(4-methoxyphenyl)-1,8dioxo-octahydroxanthene (3b). White solid, mp: 210–212°C, IR (KBr) (v_{max}): 3025, 2980, 1685, 1660, 1620, 1513, 1450, 1375, 1360, 1260, 1235, 1170, 1142, 1032, 1003, 840 cm⁻¹.

¹H NMR (CDCl₃): $\delta_{\rm H}$ 300 MHz 1.09(s, 6H), 1.22(s, 6H), 2.33–2.63 (m, 8H), 3.76 (s, 3H), 5.48 (s, 1H), 6.82 (d, 2H), 7.01 (d, 2H) (Scheme 2).

3,3,6,6-Tetramethyl-9-(4-chlorophenyl)-1,8-dioxooctahydroxanthene (3c). White solid, mp: 150–152°C, IR (KBr) (v_{max}): 3028, 2980, 1680, 1660, 1620, 1490, 1480, 1360, 1200, 1170, 1140, 1090, 1010, 1000, 850, 840 cm⁻¹.

¹H NMR (CDCl₃): $\delta_{\rm H}$ 300 MHz 1.12 (s, 6H), 1.27 (s, 6H), 2.33–2.49 (m, 8H), 5.54 (s, 1H), 7.01 (dd, 2H), 7.26 (dd, 2H) [23] (Scheme 3).

3,3,6,6-Tetramethyl-9-(4-nitrophenyl)-1,8-dioxooctahydroxanthene (3d). White solid, mp: 222°C; IR (KBr) (v_{max}) 3031, 2959, 1665, 1460, 1361, 1200, 1170, 855 cm⁻¹.

¹H NMR (DMSO-d₆) $\delta_{\rm H}$ 400 MHz 1.00 (s, 6H), 1.12 (s, 6H), 2.16 (dd, 4H), 2.41 (s, 4H), 4.46 (s, 1H), 7.50–7.63 (m, 2H), 8.06–8.16 (m, 2H) (Scheme 4).

3,3,6,6-Tetramethyl-9-(4-methylphenyl)-1,8-dioxooctahydroxanthene (3e). White solid, mp: 217–218°C; IR (KBr) (ν_{max}) 3020, 2960, 1661, 1465, 1365, 1205, 1175, 853 cm⁻¹.

¹H NMR (DMSO-d₆) $\delta_{\rm H}$ 400 MHz 1.03 (s, 6H), 1.12 (s, 6H), 2.07 (dd, 4H), 2.40 (s, 4H), 2.43 (s, 3H), 4.69 (s, 1H), 6.80–7.28 (m, 4H) [24] (Scheme 5).

Apparatus

The conductance measurements were performed using a digital Jenway conductometer, model 4510 at a frequency of 1 kHz in a water bath thermostat (LAUDA) with a precision of $\pm 0.1^{\circ}$ C. The electrolytic conductance was measured using a cell consists of two platinum electrodes to which an alternating potential was applied. A conductometric cell with a cell constant of 0.98 cm⁻¹ was used throughout the studies.



Fig. 1. Molar conductance versus mole ratio plots for (3,6,6-Tetramethyl-9-(4-chlorophenyl)-1,8-dioxo-octa-hydroxanthene·Y³⁺) complex in MeOH at different temperatures.

Method

The experimental procedure to obtain the formation constants of the complexes was as follow: 20 mL of $Y(NO_3)_3 \cdot 6H_2O$ (1.00 × 10⁻⁴ M) solution was placed in a titration cell and the conductance of the solution was measured. Then a step-by-step increase in the studied ligands solutions prepared in the same solvent (2.00 \times 10⁻³ M) was carried out by a rapid transfer to the titration cell using a pre-calibrated microburette and the conductance of a resulted solution was measured after each transfer at the desired temperature. This addition continued until the total concentration of the ligand was approximately five times higher than the total concentration of the studied metal ion. The titration curves were thus obtained in the form of the molar conductivity as function of the ligand to metalcation molar ratio.

RESULTS AND DISCUSSION

Conductance Studies

In order to evaluate the influence of adding the solutions of five different derivatives of xanthenes on the molar conductance of Y³⁺ cation in pure AN and MeOH, the conductivity of the solutions at a constant salt concentration (1.00 \times 10⁻⁴ mol L⁻¹) was monitored with increasing the concentration of the ligands at various temperatures. A typical series of molar conductance versus ligand/cation mole ratio plot for the formation of (3,6,6-Tetramethyl-9-(4-chlorophenyl)-1.8-dioxo-octahydroxanthene Y^{3+}) complex in pure MeOHat different temperatures is shown in Fig. 1. As it is seen from this figure, the molar conductivity gradually increases after addition of the ligand to the solution of Y^{3+} cation. This behavior indicates that the complexed form of the Y^{3+} cation is more mobile than the free solvated cation. In fact the complexation reac-

Medium/Ar	$\log K_{ m f}\pm{ m SD}^{ m a}$				
Weddung / K	15°C	25°C	35°C	45°C	
C ₆ H ₅ -					
Pure AN	2.70 ± 0.10	2.79 ± 0.09	2.50 ± 0.18	2.50 ± 0.17	
Pure MeOH	2.72 ± 0.08	2.62 ± 0.05	2.79 ± 0.09	2.55 ± 0.16	
4-MeOC ₆ H ₄					
Pure AN	2.82 ± 0.07	2.68 ± 0.16	2.50 ± 0.15	2.76 ± 0.10	
Pure MeOH	3.67 ± 0.06	2.55 ± 0.15	2.85 ± 0.08	2.71 ± 0.13	
4-MeC ₆ H ₄					
Pure AN	b	2.50 ± 0.23	2.53 ± 0.18	2.51 ± 0.20	
Pure MeOH	2.61 ± 0.10	2.53 ± 0.17	2.70 ± 0.13	2.53 ± 0.17	
4-ClC ₆ H ₄ -					
Pure AN	b	2.69 ± 0.26	b	b	
Pure MeOH	3.86 ± 0.11	b	3.60 ± 0.24	3.57 ± 0.17	
$4-NO_2-C_6H_4$					
Pure AN	2.74 ± 0.11	2.69 ± 0.13	2.53 ± 0.17	2.56 ± 0.14	
Pure MeOH	2.69 ± 0.15	2.76 ± 0.09	2.56 ± 0.17	2.55 ± 0.12	

Table 2. $\log K_{\rm f}$ values of the complexes formed between (phenyl, 4-methoxyphenyl, 4-methylphenyl, 4-chlorophenyl, 4-nitrophenyl) 9-substituted 1,8-dioxo-octahydroxanthene and Y³⁺ in AN and MeOH at different temperatures

^a SD standard deviation. ^b With high uncertainty.

tion is a competitive reaction between the ligand and the solvent molecules for the metal cation in solutions. Upon complexation of the Y^{3+} cation with the studied ligands, the ligands molecules replace the solvation sheath around the metal ion and as a result, the solvated complexes become less bulky and more mobile than the solvated cation, therefore, the molar conductance increases upon addition of the ligand to the cation solution. Similar behavior was observed in all of the other studied systems. The conductometric data show that in all studied solvent systems, the stoichi-



Fig. 2. The fitting and experimental (filled diamond).

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ometry of the complexes formed between the organic ligands and the metal cation is 1 : 1 [M : L].

The corresponding molar conductance versus $([L]_t/[M]_t)$ plots do not illustrate a considerable change in their slopes at a mol ratio of about 1, which indicate that the 1:1 complexes formed between the Y^{3+} cation and the studied ligands are relatively weak. In order to make more clear the 1:1 [M:L] complexation model, the fitting and experimental curves for (3,6,6-Tetramethyl-9-(4-chlorophenyl)-1,8-dioxooctahydroxanthene $\cdot Y^{3+}$) complex (at 15°C in pure MeOH) are shown in Fig. 2. As is evident in this figure, there is a very good agreement between the fitting and experimental data, which indicates a 1:1 stoichiometry for the complexes formed between the Y³⁺ cation and the organic synthesized ligands. The formation constants of the 1:1 complexes formed between the five synthesized ligands and Y^{3+} cation at each temperature were obtained from changes of the molar conductivity as a function of the ligand to metal cation molar ratios plots, using a non-linear least square computer program, GENPLOT [25]. It should be noted that, in the calculation of the stability constants of the complexes, association into ion pairs was considered to be negligible at the highly dilute experimental concentrations used. Since the ligand concentration in solutions was also sufficiently low ($<2.00 \times 10^{-3} \text{ mol } L^{-1}$), corrections for viscosity changes were also neglected.

The values of formation constant $(\log K_f)$ of the complexes formed between Y³⁺ cation and the studied

ligands in pure AN and MeOH at different temperatures are summarized in Table 2. As it clear from this table, the order of stability of the complexes formed between the organic ligands and Y³⁺cation in pure MeOH at 45°C is: (3,6,6-Tetramethyl-9-(4-chlorophenyl)-1,8-dioxo-octahydroxanthene·Y³⁺) > (3,6,6-Tetramethyl-9-(4-methoxyphenyl)-1,8-dioxo-octahydroxanthene·Y³⁺) > (3,6,6-Tetramethyl-9-(4-phenyl)-1,8-dioxo-octahydroxanthene·Y³⁺) \approx (3,6,6-Tetramethyl-9-(4-nitrophenyl)-1,8-dioxo-octahydroxanthene·Y³⁺) > (3,6,6-Tetramethyl-9-(4-methylphenyl)-1,8-dioxo-octahydroxanthene·Y³⁺), but in the case of pure AN at the same temperature the stability order changes to:

 $\begin{array}{ll} (3,6,6\mbox{-Tetramethyl-9-(4-methoxyphenyl)-1,8-dioxo-octahydroxanthene`Y^{3+}) > (3,6,6\mbox{-Tetramethyl-9-(4-nitrophenyl)-1,8-dioxo-octahydroxanthene`Y^{3+}) > (3,6,6\mbox{-Tetramethyl-9-(4-methylphenyl)-1,8-dioxo-octahydroxanthene`Y^{3+}) \approx (3,6,6\mbox{-Tetramethyl-9-(4-phenyl)-1,8-dioxo-octahydroxanthene`Y^{3+}) > (3,6,6\mbox{-Tetramethyl-9-(4-chlorophenyl)-1,8-dioxo-octahydroxanthene`Y^{3+}) > (3,6,6\mbox{-Tetramethyl-9-(4-chlorophenyl)-1,8-dioxo-octahydroxanthene}) > (3,6,6\mbox{-Tetramethyl-9-(4-chloroph$

[M:L] complexes formed between the Y^{3+} cation and the studied organic ligand containing different electron donor (OMe, Me) and electron acceptor (NO_2, Cl) aryl substituent in pure AN system at 35°C is the same. It seems that at this temperature, AN acts as a leveling solvent and level effect of the electron donor and electron acceptor aryl substituent in the complexation process. Moreover, the experimental results indicate that the stability order of the complexes may change with the temperature. These changes are probably due to the changes in the solvation number of the cations, ligand and even the resulting complexes with the nature of the medium and also temperature. These behavior sindicate the critical role of solvent in local structure optimization and complex stabilization in the host-guest recognition processes. Thus, the complex stability is known to vary drastically according to the nature of solvent in which the reaction occurs [26].

Thermodynamic Calculations

The thermodynamic quantities for complexations reactions between the Y³⁺ cation and the studied organic ligands were obtained from temperature dependence of the stability constants of the resulting 1 : 1 [M : L] complexes using the van't Hoff plots. The van't Hoff plots of $\ln K_f$ versus 1/T for all of the investigated systems were constructed. For example, the van't Hoff plot for (3,6,6-Tetramethyl-9-(4-phenyl)-1,8-dioxo-octahydroxanthene·Y³⁺) complex in AN is shown in Fig. 3. The values of the standard enthalpy (ΔH_c°) for the complexation reactions were calculated by the slope of the van't Hoff's isochors as suming that



Fig. 3. van't Hoff plots for (3,6,6-Tetramethyl-9-(4-phenyl)-1,8-dioxo-octahydroxanthene Y³⁺) complex in pure AN.

 $C_{\rm P}$ is equal to zero over the entire temperature range investigated. The standard Gibbs energy change $(\Delta G_{\rm c}^{\circ})$ for the complexation process was calculated from the following equation:

$$\Delta G_{c,298.15}^{\circ} = -RT\ln K_{\rm f}.\tag{1}$$

The changes in standard entropy (ΔS_c°) were calculated from the Gibb's–Helmholtz equation:

$$\Delta G_{c,298.15}^{\circ} = \Delta H_{c}^{\circ} - 298.15 \Delta S_{c}^{\circ}.$$
 (2)

The calculated standard thermodynamic parameters for the complexation reactions are summarized in Table 3. As is evident from this table, the calculated thermodynamic parameters for the complexation process between Y³⁺ cation and the synthesized organic ligands, show that in some cases, the changes in the standard enthalpy for the complexation reactions (ΔH_c°) are negligible, therefore, it seems that the complexation processes in these non-aqueous solvents are probably athermic, on the other hand, the values of the standard entropy (Δg°) in these systems are pasi

the standard entropy (ΔS_c°) in these systems are positive, therefore, the complexation reactions between the studied ligands and the metal cation in these organic solvents are entropy stabilized. But in some of the complexation systems, the changes in the standard enthalpy is negative, therefore, the complexation processes in these systems are exothermic.

CONCLUSIONS

The results obtained for the complexation reactions between five different 9-aryl substituted 1,8-dioxooctahydroxanthenes as organic ligands and Y^{3+} metal cation in methanol (MeOH) and acetonitrile (AN) at different temperatures using the conductometric method, show that the stability and thermodynamics of the complexation reactions are governed by the sol-

Medium/Ar	$\Delta G_{\rm c}^{\circ} \pm { m SD}^{\rm a}$ (25°C), kJ mol ⁻¹	$\Delta H_{\rm c}^{\circ} \pm { m SD}^{\rm a}$, kJ mol ⁻¹	$\Delta S_{\rm c}^{\circ} \pm { m SD}^{\rm a}$, J mol ⁻¹ K ⁻¹
C ₆ H ₅ -			
Pure AN	-15.97 ± 0.51	-12.42 ± 3.49	b
Pure MeOH	-14.96 ± 0.32	~0	50.18 ± 1.07
4-MeOC ₆ H ₄			
Pure AN	$-15.3 \ 3 \pm 0.93$	~0	52.09 ± 3.12
Pure MeOH	-14.54 ± 0.88	~0	48.77 ± 2.95
4-MeC ₆ H ₄			
Pure AN	-15.38 ± 0.76	-11.37 ± 4.44	b
Pure MeOH	-15.78 ± 0.52	b	b
4-ClC ₆ H ₄ -			
Pure AN	-15.38 ± 1.49	-45.19 ± 9.99	b
Pure MeOH	b	b	b
$4-NO_2-C_6H_4$			
Pure AN	-14.25 ± 1.32	~0	47.79 ± 4.46
Pure MeOH	-14.45 ± 0.99	~0	48.47 ± 3.32

Table 3. Thermodynamic parameters for complexes formed between (phenyl, 4-methoxyphenyl, 4-methylphenyl, 4-chlorophenyl, 4-nitrophenyl) 9-substituted 1,8-dioxo-octahydroxanthene and Y^{3+} in AN and MeOH

^aSD standard deviation. ^b With high uncertainly.

vent medium. According to the conductometric data, in all cases, the stoichiometry of the resulting complexes is 1:1 [ML]. The order of stability constant of the complexes formed between the studied ligands and Y^{3+} metal cation in pure MeOH at 45°C was found to (3,6,6-Tetramethyl-9-(4-chlorophenyl)-1,8be: dioxo-octahydroxanthene Y^{3+} > (3,6,6-Tetramethyl-9-(4-methoxyphenyl)-1,8-dioxo-octahydroxanthene Y^{3+} > (3,6,6-Tetramethyl-9-(4-phenyl)-1,8-dioxooctahydroxanthene $\cdot Y^{3+}$) \approx (3,6,6-Tetramethyl-9-(4nitrophenyl)-1,8-dioxo-octahydroxanthene $\cdot Y^{3+}$) (3,6,6-Tetramethyl-9-(4- Methylphenyl)-1,8-dioxooctahydroxanthene $\cdot Y^{3+}$), but in the case of AN at 45°C it changes to: (3,6,6-Tetramethyl-9-(4-methoxyphenyl)-1,8-dioxo-octahydroxanthene $\cdot Y^{3+}$ > (3,6,6-Tetramethyl-9-(4-nitrophenyl)-1, 8-dioxo-octahydroxanthene Y^{3+} > (3,6,6-Tetramethyl-9-(4-methylphenyl)-1, 8-dioxo-octahydroxanthene Y^{3+} \approx (3,6,6-Tetramethyl-9-(4-phenyl)-1,8-dioxo-octahydroxanthene Y^{3+} > (3.6.6-Tetramethyl-9-(4-chlorophenyl)-1,8-dioxo-octahydroxanthene $\cdot Y^{3+}$). The results obtained in this investigation indicate that the order of selectivity of the synthesized organic ligands for the Y^{3+} metal cation is changed by the nature of the non-aqueous solvent and even with the temperature. The standard thermodynamic parameters obtained for the complexation reactions show that in some cases, the complexation processes between the studied ligands and the metal cation are athermic but in the other cases, the complexation processes are exothermic and positive

values of entropy characterized the formation of some complexes in solution.

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