

The Thermodynamic Characteristic of Complex Formations of some metals with 3-(4-nitrophenylazo) pentan-2, 4-dione in Aqueous Ethanol Solution

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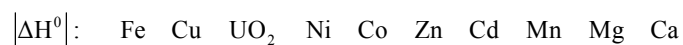
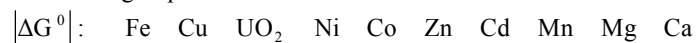
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Abstract: The method of potentiometric titrations investigates complex formation of some metals with 3-(4-nitrophenylazo)pentan-2,4-dione (**L**) in aqueous ethanol a solution at various temperatures (298 0.5; 308 0.5; 318 0.5 K). Standard thermodynamic functions of reaction of complex formation which change in the following sequence also are established:



Method MO LCAO in approximation Hückel quantum-chemical calculations determines effective charges of atoms in tautomeric forms (enol-azo, keto-azo, hydrazo) of **L**.

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1. INTRODUCTION

Thermodynamic functions of reaction of complexformation of azoderivatives of acetylacetone are fundamental characteristics for forecasting analytical opportunities of this class of organic reagents [1, 2] At complex formation of ions of metals with these reagents it dominates enthalpy factor bound with forming of quasaromatic six-membered chelate.

In the present work thermodynamic functions of reaction of complexformation of azoderivative of acetylacetone – 3-(4-nitrophenylazo)pentan-2,4-dione (**L**) with some metals are investigated by method potentiometric titrations. Besides that we established reactionary ability of tautomeric forms (enol-azo, keto-azo, hydrazo) **L** by method MO LCAO in approximation Hückel.

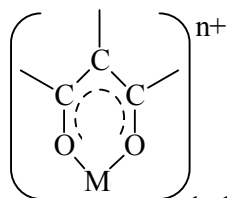
2. Experimental

L was prepared by azo coupling of diazotized *p*-nitroaniline with acetylacetone in a weakly alkaline medium in technique [3]; its structure was proved by IR and ¹H NMR spectroscopy [4].

The starting reagents were FeCl₃ · 6H₂O, CuSO₄ · 5H₂O, UO₂SO₄ · 3H₂O, NiSO₄ · 7H₂O, CoSO₄ · 7H₂O, Cd(NO₃)₂ · 4H₂O, ZnSO₄, MnCl₂ · 4H₂O, MgSO₄ · 7H₂O, Ca(NO₃)₂ (reagent grade) and solutions of **L** in aqueous ethanol. In aqueous solutions of the salts, the concentrations of Fe(III), Cu(II), Ni(II), Co(II), Zn(II), Cd(II) and Mn(II) were determined by atomic absorption spectroscopy, the concentrations of Mg(II) and Ca(II), by atomic emission spectroscopy, and the concentration of UO₂(II), by photometry [5]. Potentiometric titration of mixtures of **L** with the corresponding metal (**M**) salts was carried out in aqueous ethanol (3 : 7, v/v) with consideration of the

The molecular diagrams show that the introduction of functional groups (N N Ar) in a molecule of acetylacetone do not change the reaction centers (O and O). Most likely, the

positively charged M^{n+} ion should interact with the keto-azo tautomer of L (ambidentate form) with forming a quasiaromatic six-membered chelate ring [14, 15]:



The dissociation constants of L at different temperatures ... calculated by the equation [16]:

$$\lg K_{\text{dis}} = \text{pH} - \lg[\text{HL}] / \lg[\text{L}]; \quad \lg K_{\text{dis}} = \text{p}K.$$

The dissociation constant have been evaluated at 298, 308 and 318 K and are given in table 1. The slope of the plot ($\text{p}K$ versus $1/T$) was utilized to evaluate the enthalpy change (ΔH^0) for the dissociation process. From the Gibbs energy change (ΔG^0) and (ΔH^0) values one can deduce the entropy change (ΔS^0) using the well known relationships [17]:

$$\Delta G^0 = 2.303RT\text{p}K; \quad \Delta S^0 = (\Delta H^0 - \Delta G^0)/T.$$

TABLE 1
Thermodynamic characteristics dissociation L in aqueous ethanol a solution

T, K	pK	ΔG^0 , kJ mol ⁻¹	ΔH^0 , kJ mol ⁻¹	ΔS^0 , J mol ⁻¹ K ⁻¹
298 0.5	8.10 0.02	46.22 0.11	30.90 1.67	-51.40 1.78
308 0.5	7.95 0.03			
318 0.5	7.76 0.05			

On the basis of these given (table 1) it is possible to make the following conclusions:

1. With increase in temperature value $\text{p}K$ decreases, i.e. increases acid properties L [17, 18].
2. Positive value ΔH shows that process is endothermic [17-19].
3. Change ΔG of process is positive, therefore process dissociation does not process spontaneous [17-19].
4. A negative value of ΔS is obtained due to increased order as a result of solvation processes [18, 19].

From molecular diagrams of tautomeric forms of a reagent follows that at potentiometric titration in a proton abstraction groups it (enol-azo) and -NH- (hydrazo) values of effective charges of atoms in N more, than century

^{0.302}

O. Based on the quantum-chemical data, one can assume that K_{dis} of L characterizes proton abstraction form its hydrazo form (table 1).

The stability constants K_{st} of metal complexes with L were calculated by the Chaberek-Martell method [20]:

$$K_{\text{st}} = \frac{c_L [\text{L}][\text{x}]}{[\text{L}]^2[\text{x}]},$$

$$[\text{L}] = \frac{\{c_L(1 - a) [\text{H}^+] [\text{OH}^-]\} K_{\text{dis}}}{[\text{H}^+]},$$

$$[\text{x}] = \frac{[\text{H}^+]}{K_{\text{dis}}}, \quad a \text{ is the neutralization point,}$$

and $c_M = c_L = 1 \cdot 10^{-3}$ mol dm⁻³. The Gibbs energies and enthalpies of formation of complexes were calculated by the formulas [21]:

$$\Delta G^0 = RT \ln K_{st} \quad ;$$

$$\Delta H^0 = \left\{ R \left(\ln K_{st(T_3)} - \ln K_{st(T_1)} \right) \right\} / \left\{ \left(1/T_3 \right) - \left(1/T_1 \right) \right\}$$

The entropy of the complexation reaction was calculated by the formula

$\Delta S^0 = (\Delta H^0 - \Delta G^0)/T$. Results of calculations are submitted in table 2.

TABLE 2

Thermodynamic characteristics of reactions of complexformation L with some metals in aqueous ethanol solution

ML	T, K	lg K	ΔG^0 , kJ mol ⁻¹	ΔH^0 , kJ mol ⁻¹	ΔS^0 , J mol ⁻¹ K ⁻¹
FeL	298 0.5	8.02 0.02	-45.76 0.10	-40.89 2.18	16.34 2.28
	308 0.5	7.80 0.04			
	318 0.5	7.57 0.04			
CuL	298 0.5	7.87 0.04	-44.90 0.12	-39.07 2.12	19.56 2.24
	308 0.5	7.66 0.04			
	318 0.5	7.44 0.05			
UO ₂ L	298 0.5	7.63 0.06	-43.53 0.13	-35.44 1.94	27.15 2.07
	308 0.5	7.55 0.05			
	318 0.5	7.24 0.03			
NiL	298 0.5	7.07 0.07	-40.34 0.14	-32.71 1.81	25.60 1.95
	308 0.5	6.89 0.06			
	318 0.5	6.71 0.02			
CoL	298 0.5	6.72 0.06	-38.34 0.13	-27.26 1.52	37.18 1.65
	308 0.5	6.57 0.05			
	318 0.5	6.42 0.03			
ZnL	298 0.5	6.58 0.03	-37.54 0.10	-24.54 1.35	43.62 1.45
	308 0.5	6.44 0.05			
	318 0.5	6.31 0.04			
CdL	298 0.5	6.37 0.03	-36.35 0.10	-21.81 1.21	48.79 1.31
	308 0.5	6.25 0.05			
	318 0.5	6.13 0.05			
MnL	298 0.5	6.31 0.02	-36.00 0.08	-19.99 1.10	53.72 1.18
	308 0.5	6.20 0.06			
	318 0.5	6.09 0.03			
MgL	298 0.5	6.04 0.04	-34.46 0.10	-16.35 0.94	60.77 1.04
	308 0.5	5.95 0.04			
	318 0.5	5.86 0.05			
CaL	298 0.5	5.77 0.05	-32.92 0.11	-13.63 0.81	64.73 0.92
	308 0.5	5.69 0.05			
	318 0.5	5.62 0.06			

From table 2 it is visible that thermodynamic functions of reactions complexformation change in the following sequence:

$$\begin{array}{l} |\Delta G^0|: \text{Fe Cu UO}_2 \text{ Ni Co Zn Cd Mn Mg Ca} \\ |\Delta H^0|: \text{Fe Cu UO}_2 \text{ Ni Co Zn Cd Mn Mg Ca} \\ \Delta S^0: \text{Ca Mg Mn Cd Co Zn Co UO}_2 \text{ Cu Fe} \end{array}$$

The specified sequence of change enthalpy complexformation is connected to increase in a degree covalente communications (a "internal" part of change enthalpy) (keto-azo) and, accordingly, decrease in the electrostatic contribution (a "external" part of change enthalpy) [22, 23], and also dominate functional groups (enthalpy shift tautomeric equilibrium) depending on affinity of ions of metals with d-orbitales in complexformation.

The increase of entropy is connected to abstraction molecules of water at complexformation, and also at formation of a complex with lower charge, than at initial ions and as a result it smaller solvatasion the received complexes [24]. Increase entropy of complexformation can be, basically is caused by losses configuration entropy liganda (entropy tautomeric equilibrium).

Thus, the following conclusions received from table 2:

1. Change of temperature influences reaction of complexformation, i.e. with increase in temperature stability of complexes decreases.
2. Negative value ΔG show, that reactions of complexformation processed spontaneously [20, 21, 24].
3. Reactions of complexformation are exothermic ($\Delta H < 0$) and fofarite the role plays enthalpy at complexformation.
4. Positive change of entropy of process asserts complexformation in a solution

Results of conductometric titration in technique [26] $50 \text{ cm}^3 \text{ l } 10^{-3} \text{ L dm}^{-3}$ water solutions of the salts of metals with $10^{-2} \text{ L dm}^{-3}$ aqueous ethanol solution of reagent show, that due to mobile of ions H_3O^+ (which are more mobile) increases conductivities of system:

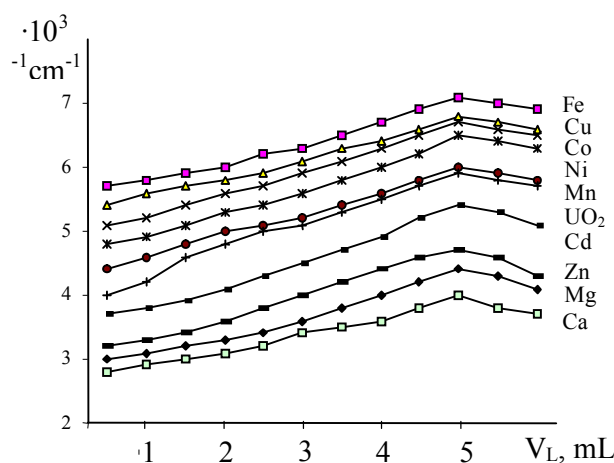
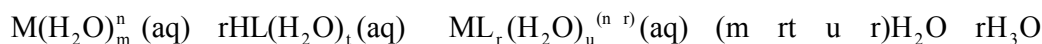


FIGURE. Conductometric titration curves of aqueous solutions of the metal salts (solution of L in aqueous ethanol as titrants) with L

Comparison of constants of stability of complexes (table 2) and their conductivity shows (figure), that the ions H_3O^+ are more abstraction at complexformation, the received complex (figure) is stable. It can be seen from figure that the conductivities decrease after the equivalence point. This is associated with the shift of the equilibrium $L + H^+ \rightleftharpoons HL$ to the right (i.e., with the protonation of L).

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