Abnormal Hyperchromism of the n→π^* Absorption Band of Acetone in Protic Solvents

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Concentration dependence (1—10^{-4} molar fraction) of the UV absorption spectra of the binary mixtures of (i) acetone–water, (ii) acetone–ethanol, and (iii) diisobutyl ketone–ethanol systems was studied. In (i) and (ii) distinct spectral changes of three steps were observed in succession, while in (iii) gradual changes in two steps were observed. The intensities of the n→π^* band of very dilute solutions for these systems are enhanced, respectively, by 40, 20, and 15 per cent. The results were interpreted as the following stepwise equilibria

$$A + B \rightleftarrows AB, \quad AB + B \rightleftarrows AB_2, \quad AB_2 + B \rightleftarrows AB_3$$

for (i) and (ii), while in (iii) the last step is obscured, where A and B denote, respectively, ketone and water or ethanol molecules. The structure of AB_3 is discussed.

The n→π^* absorption bands of ketones have been extensively studied and known to show blue shift in protic solvents.[1,2] However, most of the studies on the solvent effect of the electronic absorption spectra have been performed using dilute solutions. Above all Bayliss and Wills-Johnson extensively measured the n→π^* bands of various ketones and nitro-compounds in a number of solvents and claimed that the intensity change can be explained mainly by the dispersion force, even for the cases where hydrogen bonding exists.[3] They found that, among the various solvents studied, water has by far the most peculiar effect to increase the oscillator strength as large as 40 per cent in dilute solution, but they failed to observe the concentration dependence. Gorubunov and Naberukhin measured the concentration dependence of IR and UV spectra of acetone-water mixtures in a wide range and attributed them to the two step hydrogen bonding forming acetone–water and acetone–$(\text{water})_2$ complexes.[4] However, their conclusions are not decisive yet, since they did not analyze the intensity change. Further, Lavrik and Naberukhin proposed that cooperative effects of the hydrogen bonding of water molecules are operative in dilute aqueous non-electrolyte solutions.[5] On the other hand, Reuben explained the concentration dependence of the NMR spectra of acetone-water mixture by the existence of two different hydrogen bonding species, *i.e.*, acetone–water and $(\text{acetone})_2$–water.[6]

Summarizing these studies, it is plausible to assume at least the following three different hydrogen bonding species for explaining the spectral change of the acetone–water mixture.

$$R_2CO + HOH \rightleftarrows R_2CO \cdots HOH \qquad (AB) \qquad (1)$$

$$R_2CO \cdots HOH + R_2CO \rightleftarrows R_2CO \cdots HOH \cdots OCR_2 \qquad (A_2B) \qquad (2)$$

$$R_2CO \cdots HOH + HOH \rightleftarrows R_2CO \cdots (HOH)_2 \qquad (AB_2) \qquad (3)$$

For acetone-alcohol mixtures similar arguments may apply but without assuming the A_2B type species.

As argued from the above discussion the concentration dependence of the n→π^* absorption bands of ketone in protic solvents needs to be remeasured carefully, and also the effects of the proton donating and accepting powers of the solvent and solute should be studied in order to settle the discussions above.

In this study we have performed accurate measurements of the n→π^* absorption bands of the binary mixture of acetone–water, acetone–ethanol, and diisobutyl ketone–ethanol systems over the full concentration range, *i.e.*, from pure acetone liquid down to very dilute solutions as low as $\approx 10^{-4}$ molar fraction.[7] The conclusions obtained in this study are as follows.

i) The intensity of the n→π^* absorption bands of ketones in protic solvents such as water and alcohols increases steadily but not monotonously as the concentration of the ketone decreases, and as yet no lower limit of the concentration is obtained below which the spectrum is stable.

ii) This concentration dependence of the n→π^* absorption bands of acetone in water can be interpreted as the stepwise equilibria involving successive coordination of the protic solvent molecules through hydrogen bonding as

$$A \longrightarrow AB(A_2B) \longrightarrow AB_2 \longrightarrow AB_3.$$

Especially in the very low concentration of acetone (below 10^{-2} molar fraction), it is essential to assume the third water molecule which causes extraordinary enhancement of the n→π^* absorption band by forming AB_3 species as

$$R_2CO \cdots (HOH)_2 + HOH \rightleftarrows R_2CO \cdots (HOH)_3 \quad (AB_3). \quad (4)$$

iii) Almost the same but a little different mechanism can be applied to other combinations of ketones and protic solvents, the difference being attributed to the strength of the hydrogen bonding.

iv) It became clear that any discussion on the solvent effect is liable to be in serious error unless concentration dependence in a wide range down to lower molar fraction is studied.

Experimental

Acetone and ethanol of G. R. grade were dried over molecular sieve 3A and distilled several times until the refractive indices got close to the literature values. Water for spectral measurements was passed through the ion exchange resin and distilled. Crude diisobutyl ketone was purified by the courtesy of Shimadzu Seisakusho using a preparative gas chromatograph. It is reported that the gas chromatogram analysis assures 100% purity. The refractive index also agreed with the literature value, 1.4122. The molar fraction of the solutions was determined by weight using measuring flasks.

The UV spectra of ketones in water and ethanol of wide range of concentrations were measured with a Shimadzu D-40R recording spectrophotometer at room temperature. In order to check the linearity in the high optical density region, the influenece of the stray light of the recorded intensity was checked by using the calibrated potassium chromate in aqueous 0.05 M KOH solutions. Various fused quartz cells of the lengths, 5, 1, 0.5, and 0.1 cm, with stoppers and quartz assembling cells of 0.01 cm were used depending on the concentration of ketones. The length of the 0.01 cm cells was calibrated using a micrometer, while other cells were calibrated by measuring the standard spectra. In the case where the absorbance gets larger than 2, the reference light was diminished by using a wire net whose absorbance is nearly equal to unity in the wavelength region between 350 and 230 nm. Reproducibility of the spectra was strictly checked.

The temperature dependence of the n→π* band of acetone in water was checked in the range 20—50 °C by using a cell jacket through which water from a constant temperature bath is circulated.

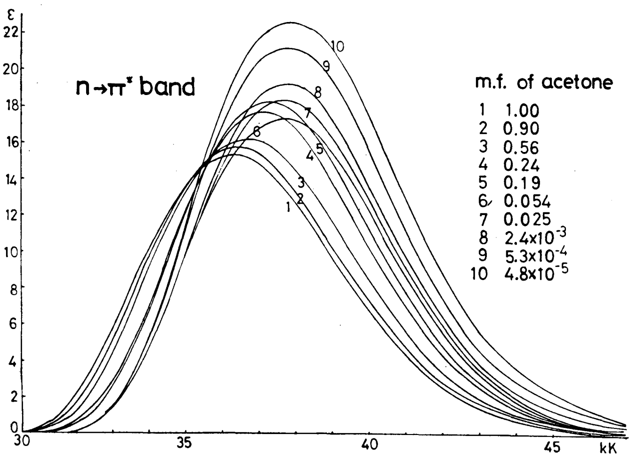


Fig. 1. The concentration dependence of the n→π* absorption band of acetone in the binary mixtures with water.

Results

Acetone–Water System. As shown in Fig. 1, the n→π* absorption band of the acetone–water system changes so slightly in the concentration range (Region I) between 1.0 and 0.15 molar fraction (x_A) that only a vague isosbestic point can be observed. Below 0.15 down to 0.05 of x_A (Region II) the intensity of the band slowly diminishes. Further, as the concentration gets lower (Region III) the intensity (ε_{max}) of the band monotonously increases and we could not observe the convergence limit at the infinite dilution.

In order to see the spectral change in more detail in the low concentration range, λ_{max} and ε_{max} are plotted against the logarithm of x_A as in Fig. 2.[8] It should be noted that both the curves have similar concentration dependence and their inflexion points are found nearly in the same concentration region. To see this more quantitatively, the plots of ε—log x_A at various wavelengths are given in Fig. 3. For a single equilibrium as $A+B \rightleftharpoons AB$, the plotted curve should be something like a sigmoid one unless the wavelength is chosen at the isosbestic point.[9] For stepwise equilibria the plotted curve is expected not exactly but approximately to be a composite of the curves of the component equilibria. If a few wavelengths are carefully chosen for this plot one can easily decompose the whole change into the component equilibria.[10] This is the case with Fig. 3, where the wavelengths 35710 and 39220 cm^{-1} are so chosen from the isosbestic points for the first and second steps, respectively, that the spectral changes in the other steps clearly come out. The wavelengths 36360 and 37380 cm^{-1} are chosen so as to get zig-zag plots and are advantageous over the region above 40000 or below 34000 cm^{-1} giving monotonously increasing or decreasing curve. Now it is unambiguous that we are really observing three distinct equilibria as in Regions I—III mentioned above.

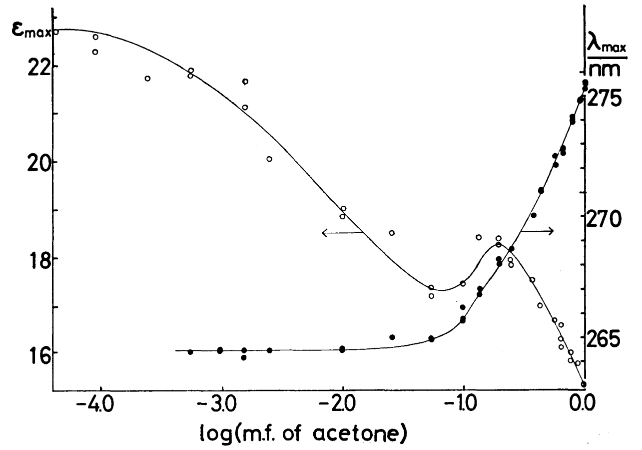


Fig. 2. The λ_{max}—log x_A and ε_{max}—log x_A plots of the acetone–water system, x_A being the molar fraction of acetone.

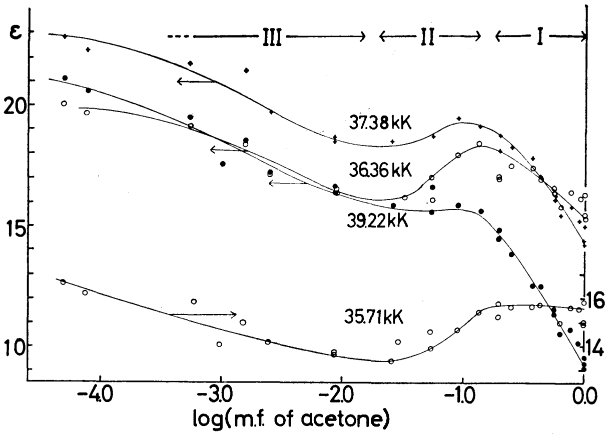


Fig. 3. The plots of ε—log x_A for the acetone–water system indicating three stepwise equilibria, Regions I—III.

Acetone–Ethanol System. As seen in Fig. 4 the n→π* band of acetone in ethanol does not effectively show wavelength shift (4 nm to blue) but gains only small fraction (about 20 per cent) of intensity as the concen-

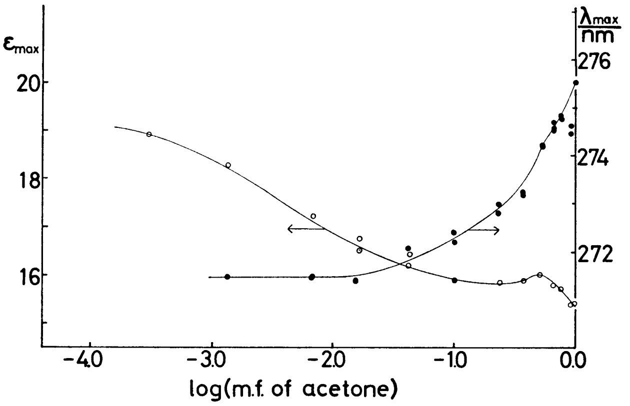


Fig. 4. The $\lambda_{\max}$—log x_A and $\varepsilon_{\max}$—log x_A plots of the acetone–ethanol system.

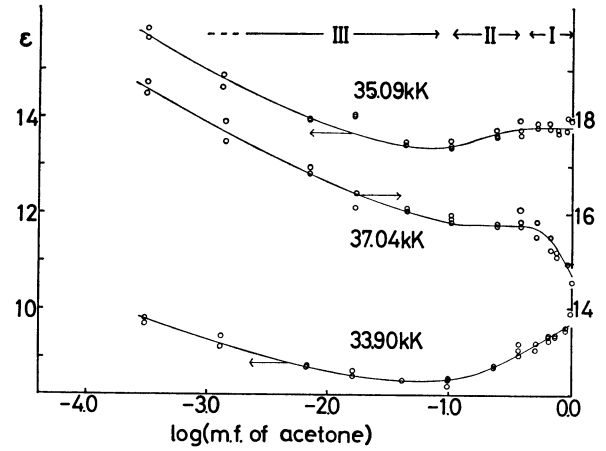


Fig. 5. The plots of ε—log x_A for the acetone–ethanol system indicating three stepwise equilibria, Regions I—III.

tration gets lower than 10^{-2} molar fraction or 0.2 M. However, if the ε—log x_A plot is taken as in Fig. 5, this spectral change also reveals three successive equilibria as in the acetone–water system. The only differences are: (i) the x_A regions in which the first and second steps occur are shifted to higher x_A values, and (ii) the degree of hyperchromism and blue shift are small. Acetone–methanol mixtures show almost the same but a little pronounced spectral changes as the acetone–ethanol system. On the other hand, the binary mixture of acetone–dioxane does not show appreciable spectral change comparable at least with that of acetone–ethanol.[11]

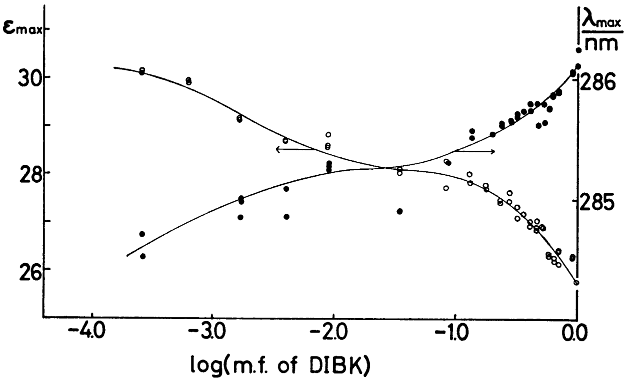


Fig. 6. The $\lambda_{\max}$—log x_A and $\varepsilon_{\max}$—log x_A plots of the diisobutyl ketone–ethanol system.

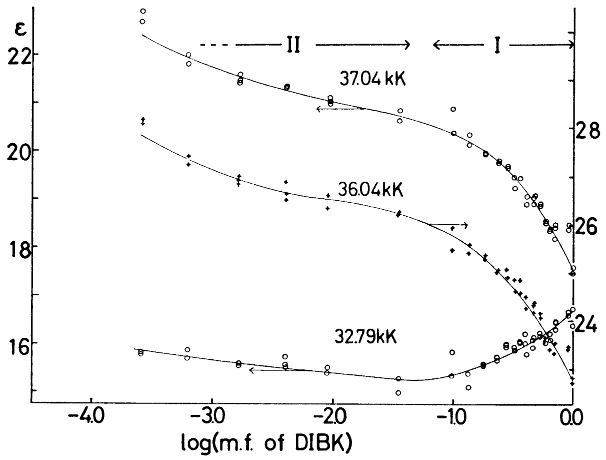


Fig. 7. The plots of ε—log x_A for the diisobutyl ketone–ethanol system.

Diisobutyl Ketone–Ethanol System. As shown in Figs. 6 and 7, the n→π* band and its concentration dependence of this binary mixture is different from the case of the acetone–ethanol mixture in three points: (i) the intensity is considerably larger, (ii) in the low concentration range the intensity is monotonously growing up with small (1.5 nm) blue shift, and (iii) only two successive equilibria can be seen below and above 0.03 molar fraction indicating the low ability of diisobutyl ketone toward hydrogen bonding.

Discussion

Expected Spectral Changes of Various Hydrogen-Bonded Species. By taking account of the several mechanisms proposed by many authors, the spectral changes obtained above can be interpreted in terms of the successive change of the equilibria (1)—(4). In the following discussion the hydrogen-bonded species composed of the *m* ketone and *n* water molecules will be denoted as A_mB_n (see Chart 1). Before going into the details in the stepwise equilibria, let us try to estimate the possible change in the intensity and the wavelength at the absorption maximum.

The blue shift of AB or A_2B relative to A is known to be due to the net stabilization of the ground state by the hydrogen bonding with protic solvent molecules. Since

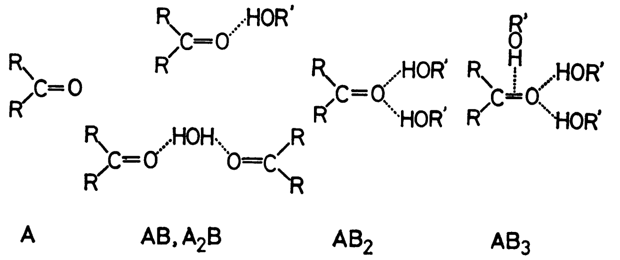


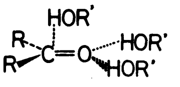
Chart 1.

we are observing the signal from the acetone molecule, it is very difficult to distinguish between AB and A_2B, if any, from the change of the $n \rightarrow \pi^*$ absorption band. Thus in the following discussion no attempt is tried to elucidate the relative ratio of AB to A_2B. However, this ambiguity has little effect on the discussion of the succeeding changes, *i.e.*, equilibria (3) and (4).

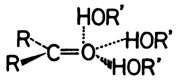
If the second solvent molecule is to attack the second lobe of the lone pairs of the carbonyl oxygen atom, further blue shift is expected for AB_2 relative to AB. According to the *ab initio* molecular orbital calculation by Iwata and Morokuma on the A, AB, and AB_2 species of formaldehyde, the same magnitude of blue shift is predicted both in the two equilibria (1) and (3).[12] It is reasonable to expect that nearly the same argument is applied to the case of acetone in water. For the case of acetone and alcohol, the magnitudes of these shifts may be smaller, reflecting the weaker hydrogen bond.

On the other hand, the intensity of the $n \rightarrow \pi^*$ band of AB is supposed to be larger than that of AB_2 since the potential of the electrons of the carbonyl group of AB has at most the C_s symmetry rather than the C_{2v} symmetry of AB_2 and releases the $n \rightarrow \pi^*$ transition from having the forbidden character. The intensity of the band of AB_2 may be a little larger than that of A due to the labile and fluctuating hydrogen bonds which distort the C_{2v} symmetry.

As to the position of the attack by the third solvent molecule, two possible structures, I and II, are proposed for AB_3, where the carbon and oxygen atoms are attacked, respectively.

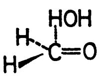


I

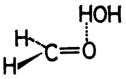


II

Since we cannot predict *a priori* which structure is more plausible for AB_3 species, let us look into the results of the *ab initio* calculation of the hydrogen bonding effect on the $n \rightarrow \pi^*$ transition of acetone. According to Iwata and Morokuma[12] the energy of the $n \rightarrow \pi^*$ transition is unchanged both for structures I′ and II′, in which a water molecule attacks from above the molecular plane of free formaldehyde.



I′



II′

However, there is no guaranty that this is also true for the attack of the third water molecule as in I and II. Del Bene has performed the population analysis for the species A and AB, where water molecules are situated in the formaldehyde plane, and found that the π-electron density of the oxygen atom is increased every time the first and second water molecules pulls the lone pair electrons through the σ-type hydrogen bonding.[13] This result is in favor of structure II but not decisive yet.

Anyway we can expect strong hyperchromism by the third water molecule to break the C_{2v} symmetry.

On the other hand, large blue shift is not expected for AB_3 species as the π-electron but not the lone pair electron is purturbed in either of the proposed structures.

Interpretation of the Spectral Changes in Terms of the Stepwise Equilibria. Now turn to the spectral change of the acetone–water system. In going from $x_A = 1$ to 0.12, the $n \rightarrow \pi^*$ band is shifted to blue by 0.15 eV with a moderate intensification. This change is in consistent with the expectation that the first water molecule attacks the carbonyl oxygen lone pair as in equilibrium (1) in agreement with the results of *ab initio* calculations.[12,13] The second change from $x_A = 0.12$ to 0.03 is a hypochromism with a further but small blue shift (0.03 eV). The symmetrical coordination of the water molecules (equilibrium (3)) may lower the intensity of the $n \rightarrow \pi^*$ band. Although two independent *ab initio* calculations[12,13] give much larger blue shift for AB_2 species there is no other candidate for explaining this spectral change in Region II.

For the concentration region below $x_A = 0.03$ (Region III) the intensity of the $n \rightarrow \pi^*$ band is monotonously growing up to the extraordinary large $\varepsilon_{\max}$ value without blue shift. That this sharp increase in the intensity is an abnormal phenomenon can be realized by replotting the curve in Fig. 2 against x_A, instead of $\log x_A$. Further, as shown in Figs. 4 and 5, a similar spectral change as Regions I, II, and III is observed also for the acetone–ethanol and the acetone–methanol (not shown) system, the same mechanism should be applied to these systems. As far as we know, only water, methanol, and ethanol are the strongly perturbing solvents for the intensity of the $n \rightarrow \pi^*$ band toward the infinite dilution without blue shift.[11]

Thus we can safely conclude that in the binary mixtures of acetone–water and acetone–alcohol the three successive hydrogen bonding equilibria (1), (3), and (4) take place. It should be noted here that although in the latter system A_2B species or equilibrium (2) is absent, the overall spectral change is essentially the same as that of the former system. This justifies the above statement that ambiguity in the ratio of AB to A_2B in the acetone–water system has little effect on the succeeding equilibria (3) and (4).

The different feature (ii) of ethanol from water stated in Results can be explained by assuming a smaller perturbation of ethanol molecule to the carbonyl group relative to that of water molecule. Whereas the main cause of the difference (i) can be attributed to the fact that, in spite of the weaker hydrogen bonding ability, ethanol molecules are more ready to associate with ketone molecules than water molecules owing to the strong tendency toward the self-association of water molecules as discussed by Gorubunov and Naberukhin.[4]

The bulky alkyl groups of a diisobutyl ketone molecule are likely to break the C_{2v} symmetry of the electronic structure of the carbonyl group reducing the forbidden character of the $n \rightarrow \pi^*$ band more than that of acetone. These bulky alkyl groups are considered to hinder ethanol molecules from associating with the carbonyl group, so that AB_2 species is difficult to be formed and a considerable amount of AB species is seen until fairly lower concentration range. The bulky alkyl groups of the diisobutyl ketone are thus responsible for the

Table 1. Absorption characteristics of the typical hydrogen-bonded species of ketones and water or ethanol

Item		a		b		c		d
Region			I		II		III	
Acetone–Water	x_A	1.0		0.133		0.054		4.82×10^{-5}
	λ_{max}/nm	275.2		267.0		264.9		264.5
	ε_{max}	15.4		18.5		17.4		22.8
	$\Delta\nu_{1/2}$/kK	6.10		6.12		6.11		6.43
Acetone–Ethanol	x_A	1.0		0.515		0.099		3.02×10^{-4}
	λ_{max}/nm	275.2		274.2		272.4		271.5
	ε_{max}	15.4		16.0		15.9		18.9
	$\Delta\nu_{1/2}$/kK	6.10		6.25		6.51		6.35
Diisobutyl Kteone–Ethanol	x_A	1.0		0.0348		6.16×10^{-4}		
	λ_{max}/nm	286.1		285.3		284.6		
	ε_{max}	25.8		28.1		31.0		
	$\Delta\nu_{1/2}$/kK	5.40		5.48		5.53		

a) Spectrum of A. b) Spectrum of $AB(A_2B)$ mixed with those of A and AB_2. c) Spectrum of AB_2 mixed with those of AB and AB_3. d) Spectrum of AB_3 mixed with that of AB_2. See text for further explanation.

differences (i) and (iii) stated above. The difference (ii) is also attributed to the bulky alkyl groups. Although in the previous section, the geometry of AB_2 species does not break the C_{2v} symmetry of the carbonyl group, it is reasonable to consider that this is not the case for bulky alkyl groups which may be twisted by the two ethanol molecules to make the intensity of the $n\to\pi^*$ band increase accompanying blue shift. As the result the intensity of the $n\to\pi^*$ band increases with blue shift.

Summarizing the above discussion absorption characteristics of the typical hydrogen-bonded species of ketones and water or ethanol are given in Table 1. Note, however, that this table was prepared so as to demonstrate how the spectrum of ketones changes with the decrease of the concentration in water and alcohols. The spectra of the pure liquid acetone and diisobutyl ketone are given under item a. The values under item b do not represent the spectrum of pure AB or A_2B species but that of the liquid mixtures at the border of Regions I and II, where AB or A_2B is thought to be predominant. The value under item c corresponds to the mixture at the border of Regions II and III, where AB_2 species predominates. Since the spectra of acetone under item d are the observed limits, the intensity of the band of pure AB_3 species is expected to be larger.

Although the change in the oscillator strength is not given in Table 1, it can be estimated to be roughly proportional to the change of ε_{max} as the half-band width is kept constant in a wide range for each system.

Other Theories. Bayliss and Wills-Johnson[3] calculated the change in the oscillator strength of the $n\to\pi^*$ bands of ketones and nitroalkanes based on their quantum mechanical model in which the total fluctuating field

$$\boldsymbol{R}^* = \alpha_s(\nu)\boldsymbol{m}\sum_k r_k^{-6}[\boldsymbol{m}-3(\boldsymbol{m}\cdot\boldsymbol{r}_k)\boldsymbol{r}_k]$$

caused by the solvent molecules surrounding the cavity acts on the solute chromophore, where $\alpha_s(\nu)$ is the solvent polarizability, $\boldsymbol{m}$ is the dipole moment of the solute, and $\boldsymbol{r}_k$ is the distance vector pointing to the k-th solvent molecule from the solute molecule. Although these authors could explain the "solvent dependence" of the relative intensity of the $n\to\pi^*$ band even for the aqueous solution, this model cannot explain the "concentration dependence," *i.e.*, the sudden rise in the intensity in the low concentration range below 10^{-2} molar fraction in water and even in ethanol, because it is impossible for any of the quantity, $\alpha_s(\nu)$, $\boldsymbol{m}$, or $\boldsymbol{r}_k$ to change sharply in this region.[14]

According to Lavrik and Naberukhin,[5] in the binary mixtures of water and non-electrolyte the cooperative effect of the hydrogen-bonded network of the liquid water predominates below 0.05 molar fraction of the non-electrolyte and this effect is greatly diminished either in ethanol or at high temperature around 60 °C. However, we have found that the behavior of the $n\to\pi^*$ band observed in the acetone–ethanol system as shown in Figs. 4 and 5 is essentially the same as that for the acetone–water system and that the intensity of the $n\to\pi^*$ band of acetone in water is even five per cent larger than the value at 20 °C. Thus we can conclude that contrary to the case of the Raman band intensity the cooperative effect of water is not responsible for the enhancement of the $n\to\pi^*$ band of ketones in dilute aqueous solutions.

It is generally accepted that the "solvent effect" of the electronic absorption spectra of most organic compounds can well be understood in terms of the polarizability, dielectric constant, dipole moment of the solvent, and the relevant interactions between the solute and solvent. However, the experimental data to be considered are usually taken from the measurements on "dilute solutions," and no systematic analysis has been done on the concentration dependence rather than the solvent dependence of the solvent effect, since it has not been realized that the former effect happens to compete with the latter as in this study. Thus one of the most important consequences of the present investigation is to give a warning that any discussion on the solvent effect of the electronic spectra is liable to be in serious error unless concentration dependence in a wide range down to lower concentrations is studied.

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7) Sterically crowded diisobutyl ketone is hardly soluble in water.

8) To the authors' awareness the concentration dependence of the $n \to \pi^*$ band of acetone in water has never been reported in the full concentration range except by Gorubunov and Naberukhin,[4] who, however, observed only the λ_{max} change as in Fig. 2.

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14) According to the observed concentration dependence of the refractive index (present study) and dielectric constant[15] of the binary mixtures of acetone and water, there is no sharp change in the low acetone concentration region.

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