

MEASUREMENT OF THE SPECTROSCOPIC PROPERTIES OF OXALIC ACID-SOLVENT SYSTEMS BY UV-SPECTROPHOTOMETRY

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Özet - Bu çalışmada, dissosiasyon ortamında okzalik asit çözeltilerinin sıcaklık ve konsantrasyon ile dissosiasyon özelliklerinin değişimi UV-VIS Spektrofotometrik yöntem ile incelenmiştir. Her çözelti sistemi için, farklı sıcaklıklarda konsantrasyon, c , ve absorbans, A , arasındaki ilişkiler belirlenmiştir. Elde edilen sonuçlar, etil alkol, n-propil alkol, iso-propil alkol and N,N-dimetilformamid çözücüleriyle hazırlanan çözeltiler için Lambert-Beer yasasının sırasıyla $1.00 \times 10^{-2} M$ ile $6.25 \times 10^{-4} M$; $1.00 \times 10^{-2} M$ ile $6.25 \times 10^{-4} M$; $3.00 \times 10^{-3} M$ ile $1.875 \times 10^{-4} M$; $3.00 \times 10^{-2} M$ ile $1.875 \times 10^{-3} M$ derişim aralıklarında geçerli olduğunu göstermiştir. Çözeltilerin molar sönüm katsayıları Lambert-Beer kanunu yardımıyla hesaplanmıştır. Her çözelti sistemi için molar sönüm katsayısının sıcaklık bağımlılığı belirlenmiştir.

Anahtar Kelimeler - UV-spektroskopisi, molar sönüm katsayısı, okzalik asit, dissosiasyon.

Summary - In this study, the properties of oxalic acid that change with temperature and concentration in the dissociation media were investigated by UV-VIS spectrophotometry. For every solution systems, the relationships between absorbance, A , and concentration, c , were obtained at different temperatures. The results were indicated that the Lambert-Beer law was obeyed in the concentration range of $1.00 \times 10^{-2} M$ to $6.25 \times 10^{-4} M$; $1.00 \times 10^{-2} M$ to $6.25 \times 10^{-4} M$; $3.00 \times 10^{-3} M$ to $1.875 \times 10^{-4} M$; $3.00 \times 10^{-2} M$ to $1.875 \times 10^{-3} M$ for the solutions which are prepared with ethyl alcohol, n-propyl alcohol, iso-propyl alcohol and N,N-dimethylformamide; respectively. Molar absorptivities of the solutions were calculated by using the Lambert-Beer law. The temperature dependence of the molar absorptivity of each solution was determined.

Keywords - UV-spectroscopy, molar absorptivity, oxalic acid, dissociation.

I. INTRODUCTION

Physical and chemical properties of a molecule depend on atoms, strength and the species of chemical bonding [1]. A vast majority of chemical reaction takes place in solutions. Both H-bonding and Van der Waals bonding are important in a solution media. Electronic structure of a molecular system, dimension, geometry, concentration of molecules and distance between molecules depend on interaction species [2,3].

The absorption of light in a molecule depends on interaction species in media. Two empirical laws have been formulated about the absorption intensity. Lambert's law states that the fraction of the incident light absorbed is independent of the intensity of the source. Beer's law states that the absorption is proportional to the number of absorbing molecules. From these laws, the Equation 1 was determined. [4,5].

$$\log \frac{I_0}{I} = A = \epsilon \cdot c \cdot l \quad (1)$$

I_0 and I are the intensities of the incident and transmitted light respectively, l is the path length of the absorbing solution in centimeter, and c is the concentration in moles/liter. $\log_{10}(I_0/I)$ is the absorbance or optical density; ϵ is known as the molar extinction [4-6].

Molar absorptivity changes with wavelength and frequency of the radiation. It is a characteristic quantity for studied atomic or molecular system. Therefore, molar absorptivity should be measured for atomic or molecular system in different media [7,8].

The Lambert-Beer law is a limited law for dilute solutions, the assertion that the extinction coefficient, ϵ , is independent of the concentration of a substance at the given wavelength, λ , applies only to dilute solutions. ϵ is no longer constant for concentrated solutions but it depends on the

refractive index of solutions [9,10]. According to Lambert-Beer law, the temperature and wavelength are both constant. Whereas, if the temperature changes, the concentration, volume and refractive index of the solutions can change, too. [11,12].

If a concentration of solution changes, the shape of an absorbance curve can change too. This phenomena is occurred with interactions between a solute and a solvent [9]. The first aim of this study is that the representation of the limitations of the Lambert-Beer law. Our second aim is to determine relationship between molar absorptivity and temperature.

II. EXPERIMENTAL

The spectra were recorded in the UV region and were measured using a Variation 1E UV-VIS Spectrophotometer for solutions of oxalic acid in the range between $20^\circ C$ and $45^\circ C$. Measurements were performed in 1mL quartz-cells. The temperature of the thermostatic bath was controlled within $\pm 0.2^\circ C$ in the range between $0^\circ C$ and $50^\circ C$ and within $\pm 0.5^\circ C$.

Solutions were prepared using solvents which have different dielectric constants such as ethyl alcohol, n-propyl alcohol, iso-propyl alcohol and N,N-dimethylformamide. Oxalic acid concentration range of the solutions are $8.00 \times 10^{-2} M$ to $6.25 \times 10^{-4} M$; $1.60 \times 10^{-1} M$ to $6.25 \times 10^{-4} M$; $4.80 \times 10^{-2} M$ to $1.875 \times 10^{-4} M$; $4.00 \times 10^{-1} M$ to $1.875 \times 10^{-3} M$ in ethyl alcohol, n-propyl alcohol, iso-propyl alcohol and N,N-dimethylformamide; respectively.

III. RESULTS AND DISCUSSION

The maximum wavelengths of the solutions were determined. The maximum wavelength values are 210nm, 218nm, 261nm and 270nm of oxalic acid solutions in ethyl alcohol, n-propyl alcohol, iso-propyl alcohol and N,N-dimethylformamide; respectively. These values are shown in Fig. 1.

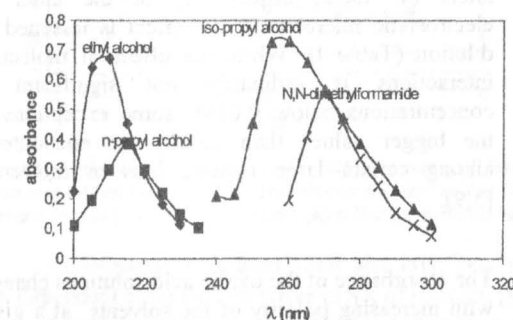
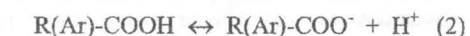


Figure 1. Spectra of oxalic acid solutions in different solvents at $20^\circ C$. Oxalic acid concentration is $1 \times 10^{-2} M$, $5 \times 10^{-3} M$, $3 \times 10^{-3} M$ and $1.5 \times 10^{-2} M$ in ethyl alcohol, n-propyl alcohol, iso-propyl alcohol and N,N-dimethylformamide; respectively.

The oxalic acid molecules are dissociated in the solvents. Ionic dissociation equilibria of oxalic acid is shown in following.



The absorbances of the solutions were measured during ten minutes at maximum wavelength of every solutions. Absorbance dependence on time is shown Fig. 2. The dissociation of oxalic acid molecules in the solvents is entirely to completed at five minutes and the system is stable. Therefore, the absorbance values of five minutes were used.

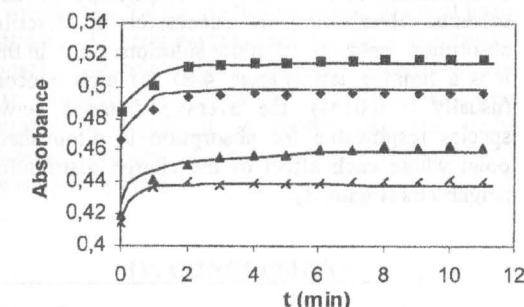
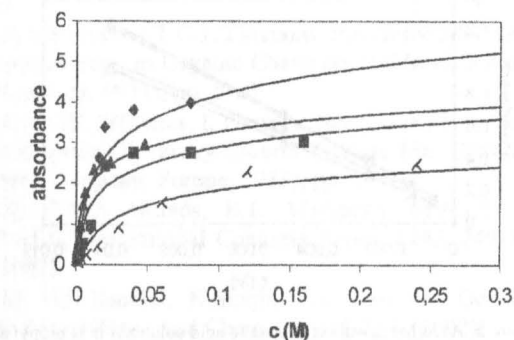


Figure 2. Absorbance dependence on time. The solvents are ethyl alcohol (\blacklozenge); n-propyl alcohol (\circ); iso-propyl alcohol (\blacktriangle); N,N-Dimethylformamide (\times).

The relationship between absorbance and concentration of the solutions is shown that in Figure 3. The Lambert-Beer law was obeyed in the concentration range of $1.00 \times 10^{-2} M$ to $6.25 \times 10^{-4} M$; $1.00 \times 10^{-2} M$ to $6.25 \times 10^{-4} M$; $3.00 \times 10^{-3} M$ to $1.875 \times 10^{-4} M$; $3.00 \times 10^{-2} M$ to $1.875 \times 10^{-3} M$ for the solutions which are prepared with ethyl alcohol, n-propyl alcohol, iso-propyl alcohol and N,N-dimethylformamide; respectively.

Figure 3. Absorbance value of oxalic acid solutions in different solvents at $20^\circ C$. The solvents are ethyl alcohol (\blacklozenge), n-propyl



alcohol (\circ), iso-propyl alcohol (\blacktriangle), N,N-dimethylformamide (\times)

Few exceptions are found to the generalization that absorbance is linearly related to path length. On the other hand, deviations from the direct proportionality between the measured absorbance and concentration when l is constant are frequently encountered. Some of these deviations are fundamental and they represent real limitations of the law (Figure 3). Others occur as a consequence of the manner in which the absorbance measurements are made or as a result of chemical changes associated with concentration changes; the latter two are sometimes known, respectively, as instrumental deviations and chemical deviations [1,9].

In Figure 4-7, the absorbance is plotted against concentration at the different temperature in the several solvents. Beer's law is successful in describing the absorption behavior of dilute solutions only; in this sense, it is a limiting law (Figure 4-8). At high concentrations (usually $> 0.01M$), the average distance between the species responsible for absorption is diminished to the point where each affect of the charge distribution of its neighbours (Figure 3).

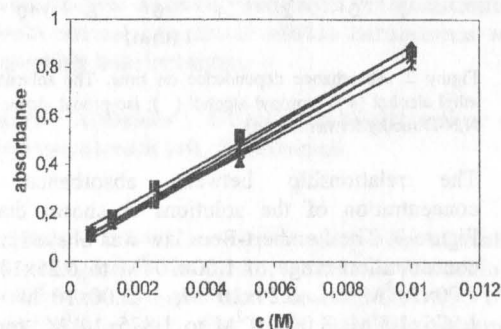


Figure 4. Absorbance values of oxalic acid solutions in ethyl alcohol at different temperatures. The temperature is 20°C (♦), 25°C (◻), 30°C (▲), 35°C (x), 40°C (*).

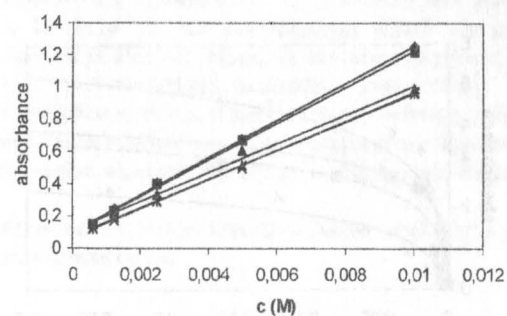


Figure 5. Absorbance values of oxalic acid solutions in n-propyl alcohol at different temperatures. The temperature is 20°C (♦), 25°C (◻), 30°C (▲), 35°C (x), 40°C (*).

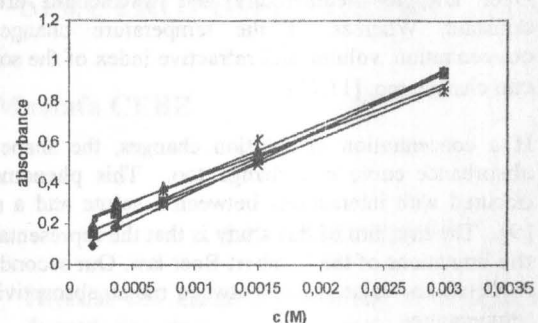


Figure 6. Absorbance values of oxalic acid solutions in iso-propyl alcohol at different temperatures. The temperature is 20°C (♦), 25°C (◻), 30°C (▲), 35°C (x), 40°C (*).

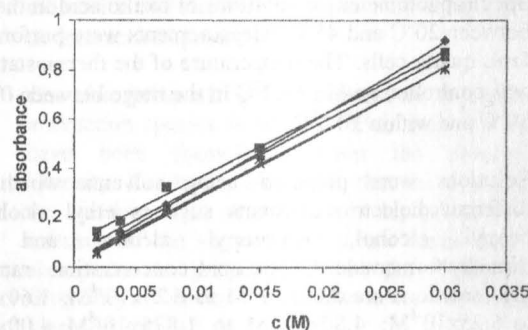


Figure 7. Absorbance values of oxalic acid solutions in N,N-dimethyl formamide at different temperatures. The temperature is 20°C (♦), 25°C (◻), 30°C (▲), 35°C (x), 40°C (*).

These interactions, in turn, can alter the species ability to absorb a given wavelength of radiation. Because the extent of interaction depends on concentration, the occurrence of this phenomenon causes deviations from the linear relationship between absorbance and concentration (Figure 3) [2,9]. The close proximity of ions to the absorber alters the molar absorptivity of the latter by electrostatic interactions; the effect is lessened by dilution (Table I). While the effect of molecular interactions is ordinarily not significant at concentrations below 0.01M, some exceptions as the bigger values than 0.01M are encountered among certain large organic ions or molecules [3,9].

The absorbance of the oxalic acid solutions changes with increasing polarity of the solvents at a given temperature. This effect is shown in Fig.8.

Table I. Molar absorptivity of oxalic acid solutions in different solvents at different temperatures.

Solvent	Molar Extinction Coefficient, ϵ ($M^{-1}cm^{-1}$) ^a				
	20°C	25°C	30°C	35°C	40°C
Ethy Alcohol	83 ± 2	79 ± 4	81 ± 3	79 ± 1	74 ± 2
n-Propyl Alcohol	116 ± 2	113 ± 2	90 ± 4	90 ± 1	89 ± 1
İso-Propyl Alcohol	299 ± 8	275 ± 10	256 ± 14	249 ± 11	231 ± 23
N,N-dimethylformamide	30 ± 0.9	26 ± 0.8	27 ± 0.5	27 ± 0.3	26 ± 0.8

^a [13]

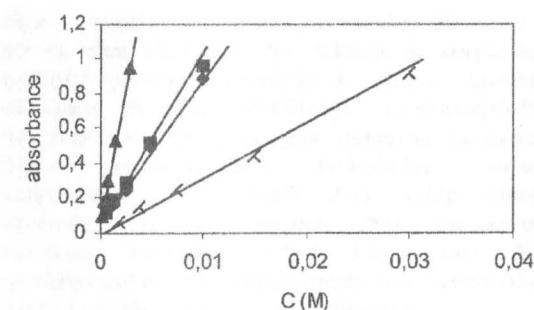


Figure 8. Absorbance of the solutions as a function species of the solvents at 20°C. The solvents are ethyl alcohol (♦), n-propyl alcohol (◻), iso-propyl alcohol (▲), N,N-dimethylformamide (x)

The relationships between absorbances and concentrations are clearly linear, and the values of the molar absorptivity at different temperature can be deduced from the slope of these lines. The molar absorptivities are shown in Table I. The relationship between molar absorptivity and temperature is shown in Fig. 9.

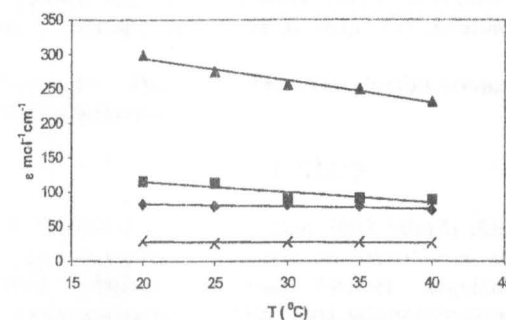


Figure 9. Molar absorptivities of oxalic acid solutions in different solvents at different temperatures. The solvents are ethyl alcohol (♦), n-propyl alcohol (◻), iso-propyl alcohol (▲), N,N-dimethylformamide (x).

Deviations from Beer's law also arise because ϵ is dependent upon the refractive index of solution [9]. Thus, if concentration and temperature change because of the significant alterations in the refractive index n of a solution, departures from Beer's law are observed

[4,9]. Therefore, molar absorptivity of the solutions are not constant and they are changed (Fig. 9).

The results of ϵ for the studied solutions showed linear variation with temperature, within the experimental accuracy. The relationship between temperature and molar absorptivity values of the solutions were illustrated in Fig.9. It is shown that the molar absorptivity values of the solutions decrease with increasing temperature.

IV. CONCLUSIONS

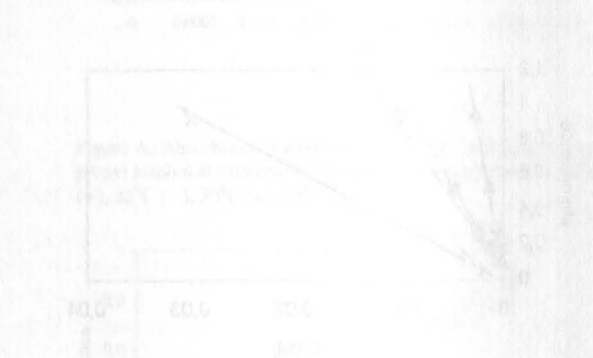
In this study, the Lambert-Beer law is applied to our experimental data and the suitable concentration ranges are determined. Our results showed that Lambert-Beer law was obeyed in the concentration range of $1.00 \times 10^{-2}M$ to $6.25 \times 10^{-4}M$; $1.00 \times 10^{-2}M$ to $6.25 \times 10^{-4}M$; $3.00 \times 10^{-3}M$ to $1.875 \times 10^{-4}M$; $3.00 \times 10^{-2}M$ to $1.875 \times 10^{-3}M$ for the studied solutions which are prepared with ethyl alcohol, n-propyl alcohol, iso-propyl alcohol and N,N-dimethylformamide; respectively.

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Molar Extinction Coefficient	20°C	30°C
ϵ_{250}	1.10 ± 2	81 ± 2
ϵ_{260}	1.03 ± 1	79 ± 4
ϵ_{270}	0.87 ± 10	67 ± 10
ϵ_{280}	0.70 ± 10	50 ± 10



The molar extinction coefficient of oxalic acid-solvent systems was measured at different temperatures. The results are shown in Figure 1. It is seen that the molar extinction coefficient of oxalic acid-solvent systems decreases with increasing temperature. This is due to the fact that the equilibrium constant of the dissociation reaction of oxalic acid increases with increasing temperature. As a result, the concentration of the oxalic acid molecules in the solution decreases, and the molar extinction coefficient of the solution decreases.

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