

SOLVENT EFFECT ON ULTRAVIOLET SPECTRUM OF STYRENE

WEERASAK SOPITKITTIKUL^a, RUANGSRI WATANESK^b AND SURASAK WATANESK

Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50202, Thailand.

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ABSTRACT

The effect of solvents on the ultraviolet spectrum of styrene was studied by considering the absorption ratios (R_{pv}) at peak and valley of benzenoid bands. These ratios varied with the change of electrical environment that could be monitored through the dielectric constant of the solvent. It was found that the R_{pv} values of the solvent-induced (s-i) bands of styrene decreased as the polarity of solvent increased. In addition, at higher temperature, those values of R_{pv} turned out to be lower, especially in polar solvents.

INTRODUCTION

The ultraviolet (UV) spectra of aromatic molecules, particularly benzene, has been extensively studied¹⁻³. These spectra of benzene in solution have a solvent-induced (s-i) band which is absent in the vapor phase and often sensitive to the nature of local environment in solution. Spectral changes of benzene and its derivatives induced by solvent polarity could be observed through dielectric constant measurement². Styrene is also one of benzene derivatives which is normally used as monomer in suspension and emulsion polymerization⁴⁻⁵ for polystyrene production. The spectral change of styrene in different local environment might be used to predict the behavior of styrene environment in polymerization processes.

This paper reveals the effect of electrical environment from solvents on the absorption ratios (R_{pv}) of the s-i bands of styrene. These ratios show considerably sensitive to the variation in polarity of solvents of graded hydrophobic character namely heptane and some monohydric alcohols, and water. Moreover, the R_{pv} value of the s-i bands was also found to be a function of temperature.

MATERIALS AND METHODS

Chemicals

All chemicals used were of analytical grade. Styrene was obtained from Fluka (Buchs, Switzerland). Ethanol was obtained from Merck (Darmstadt, Germany). n-Heptane and 2-propanol were obtained from BDH (Poole, England). Methanol was obtained from JT-Baker (Philipsburg, U.S.A.). Water was deionized grade.

Measurements

UV

All UV measurements in this work were carried out by the same procedure as Mukerjee's². The styrene was dissolved in the studied solvents then heated close to the studied temperature. Then the UV spectra of the solutions were recorded from 400 nm to 240 nm by a UV-265 spectrophotometer (Shimadzu, Japan) with the temperature control. The absorption ratios (R_{pv}) between the absorbances at peak and valley were calculated. These ratios were obtained as the average of three measurements using the solvent as the blank.

Dielectric Constant

Measurement of the dielectric constants of solvents were carried out by a dipolmeter, model DM-01 (Wiss-Techn.-Werkstätten, Germany) at the desired temperature of 20, 30, 40,

and 50°C. The measurement cells were firstly calibrated and the dielectric constant of the studied solvent were then measured. Four measurements were carried out for each solution and then the mean value was calculated.

RESULTS AND DISCUSSION

Figure 1 shows the 240 - 400 nm region absorption spectra of styrene at various concentrations in n-heptane; which is used as a reference due to its low interaction with styrene molecules. Only two peaks in these spectra are concerned due to the non-overlapping with other adjacent bands. One is the P_1 peak at $\lambda_{\max 1} \sim 281$ nm and the other is the P_2 peak at $\lambda_{\max 2} \sim 290$ nm. These peaks in benzene are often called the solvent-induced (s-i) bands^{2,3}, because the absorption intensities of these bands vary with its surrounding. These variations could be monitored through the absorption ratios between the intensities at peak and valley of the s-i bands.

Figure 2 shows the variation of the absorption ratios between peak and valley (shorter λ than peak) of peak P_1 (R_{pv1}) and of peak P_2 (R_{pv2}) of the s - i bands of styrene at the concentration ranges of 0.01 - 0.10 g/l in different solvents. The studied solvents were as follows : n-heptane, 2-propanol, ethanol, methanol and water in order of increasing polarity. These absorption ratios R_{pv1} and R_{pv2} of each solution were found constant at the styrene concentration higher than 0.04 g/l, with the values of about 1.2 and 1.6, respectively, for styrene in nonpolar solvents and 1.1 and 1.3, respectively, for styrene in water. From these constant ratios of both R_{pv1} and R_{pv2} , the optimum concentration of styrene could be chosen for further study.

Figure 3 shows the effect of solvent polarity, at 30°C, on the absorption ratios of styrene solution. The electrical behavior of solvents at the optimum styrene concentration with constant R_{pv1} and R_{pv2} could be observed by the dielectric constant measurements. The values of the dielectric constants (ϵ) of nonpolar to polar solvents range from 2 for n-heptane to 76 for water. It could be noticed that the absorption ratios (both R_{pv1} and R_{pv2}) of styrene

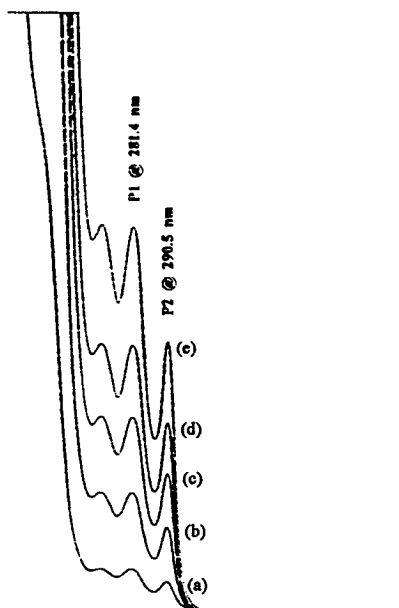


Fig.1 UV absorption spectra of styrene at various concentrations (g/l) in n-heptane : (a) 0.01 (b) 0.03 (c) 0.05 (d) 0.07 (e) 0.10

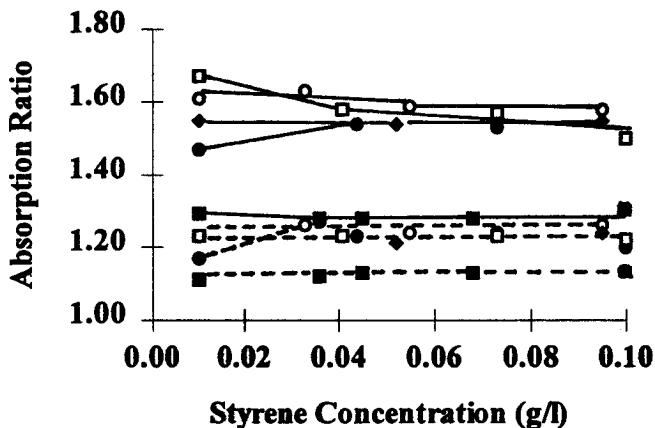


Fig.2 Absorption ratios : R_{pv1} (broken lines) and R_{pv2} (solid lines) of the s-i bands at various styrene concentrations in different solvents : n-heptane (\square), 2-propanol (\circ), ethanol (\blacklozenge), methanol (\bullet) and water (\blacksquare).

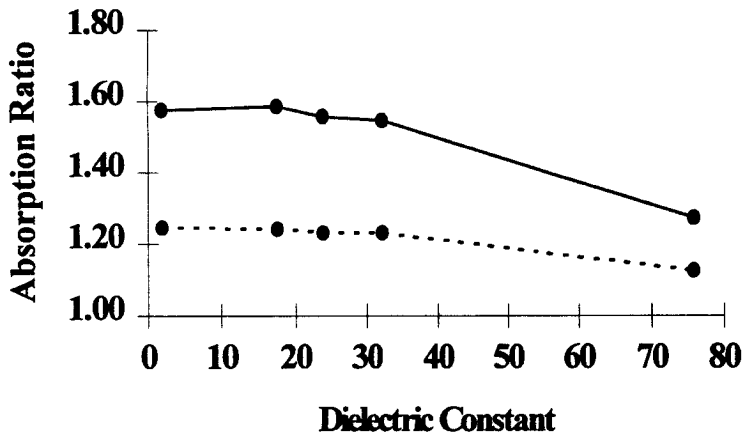


Fig.3 Absorption ratios : R_{pv1} (broken line) and R_{pv2} (solid line) of the s-i bands at optimum styrene concentration in various solvents with different dielectric constants at 30°C.

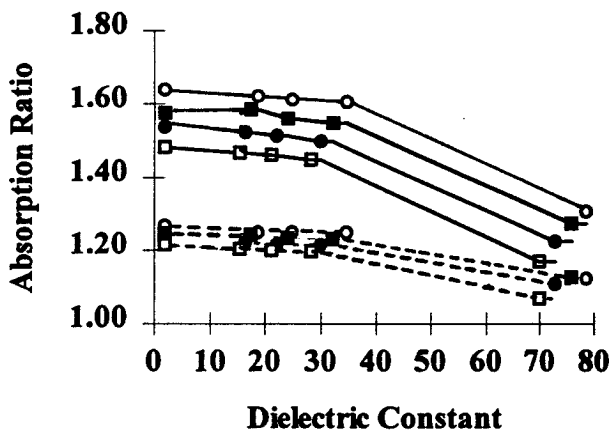


Fig.4 Absorption ratios : R_{pv1} (broken lines) and R_{pv2} (solid lines) of the s-i bands at optimum styrene concentration in different dielectric constant solvents at various temperatures : 20°C (\circ), 30°C (\blacksquare), 40°C (\bullet) and 50°C (\square).

decreased with the increasing of the dielectric constant of solvent, especially in higher polarity solvents. But the decrease of both R_{pv1} and R_{pv2} of styrene in solvents with $\epsilon > 30$ were quite significant compared to those with lower ϵ . This means that the intensity of the s-i bands of styrene were affected by the induction strength of solvents, especially in more polar solvents. This effect was also observed by Mukerjee² in UV spectrum of benzene.

When styrene molecules were perturbed by the electrical field of the solvents, it would increase the radiationless internal conversion of excited states that caused the intensity of s-i bands of styrene to become higher^{1,6-8}. For lower dielectric constant solvents which have more hydrocarbon groups, it could be observed that the interacting forces between benzene groups of the styrene and solvents could be either induced dipole-induced dipole interaction or dispersion forces. Whereas higher dielectric constant solvents would encounter the interaction of dipole-induced dipole due to the hydroxyl groups on solvent molecules. Moreover, for solvents with ϵ in the region of 30-76, a strong tendency of hydrogen bonding between hydroxyl groups of solvent and the π electrons of benzene group in styrene would be possible. This H-bond would cause a large increase of the s-i band intensity of styrene at the optimum concentration (Figure 3). The increase of the s-i band intensities of styrene due to the changing polarity of the environment could be described in the same manner as those of benzene and its other derivatives². The increase of the electronic transition could be accomplished by creating more interaction between benzene group and the perturber⁷ which is the solvent in this case.

The effect of the temperature on s-i bands of styrene in various solvents at the optimum concentration was also studied by recording the UV spectra of styrene at different temperatures. It was observed from Figure 4 that the values of the R_{pv} tended to decrease in the same fashion at all of the studied temperatures. The higher the temperature is, the lower the values of the R_{pv} . This is because at high temperature, more collision among molecules in the system occurred, especially the collision between solvent molecule and styrene molecule which would promote more conversion of the radiationless transition.

CONCLUSIONS

Styrene molecule has similar behavior to benzene which has been extensively studied. It could be perturbed by the static electrical environment of solvents which was measured in terms of dielectric constant ϵ . This behavior could be noticed from the decrease of the absorption ratios (R_{pv}) of the UV solvent-induced (s-i) bands in the benzenoid region with the increase of solvent polarity. This solvent induction caused the change in radiationless internal conversion of excited state electronic transition of styrene.

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บทคัดย่อ

ได้ศึกษาถึงอิทธิพลของตัวทำละลาย ที่มีต่ออัตราไวโอเลตสเปกตรัมของสไตรีน โดยพิจารณาจากอัตราส่วนของการดูดกลืนแสง (R_{pv}) ที่เกิดและฐานของพีคบริเวณเบนซินของสไตรีน อัตราส่วนนี้เปลี่ยนแปลงกับสภาพทางไฟฟ้าของสภาวะแวดล้อมที่สามารถติดตามได้จากค่าคงที่ไดโพลทริกของตัวทำละลาย พบว่าค่า R_{pv} ของแบนด์ที่เหนี่ยวนำด้วยตัวทำละลาย จะลดลงตามการเพิ่มของสภาพขั้วของตัวทำละลาย นอกจากนี้ ที่อุณหภูมิสูงกว่าอัตราส่วนเหล่านั้นจะมีค่าน้อยกว่า โดยเฉพาะอย่างยิ่งในตัวทำละลายที่มีขั้ว