Front. Chem. China 2011, 6(3): 248–252
DOI 10.1007/s11458-011-0247-4

RESEARCH ARTICLE

Investigation of the interaction of ethyl acetoacetate with nano alumina particle as Lewis acid in acetonitrile solvent

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The enol form of ethyl acetoacetate (EAA) displays interesting spectroscopic characteristics; this form of ethyl acetylacetate is very important in condensation reaction. In this investigation, we have studied the interactions and the complex formation constants (K_f) with nano alumina (10–20 nm) particle and alumina (mesh 135) compounds as Lewis acids in the acetonitrile solvent using absorption spectroscopy and related calculations. Furthermore, in this study we calculated the thermodynamic parameters of this reaction. The trend of reactivity of the ethyl acetoacetate (EAA) complexes toward the above Lewis acids, based on the solvent as follows: nano alumina compound > alumina compound.

Keywords complex formation constant, ethyl acetoacetate, nano alumina, alumina, thermodynamic

1 Introduction

β-diketones are important compounds in chemistry. They are among the most widely used ligands in coordination chemistry [1]. β-diketones are in solutions as keto and enol tautomers. Since the enolic hydrogen is labile, it can be replaced by a metal cation to form a six-member chelate ring. The β-diketonate complexes thus formed have been the topic of hundreds of papers and reviews [1–5], and widely used in a lot of aspects in industry, such as organic electroluminescent technology, luminescent materials, sensors for bioinorganic applications, luminescent labels in bioaffinity assays [1,2], NMR shift reagents [6–8], laser chelates [9,10], extraction agents [11–13], heat stabilizers for polymers, drugs [14,15], chemical and photochemical catalysts [16]. Moreover, they are used in manufacturing supra-conductors [17,18] and gas chromatography [19,20]. A few papers have also appeared in which β-diketones have been shown to act as neutral ligands by establishing a coordinative interaction with the metal cation [21–26].

However, in this paper, we report the thermodynamic studies on the complexes formation constants (K_f) of ethyl acetoacatate with nano alumina particle and alumina compounds as Lewis acids in acetonitrile solvents by Scatchard's Eq. (1) [27] and the evaluation of the effect of the size of the Lewis acids on K_f of complexes. (Scheme 1)

2 Experimental

2.1 Materials and apparatus

The materials, ethyl acetoacetate (EAA), the solvent and Lewis acids were obtained from Merck, Fluka and Aldrich. All of the scanning UV-Vis spectra were recorded by Cintra 101 spectrophotometer.

2.2 Electronic spectra

The electronic spectra of all investigated complexes show an absorption band at 300–200 nm in this solvent in various temperatures. All complexes show an intensive absorption band at 270–220 nm. During the reactions, we could not observe the isobestic point in all solutions. Fig. 1 shows the spectrum of complex EAA with Al_2O_3 (nano) compound as Lewis acids in acetonitrile as solvent at different temperatures. The other spectrum of EAA complex with the Al_2O_3 compound as Lewis acid is similar to Fig. 1. All measurements for the thermodynamic studies were carried out at maximum wavelength (λ_{max} = 242 nm) (Table 1).

3 Results and discussion

A solution from each complex with a concentration of about 10^{-3} mol/L was prepared. The formation constants and the thermodynamic parameters were measured spectrophotometrically. The complex formation measurements were carried out using the Lewis acids in acetonitrile solvent at various temperatures (Scheme 1). The formation constants of EAA complexes were calculated by Scatchard's Eq. (1) in which b_0 and a_0 are the initial concentrations of the acceptor (Lewis acid) and the donor (EAA) respectively; D (λ) is the optical density of the solution including the acceptor (Lewis acid) and the donor (EAA). ε_{AB} (λ) is the molar extinction coefficients

Received July 1, 2011; accepted July 20, 2011
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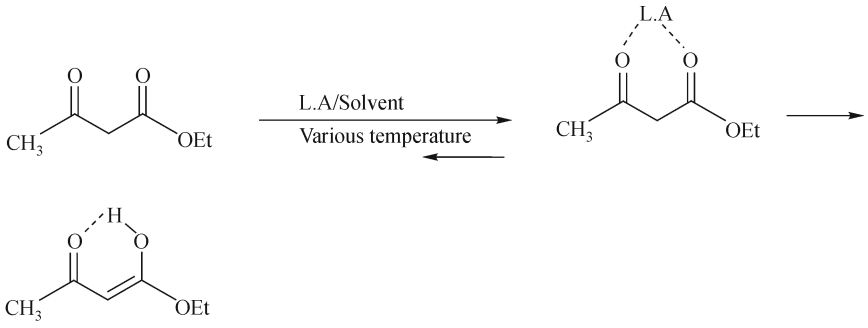

Scheme 1 Keto-enol tautomerization of EAA with different Lewis acids in the acetonitrile solvent at various temperatures

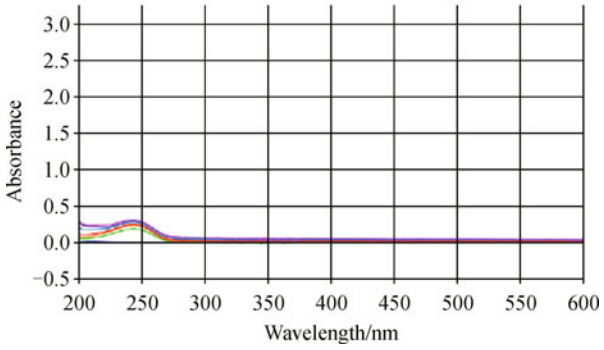

Figure 1 The absorption spectra of EAA with Al_2O_3 (nano) in acetonitrile as solvent at different temperatures

Table 1 Data of wavelengths (λ_{max}/nm) and absorption bond (A) of ethyl acetoacetate in acetonitrile solvent at room temperature

Solvent	Concentration of EAA	λ_{max} /nm	A
Acetonitrile	2×10^{-3}	242.9	0.182

of the complex. The absorption bond data of EAA concentration at room temperature are reported in Table 1 and the concentration of Lewis acids is constant (3.92×10^{-4} mol/L). The fixed wavelength (242 nm) and absorption bond of EAA complexes in various systems at room temperature are listed in Table 2. K is the formation constant of the complex formed, and the cell optical path is 1 cm.

$$Kb_0\varepsilon_{AB}(\lambda) - KD(\lambda) = D(\lambda)/a_0 \quad (1)$$

Restrictions:

$$a_0b_0 >> C^2AB;\ a_0 > b_0;\ b_0 = \text{constant}$$

In Fig. 2 (A and B), we show a plot of $D(\lambda)/a_0$ vs. $D(\lambda)$ for EAA complexes in the acetonitrile solvent at various temperatures. The curves in this figure show that in EAA reactions with two Lewis acids, only 1:1 complex is formed since all the lines are straight while a mixture of 1:1 and 1:2 or only 1:2 complex in a system would lead to a curve [28]. According to the data reported in Tables 1 and 2 and Scatchard's Eq. (1), the formation constants of the studied EAA complexes were calculated from the slope of line in the diagram.

Table 2 The fixed wavelengths (242 nm) and absorption bond (A) of EAA in various systems at room temperature

Lewis acid	Solvent	A
Al_2O_3 (nano)	Acetonitrile	0.240
Al_2O_3	Acetonitrile	0.328

The thermodynamic parameters of the studied EAA complexes with two Lewis acids in the various conditions were calculated by use of the well-known, van'tHoff Equation (Eq. (2)):

$$\ln K = -\Delta H^\circ/RT + \Delta S^\circ/R \quad (2)$$

where K is the formation constant, R is the gas constant and T is the temperature in Kelvin scale. The formation constant of the studied EAA complexes were not obtained by the linear plots of $\ln K$ vs. $1/T$ because the range of temperature is not wide. In Fig. 3, we show the scatter data and linear plots for EAA complexes with two Lewis acids at various temperatures and in acetonitrile solvent. The data for the calculations are reported in Tables 3 and 4.

We can calculate the values of ΔH° and ΔS° parameters from the slope and the intercept of plot $\ln K$ vs. $1/T$ respectively; Then according to Eq. (3), the values of ΔG° of complex formations were obtained. The thermodynamic parameters are listed in Tables 5 and 6.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (3)$$

3.1 The effect of temperature on the electronic spectra

The formation constants in the same solvent and ligand are dependent on the temperature; however, in the present study, we obtained the data of EAA complexes at various temperatures. The data are reported in Table 7.

According to the data reported in Table 7, it seems that the temperature is very influential for the formation constants of EAA complexes.

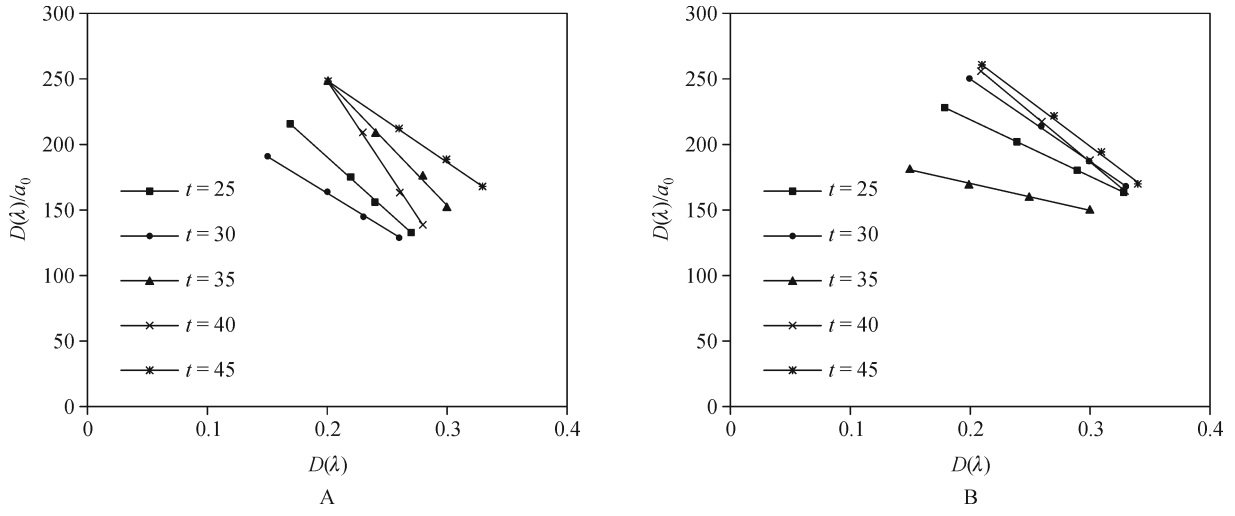

Figure 2 A) Plots of $D(\lambda) / a_0$ vs. $D(\lambda)$ for EAA complex with Al_2O_3 (nano) at various temperatures (t = 25°C–45°C) in acetonitrile; B) Plots of $D(\lambda) / a_0$ vs. $D(\lambda)$ for EAA complex with Al_2O_3 at various temperatures (t = 25°C–45°C) in acetonitrile.

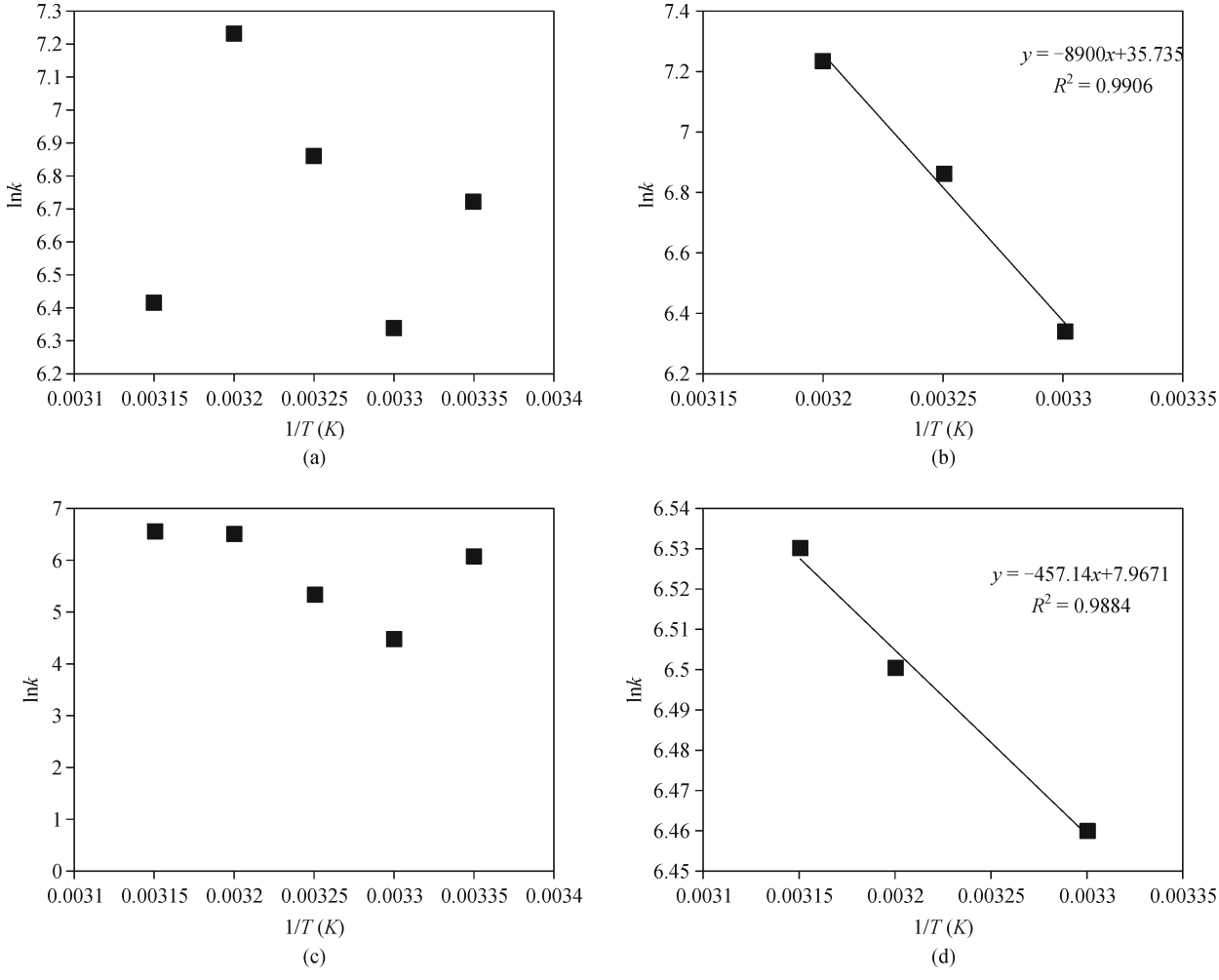

Figure 3 (a) Plot of ln$K$ vs. $1/T$ for EAA complex with Al_2O_3 (nano) in acetonitrile; (b)–(d) Plot of ln$K$ vs. $1/T$ for EAA complex with Al_2O_3 in acetonitrile

Table 3 The formation constants K (mol/L) for EAA complex with Al_2O_3 (nano) (10–20 nm) in acetonitrile solvent

T (K)	298	303	308	313	318
CH_3CN	828.57±10	567.21±12	952.15±20	1380.90±15	612.87±20

Table 4 The formation constants K (mol/L) for EAA complex with Al_2O_3 (mesh 135) in acetonitrile solvent

T (K)	298	303	308	313	318
CH_3CN	430.36±15	638.47±8	205.57±13	750.36±15	688.25±10

Table 5 The thermodynamic parameter values (ΔH°, ΔS° and ΔG°) for EAA with Al_2O_3 (nano) in acetonitrile solvent at room temperature

Solvent	ΔH° /(kJ·mol^{-1})	−ΔG° /(kJ·mol^{-1})	ΔS° /(kJ·mol^{-1})
CH_3CN	73.990	14.516	0.297

Table 6 The thermodynamic parameter values (ΔH°, ΔS° and ΔG°) for EAA with Al_2O_3 in acetonitrile solvent at room temperature

Solvent	ΔH° /(kJ·mol^{-1})	−ΔG° /(kJ·mol^{-1})	ΔS° /(kJ·mol^{-1})
CH_3CN	3.800	23.318	0.091

Table 7 Data of wavelengths (λ_{max} /nm) and absorption bonds (A) of ethyl acetoacetate (EAA) in acetonitrile solvent with two Lewis acids at various temperatures

Lewis acid	Solvent	T/°C	Concentration of EAA	λ_{max} /nm	A
		25		243.3	0.240
		30		243.3	0.256
Al_2O_3 (nano)	Acetonitrile	35	2×10^{-3}	242.9	0.292
		40		243.3	0.282
		45		242.5	0.312
		25		242.5	0.328
		30		242.9	0.335
Al_2O_3	Acetonitrile	35	2×10^{-3}	242.9	0.340
		40		243.3	0.339
		45		243.3	0.339

3.2 Thermodynamic parameters

The value of thermodynamic parameters as ΔH°, ΔG° and ΔS° are dependent on the heat of formation of the complex and the solvent effect [28]. In all EAA complexes with two Lewis acids, it is found that the ΔH° values are positive. This shows that the complex-formation contribution of ΔH° values is more important. The ΔH° value for Al_2O_3 (nano) (10–20 nm) complex as Lewis acid in acetonitrile solvent is more positive than Al_2O_3 (mesh 135) as Lewis acid in the same solvent. This shows that the complex formation for these complexes within acetonitrile is more important because the EAA complexes are very important in the synthesis of organic compounds such as synthesis of 3,4-dihydropyrimidinones [29].

The ΔS° value and its signs are also dependent on the differences in the number of particles of the initial substance and the product complexes, and the liberation of the solvent molecule from EAA complexes. In this work, we do not separate the products, an evolution from the liberation of the solvent molecule from these complexes.

However, according to the data reported in Tables 5 and 6, it is found that the ΔG° values in all EAA complexes are negative.

4 Conclusion

By considering the formation constants, K_f, and ΔG° of the formation for EAA complexes as the donor and two Lewis acids as the acceptor, we propose the following conclusions:

1) The reactions of EAA with two Lewis acids in the acetonitrile solvent are endothermic. $\Delta H^\circ > 0$.

2) The formation constant in two Lewis acids in these complexes changes according to the following trend in acetonitrile solvent: Al_2O_3 (nano) (10–20 nm) > Al_2O_3 (mesh 135).

3) The results of the present work show that the thermodynamic parameters in the ethyl acetoacatate with Al_2O_3 (nano) increase with respect to Al_2O_3, as the homogeneous distribution of the reactants throughout the

solution makes a strong case in the increase of these parameters.

4) According to the data obtained for EAA complexes, it seems that the rate of EAA in the organic synthesis is dependent on the thermodynamic parameters.

5) The aim of this study is to obtain the formation constants of EAA in various conditions that are very important in the investigation of the rate of condensation reaction of EAA in organic reactions.

6) The collective data available for the present work strongly suggest that β-diketones can have different behavior in various conditions.

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