

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

Nalan TEKİN

Department of Chemistry, Balıkesir University, 10100 Balıkesir, Turkey

ABSTRACT

In this study, the dissociation properties of benzoic 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 $1.00 \times 10^{-3} \text{M}$ to $6.25 \times 10^{-5} \text{M}$; $1.00 \times 10^{-4} \text{M}$ to $6.25 \times 10^{-6} \text{M}$; $1.25 \times 10^{-3} \text{M}$ to $7.80 \times 10^{-5} \text{M}$; $2.00 \times 10^{-4} \text{M}$ to $1.25 \times 10^{-5} \text{M}$; $1.00 \times 10^{-3} \text{M}$ to $6.25 \times 10^{-5} \text{M}$ for the solutions which are prepared with benzene, 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, benzoic acid, dissociation

ÖZET

Bu çalışmada, dissosiasyon ortamında benzoik 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, benzen, etil alkol, n-propil alkol, iso-propil alkol and N,N-dimetilformamid çözücülerıyla hazırlanan çözeltiler için Lambert-Beer yasasının sırasıyla $1.00 \times 10^{-3} \text{M}$ to $6.25 \times 10^{-5} \text{M}$; $1.00 \times 10^{-4} \text{M}$ to $6.25 \times 10^{-6} \text{M}$; $1.25 \times 10^{-3} \text{M}$ to $7.80 \times 10^{-5} \text{M}$; $2.00 \times 10^{-4} \text{M}$ to $1.25 \times 10^{-5} \text{M}$; $1.00 \times 10^{-3} \text{M}$ to $6.25 \times 10^{-5} \text{M}$ 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, benzoik asit, dissosiasyon

1. 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].

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

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

Molar absorptivity changes with wavelength 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 the concentration of a solution changes, there would be some changes on absorbance curve as well. 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.

2. EXPERIMENTAL

The spectra were recorded in the UV region and were measured using a Variation 1E UV-VIS Spectrophotometer for solutions of benzoic acid in the range between 20⁰C and 45⁰C. Measurements were performed in 1mL quartz-cells. The temperature of the thermostatic bath was controlled within $\pm 0.2^{\circ}\text{C}$ in the range between 0⁰C and 50⁰C and within $\pm 0.5^{\circ}\text{C}$.

Solutions were prepared using solvents which have different dielectric constants such as benzene, ethyl alcohol, n-propyl alcohol, iso-propyl alcohol and N,N-dimethylformamide. Benzoic acid concentration range of the solutions are 1.60x10⁻²M to 6.25x10⁻⁵M; 1.60x10⁻³M to 6.25x10⁻⁶M; 1.00x10⁻²M to 7.80x10⁻⁵M; 8.00x10⁻⁴M to 1.25x10⁻⁵M; 1.60x10⁻²M to 6.25x10⁻⁵M in benzene, ethyl alcohol, n-propyl alcohol, iso-propyl alcohol and N,N-dimethylformamide; respectively.

3. RESULTS AND DISCUSSION

The maximum wavelengths of the solutions were determined. The maximum wavelength values of benzoic acid solutions in ethyl alcohol, n-propyl alcohol, iso-propyl alcohol, benzene and N,N-dimethylformamide are 225nm, 225nm, 235nm, 280nm and 270nm, respectively. These values are shown in Figure 1.

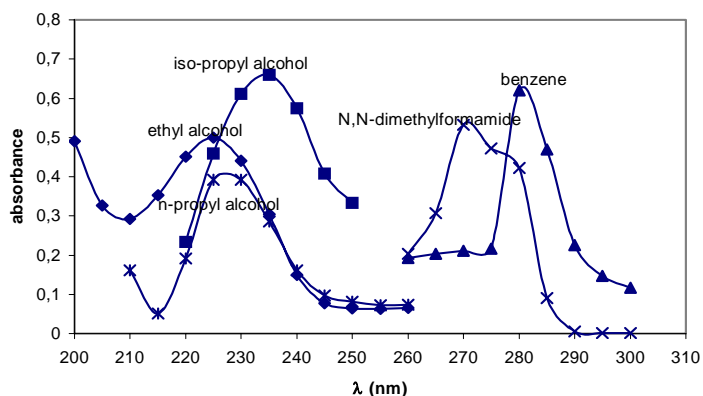


Figure 1. Spectra of benzoic acid solutions in different solvents at 20°C. Benzoic acid concentration is $5 \times 10^{-4} \text{M}$, $5 \times 10^{-5} \text{M}$, $6 \times 10^{-4} \text{M}$, $1 \times 10^{-4} \text{M}$ and $6 \times 10^{-4} \text{M}$ in benzene, ethyl alcohol, n-propyl alcohol, iso-propyl alcohol and N,N-dimethylformamide, respectively.

The benzoic acid molecules are dissociated in the solvents used. Ionic dissociation equilibria of benzoic acid is shown by the equation;



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

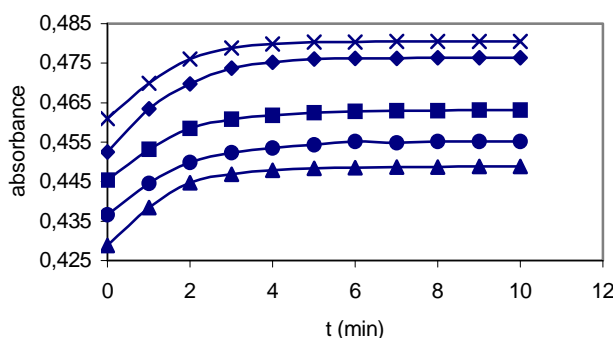


Figure 2. Absorbance dependence of benzoic acid on time. The solvents are benzene (◆); n-propyl alcohol (■); iso-propyl alcohol (▲); N,N-Dimethylformamide (●) and ethyl alcohol (x).

The relationship between absorbance and benzoic acid concentration of the solutions is shown that in Figure 3. The Lambert-Beer law was obeyed in the concentration range of $6.25 \times 10^{-5} \text{M}$ to $1.00 \times 10^{-3} \text{M}$; $6.25 \times 10^{-6} \text{M}$ to $1.00 \times 10^{-4} \text{M}$; $7.80 \times 10^{-5} \text{M}$ to $1.25 \times 10^{-3} \text{M}$; $1.25 \times 10^{-5} \text{M}$ to $2.00 \times 10^{-4} \text{M}$; $6.25 \times 10^{-5} \text{M}$ to $1.00 \times 10^{-3} \text{M}$ for the solutions which are prepared with benzene, ethyl alcohol, n-propyl alcohol, iso-propyl alcohol and N,N-dimethylformamide; respectively.

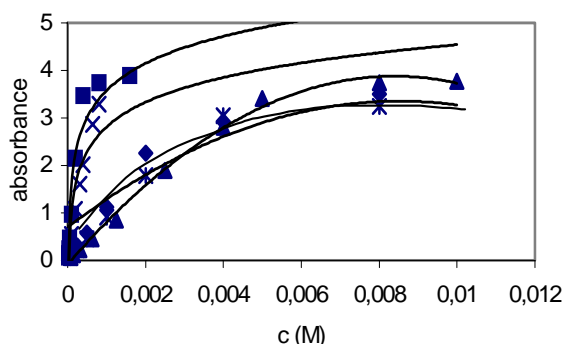


Figure 3. Absorbance value of benzoic acid solutions in different solvents at 20°C . The solvents are benzene (◆), ethyl alcohol (■), n-propyl alcohol (▲), iso-propyl alcohol (x), N,N-dimethylformamide (*).

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 4-8, 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 $> 0.01\text{M}$), the average distance between the species responsible for absorption is diminished to the point where each species affect the charge distribution of its neighbours (Figure 3).

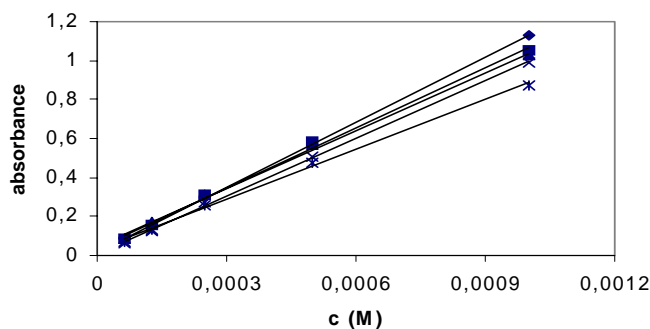


Figure 4. Absorbance values of benzoic acid solutions in benzene at different temperatures. The temperature is 20°C (\blacklozenge), 25°C (\blacksquare), 30°C (\blacktriangle), 35°C (\times), 40°C ($*$).

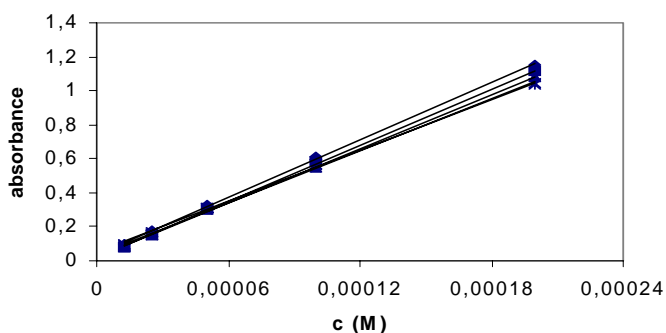


Figure 5. Absorbance values of benzoic acid solutions in ethyl alcohol at different temperatures. The temperature is 20°C (\blacklozenge), 25°C (\blacksquare), 30°C (\blacktriangle), 35°C (\times), 40°C ($*$).

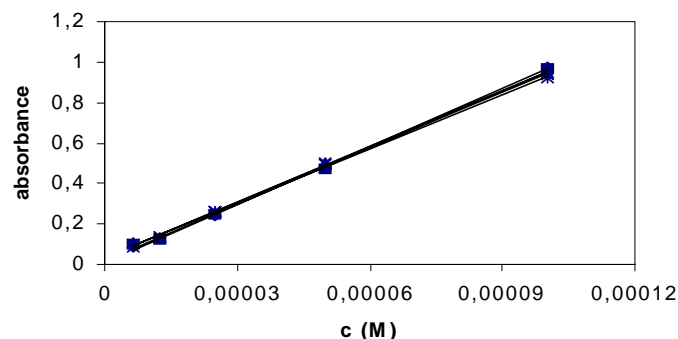


Figure 6. Absorbance values of benzoic acid solutions in n-propyl alcohol at different temperatures. The temperature is 20°C (\blacklozenge), 25°C (\blacksquare), 30°C (\blacktriangle), 35°C (\times), 40°C ($*$).

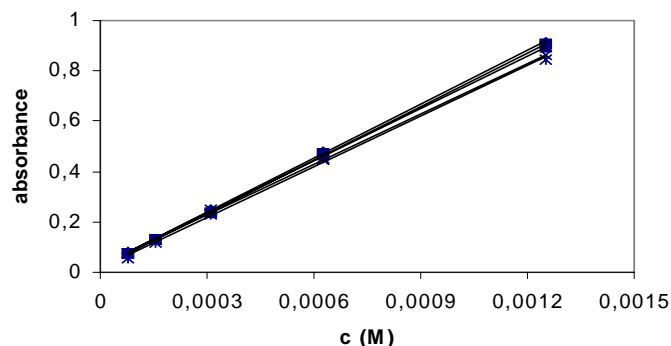


Figure 7. Absorbance values of benzoic acid solutions in iso-propyl alcohol at different temperatures. The temperature is 20⁰C (♦), 25⁰C (■), 30⁰C (▲), 35⁰C (x), 40⁰C (*).

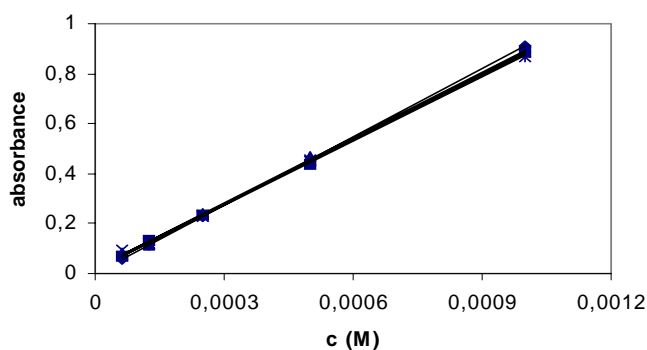


Figure 8. Absorbance values of benzoic acid solutions in N,N-dimethylformamide at different temperatures. The temperature is 20⁰C (♦), 25⁰C (■), 30⁰C (▲), 35⁰C (x), 40⁰C (*).

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 are encountered among certain large organic ions or molecules [3,9].

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

| Solvent | Molar absorptivity, ϵ ($M^{-1}cm^{-1}$) | | | | |
|-----------------------|--|-------------------|-------------------|-------------------|-------------------|
| | 20 ⁰ C | 25 ⁰ C | 30 ⁰ C | 35 ⁰ C | 40 ⁰ C |
| Benzene | 1107 ± 4 | 1031 ± 32 | 992 ± 28 | 987 ± 15 | 854 ± 25 |
| Ethy Alcohol | 9585 ± 179 | 9386 ± 236 | 9155 ± 206 | 9141 ± 120 | 8891 ± 143 |
| n-Propyl Alcohol | 715 ± 5 | 711 ± 7 | 696 ± 8 | 665 ± 6 | 673 ± 14 |
| Iso-Propyl Alcohol | 5594 ± 79 | 5481 ± 81 | 5310 ± 74 | 5090 ± 126 | 4977 ± 118 |
| N,N-dimethylformamide | 909 ± 3 | 871 ± 12 | 868 ± 15 | 857 ± 14 | 855 ± 7 |

The absorbance of the benzoic acid solutions changes with increasing polarity of the solvents at a given temperature. This effect is shown in Figure 9.

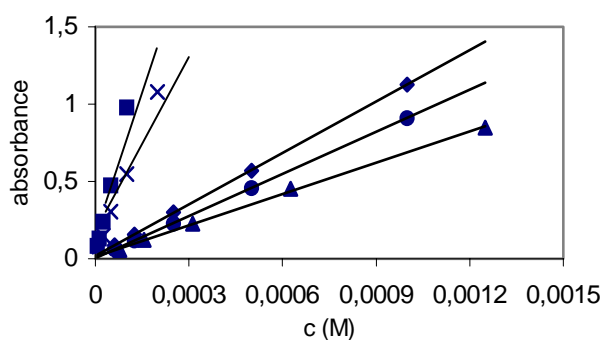


Figure 9. Calibration curves for benzoic acid in different solvents at 20⁰C. The solvents are benzene (◆), ethyl alcohol (■), n-propyl alcohol (▲), iso-propyl alcohol (x), N,N-dimethylformamide (●).

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 Figure 10.

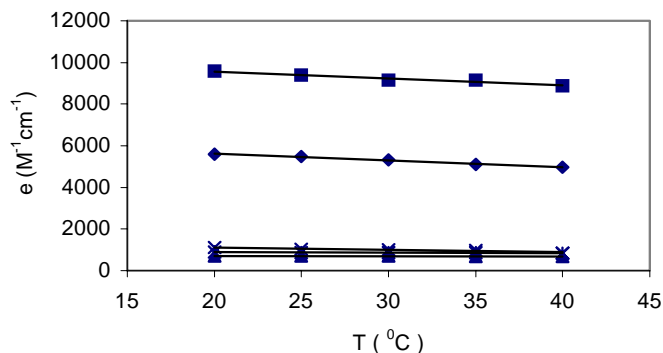


Figure 10. Molar absorptivities of benzoic acid solutions in different solvents at different temperatures. The solvents are iso-propyl alcohol (◆), ethyl alcohol (■), n-propyl alcohol (▲), benzene (x), N,N-dimethylformamide (*).

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 (Figure 10).

In this study, the Lambert-Beer law is applied to our experimental data and the suitable concentration ranges are determined. Our results showed that the Lambert-Beer law was obeyed in the concentration range of $6.25 \times 10^{-5} M$ to $1.00 \times 10^{-3} M$; $6.25 \times 10^{-6} M$ to $1.00 \times 10^{-4} M$; $7.80 \times 10^{-5} M$ to $1.25 \times 10^{-3} M$; $1.25 \times 10^{-5} M$ to $2.00 \times 10^{-4} M$; $6.25 \times 10^{-5} M$ to $1.00 \times 10^{-3} M$ for the solutions which are prepared with benzene, ethyl alcohol, n-propyl alcohol, iso-propyl alcohol and N,N-dimethylformamide; respectively.

REFERENCES

- [1] Rao C.N.R. "Ultraviolet and Visible Spectroscopy", London, Butterworths, pp. 1-20 (1961).
- [2] Murrell J.N. "The Theory of the Electronic Spectra of Organic Molecules", London, Methuen, pp. 4-18 (1963).
- [3] Stern E.S. and Timmons T.C.J. "Electronic Absorption Spectroscopy in Organic Chemistry", New York, StMartin's Press, pp. 5-10 (1971).
- [4] Williams D. H. and Fleming I. "Spectroscopic Methods in Organic Chemistry", Fourth Edition, Mc. Graw-Hill Book company Europe, pp. 1-29 (1989).
- [5] Brands C. M. J., Wedzicha B. L. and van Boekel M.A.J.S, "The use of radiolabelled sugar to estimate the extinction coefficient of melanoidins formed in heated sugar-casein systems", **International Congress Series**, 1245, 249-253, (2002).
- [6] Sandhu G.K., Singh K., Lark B.S. and Gerward L., "Molar extinction coefficients of some fatty acids", **Radiation Phys. And Chem.** 65, 211-215, (2002).
- [7] Barrow G.M. "Physical Chemistry", Fifth Edition, McGraw-Hill, pp. 541-549 (1988).

- [8] Grebenyuk S.A., Perepichka I.F. and Popov A.F., "Evaluation of the parameters of 1:1 charge transfer complexes from spectrophotometric data by non-linear numerical method", **Spectrochimica Acta Part A** 58, 2913-2923, (2002).
- [9] Skoog/Leary, "Principles of Instrumental Analysis", Fourth Edition, Saunders College Publishing, pp. 1-28. (1992).
- [10] Perkampus H.H., "UV-VIS Spectroscopy and Its Applications", Springer-Verlag Berlin Heidelberg, Springer Laboratory, pp.3-24 (1992).
- [11] Fenter F.F., Catoire V., Lesclaux R. and Lightfoot P.D. , " The ethylperoxy radical: Its ultraviolet spectrum, self-reaction, and reaction with HO₂, each studied as a function of temperature", **J. Phys. Chem** 97, 3530-3538, (1993).
- [12] Schwell M., Wachter N.K., RiceJ.H., Galaup J.P., Leach S., Taylor R. and Bensasson R.V., "Coupling a dendrimer and a fullerene chromophore: A study of excited state properties of C₆₁(poly(aryl)acetylene)₂ ", **Chem. Phys. Lett.** 339, 29-35, (2001).