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EVALUATION OF CMC OF SURFACTANTS THROUGH THE UV S-I BANDS OF STYRENE

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ABSTRACT

The effect of surfactants on the ultraviolet spectrum of aqueous styrene solution was studied by considering the absorption ratios (R_{pv}) at peak and valley of the solvent-induced (s-i) bands. These ratios varied with the change of electrical environment that could be monitored through the conductance measurement of the solution. Deflection of the R_{pv} values of styrene in styrene-sodium dodecylsulfate (SDS) solution could be observed in the critical micelle concentration (CMC) region of SDS, but not noticeable in styrene-polyvinyl alcohol (PVA) solution. The result from the appearance of the CMC of SDS deduced from the R_{pv} values of styrene in styrene-SDS solution corresponded to those obtained by other methods such as conductivity and UV absorption measurements.

INTRODUCTION

Styrene is one of benzene derivatives which is normally used as a monomer in suspension or emulsion polymerization for polystyrene production[1-2]. In emulsion polymerization, anionic surfactant such as sodium dodecylsulfate (SDS) acts as an emulsifier due to its lyophobic and lyophilic properties. Whilst, in suspension polymerization, nonionic surfactant like polyvinyl alcohol (PVA) is used as a suspension stabilizer to prevent coalescence occurring during the polymerization process. The effect of solvents on the ultraviolet (UV) spectra of styrene was studied[3] by considering the absorption ratio (R_{pv}) at peak and valley of the solvent induced (s-i) bands in benzenoid region[4-6]. These ratios of intensity decreased with the increase of solvent polarity due to the change of static electrical environment in solution.

In this paper we aim to report the effect of surfactants on the R_{pv} of the s-i bands of styrene. The surfactants used were SDS and PVA. Study of the UV spectra of styrene in surfactant solution might be used for predicting the behavior of styrene in the environment of emulsifier and suspension stabilizer in polymerization processes.

MATERIALS AND METHODS

Chemicals

All chemicals used were of analytical grade. Styrene and sodium dodecylsulfate (SDS) were obtained from Fluka (Buchs, Switzerland). Polyvinyl alcohol (PVA) was obtained from Sigma (St. Louis, U.S.A.). Water was deionized grade.

Measurements

UV

All UV measurements in this work were carried out as the same procedure as Watanesk's[3].

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Conductivity

The conductivities of the concerned solutions were measured by means of a conductivity meter (Weilheim, Germany) at 30°C. Three measurements of each solution were then averaged. Accuracy of the conductivity meter was firstly calibrated with KCl solution before making measurements.

RESULTS AND DISCUSSION

In general, in any solution containing surfactant, changes in physico-chemical properties of solution relate to the changes in surfactant concentration. Therefore it is necessary to determine the critical micelle concentration (CMC) of surfactant in that solution in order to determine the optimum surfactant concentration for a further study. In the region of CMC, arrangement of surfactant molecules in solution is quite different from dilute condition due to the formation of micelle. This micelle formation could change electrical environment for the bulk of solution and might affect the intensities of the s-i bands of styrene. The CMC determination of surfactants in water were carried out by conductivity measurement and reassured by spectrophotometric measurement. The aqueous solutions of surfactants were prepared by dissolving various amounts of the surfactant in 25-ml volumetric flasks and filled up with deionized water. Then the conductivity of each solution was measured along with the absorbance reading at 220 nm.

Figure 1 shows the variations of specific conductivity and absorbance of SDS with its concentration. It was noticeable from these plots that both conductivity and absorbance measurements exhibited corresponding deflection zones within the SDS concentration of about 2.0 g/l within the conductivity range of 700 - 800 μS/cm. This zone could be regarded as the CMC for micelle formation of SDS which corresponded to those obtained by other methods[7-8].

The variation of specific conductivity with the concentration of SDS happened in the manner that as the SDS concentration increased, the specific conductivity started rising because more ions were introduced to the solution. When the dodecylsulfate ions commenced aggregation, slower rising in conductivity occurred because of the bulkiness of the aggregated species. After the micelle formation had completed, the excess dodecylsulfate ions could move freely and again caused the increase in conductivity. Likewise, in absorbance measurement, the absorbancy of the SDS solution became stall in the CMC region due to the association of dodecylsulfate ions.

The effect of surfactants on the absorption ratios, R_{pv1} and R_{pv2} ,of styrene was studied at $\lambda_{max1} \sim 281$ nm and $\lambda_{max2} \sim 290$ nm, respectively. The wavelength shift of these bands was not evidently noticed after adding surfactant into the styrene solution. Then effect of electrical environment due to anionic SDS on the styrene was followed by measuring the conductivities of styrene-SDS solutions. Styrene in aqueous solutions of SDS were prepared by pipetting 30 μl of 1.1 g/l of the styrene solution into each 25-ml volumetric flask. Then made up the volume in each flask with the SDS solution of various concentrations. The UV spectra and the conductivities of those solutions were later measured at 30°C. Fixed amount of 0.1 g/l of styrene in SDS solution was chosen from the previous study[3] that would result in only variation of the styrene intensity with SDS.

Figure 2 shows the effects of SDS concentration on the R_{pv1} and R_{pv2} of the s-i bands of styrene and specific conductivity of styrene-SDS solution. Deflections of those curves were observed at the SDS concentration of about 2.0 g/l which corresponded to the CMC of SDS in water found in Figure 1.

In dilute styrene-SDS solutions, the values of Rpv should have increased with the increase of SDS concentration because the increasing numbers of its long chain hydrophobic portion created the lower polarity of the solution comparing to water[3]. It was observed from the solid line plot in Figure 2 that when styrene was present in a highly diluted SDS solution, the R_{pv} values of styrene increased from that of water. This confirmed the result obtained in previous report that the R_{pv} value increased with the decrease of the solvent polarity. But once the concentration of SDS solution increased to the range of 0.5-1.25 g/l, the Rpv values tended to decrease and converged to a higher value at the SDS concentration of about 2.0 g/l. The reason for such change is due to the fact that at low concentration; the dodecylsulfate ions try to arrange their orientation to form micelle by turning their hydroophobic parts to each other and pointing out their hydrophilic ends toward medium. This arrangement would create higher electrical atmosphere to styrene that caused the decrease of the R_{pv} values. When the SDS concentration was high enough to reach the value of CMC, the SDS micelle formation occurred. The larger structure of the micelle would reduce its energetic motion, resulting in the increase of the R_{pv} values of styrene. At concentration of SDS higher than the CMC value (about 2.0 g/l), the R_{pv} value was again observed to be decreasing which was caused by the presence of excess dodecylsulfate. This behavior could be reasoned as the repetition of the other micellar shape formation such as rod and/or lamella.

The change in electrical environment of the solution which would influence the spectroscopic behavior of styrene was also measured conductometrically. Deflection point in specific conductivity, shown by the broken line in Figure 2, was again observed in the CMC region of SDS similar to that observed in Figure 1. It was noticeable that both of the deflection point of specific conductivity and converging point of the R_{pv} value occurred at the same region of the CMC of SDS. Despite both deflection and converging points in Figures 1 and 2, especially in Figure 2, seem not to be so distinctive, but regarding to the standard deviations of the measurements as indicated by the error bars, this could still confirmed the existence of those points. Therefore, the spectroscopic behavior of styrene in SDS solution would, in turn, indicate and confirm the micelle formation of the dodecylsulfate.

The role of spectroscopic behavior of styrene influenced by the change in electrical environment of the solution containing surfactant could further be revealed when nonionic PVA was present in the solution of styrene. In this study, styrene in aqueous solutions of PVA were prepared by the same procedure as in styrene-SDS solution described above. The UV spectra and conductivities of the solutions were also measured at 30°C. It was found from Figure 3 that no deflection neither of the R_{pv} values nor the conductivity of the solution could be noticed for indicating the existence of micelle in the styrene-PVA solution. The presence of PVA in styrene solution did not affect the s-i bands of styrene due to their nonpolarity of PVA molecules. This happening occurred as expected because PVA molecules were very slightly polar and the dissolution in aqueous solution was quite low. Therefore, the concentration of PVA would not be high enough for inducing the aggregation of PVA molecules in micelle formation which resulted in no noticeable change in both the R_{pv} values of the s-i bands of styrene and the conductivities of the solution.

By now, it is evident that the change of the R_{pv} values of the s-i bands of styrene indicated the behavior of styrene environment affected by different types of surfactants. For anionic surfactant such as SDS, the deflection of the R_{pv} values of styrene indicates the occurrence of the micelle formation of SDS which is not exhibited by nonionic PVA.

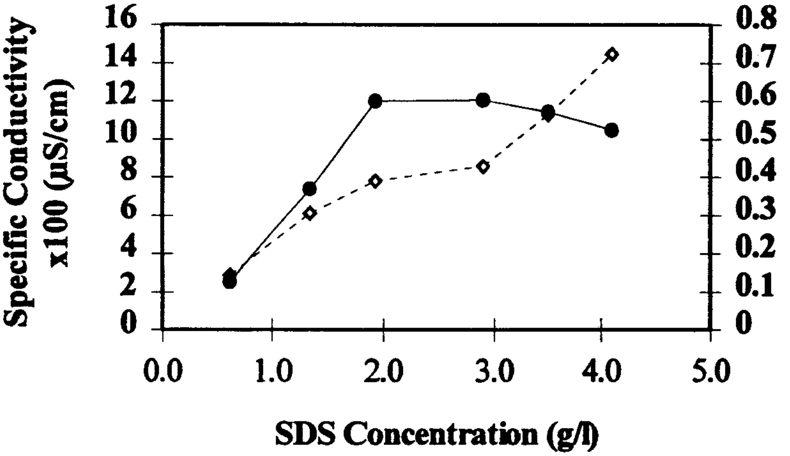

Fig.1. Variations of specific conductivity (broken line) and absorbance reading at 220 nm (solid line) of SDS solution with its concentration.

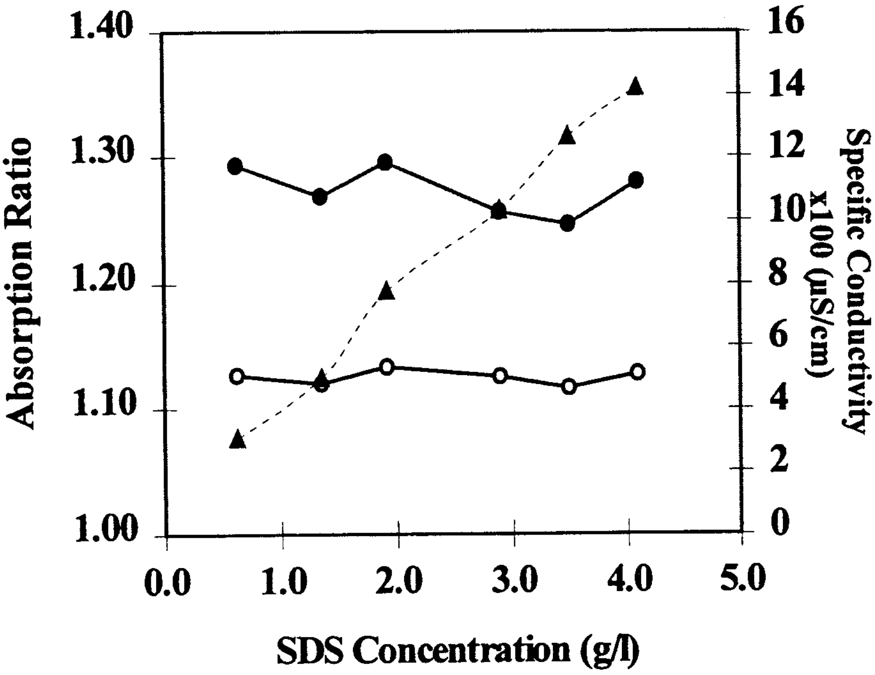

Fig.2. Variation of the absorption ratios (solid line) : R_{pv1} (o) and R_{pv2} (●) of the s-i bands and specific conductivity (broken line) of styrene-SDS solution with the SDS concentration.

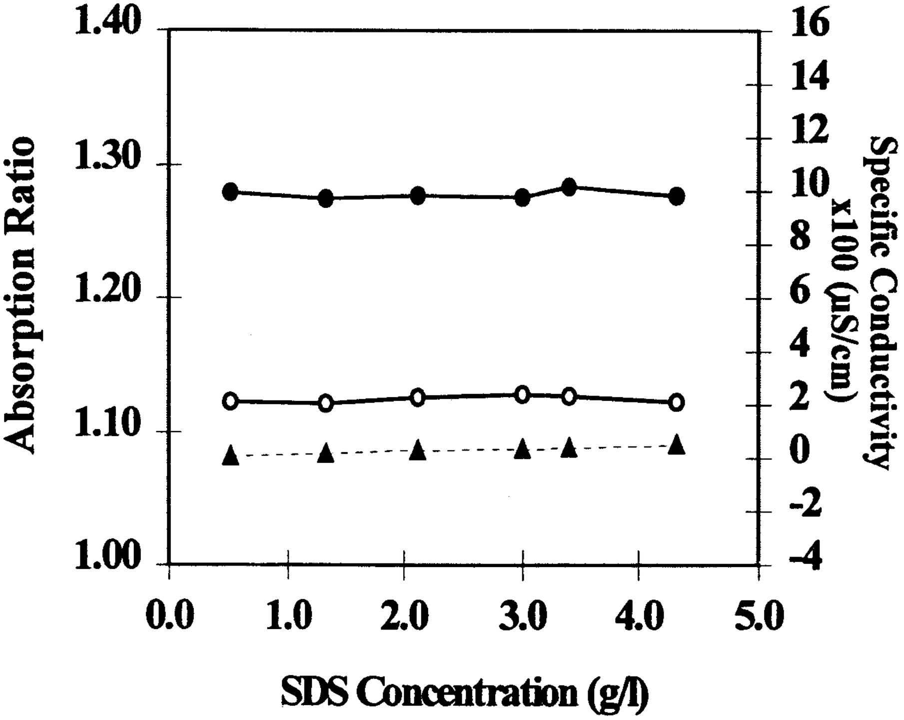

Fig.3. Absorption ratios (solid line) : R_{pv1} (o) and R_{pv2} (●) of the s-i- bands and specific conductivity (broken line) of styrene-PVA solution with the PVA concentration.

CONCLUSIONS

Styrene molecules could be perturbed by electrical environment of anionic surfactant such as sodium dodecylsulfate but not by nonionic surfactant like polyvinyl alcohol. The perturbation could be observed from the absorption ratios (R_{pv}) at the peak and valley of the solvent induced (s-i) bands of styrene. These ratios were affected by the surfactant concentration, especially in the CMC region. The CMC value of SDS deduced from deflection of the R_{pv} values of styrene corresponded to those obtained by other methods.

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บทคัดย่อ

ได้ศึกษาถึงอิทธิพลของสารลดแรงตึงผิวชนิดแอนไอออนิกที่มีต่ออัลตราไวโอเลตสเปกตรัมของสไตรีนในน้ำ โดยพิจารณาจากอัตราส่วนของการดูดกลืนแสง (R_{pv}) ที่พีคและฐานของพีคที่ถูกเหนี่ยวนำด้วยตัวทำละลาย ที่เปลี่ยนแปลงไปกับสภาพทางไฟฟ้าของสิ่งแวดล้อม ซึ่งสามารถติดตามได้จากการวัดค่าการนำไฟฟ้าของสารละลาย พบการเปลี่ยนแนวของค่า R_{pv} เกิดขึ้นบริเวณความเข้มข้นวิกฤติของไมเซลล์ (ซีเอ็มซี) ของโซเดียมโดเดคิลซัลเฟต (เอสดีเอส) ในสารละลายสไตรีน-เอสดีเอส แต่ไม่พบในสารละลายสไตรีน-พอลิไวนิลแอลกอฮอล์ (พีวีเอ) ผลที่ได้จากการเกิดซีเอ็มซีของเอสดีเอส สรุปจากค่าของ R_{pv} ของสไตรีนในสารละลายสไตรีน-เอสดีเอส สอดคล้องกับค่าที่หาได้จากวิธีอื่น เช่น จากการวัดค่าการนำไฟฟ้าและการวัดค่าการดูดกลืนแสงอัลตราไวโอเลต