The Hydration of Some Organic Compounds in an Aqueous Solution. I. Studies of Aliphatic Aldehydes by Raman-effect Observation

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It has long been recognized that acetaldehyde is partly hydrated in an aqueous solution to the $CH_3CH(OH)_2$ molecule; Bell and his co-workers have summarized this evidence[1] and have reported kinetic measurements[2] of the reversible hydration process. The hydrate in question could not be isolated except for those from chloro-substituted aldehydes, and such a structure as $=C(OH)_2$ is often mentioned as a reactive intermediate in the organic reactions. It is, therefore, of interest to examine the species existing only in solution from the spectral point of view. Moreover, it seems worthwhile to pay attention to the infinite solubility with which formaldehyde and acetaldehyde dissolve, in water as well as in organic solvents. Since the formation of hydrates obviously helps their solubility, to obtain hydration energy is also of interest. The present paper aims at obtaining the molecular vibrational spectra characteristic of the hydrated structure; it also aims at elucidating molecular interactions through measurement of the changes in the relative intensities of suitable Raman lines produced by changes in temperature.

In the case of formaldehyde, an interesting phenomenon was observed by Hibben[3] in the Raman spectrum in an aqueous solution. The spectrum in solution has a relatively close similarity to that of glycol: $CH_2O+H_2O \rightleftharpoons CH_2(OH)_2$. The simplicity of the Raman spectrum of water led us to hope that the Raman effect technique would prove useful in detecting the species existing in an aqueous solution. Further, it seemed reasonable to expect that each spectrum corresponding to aldehyde and its hydrate would change in intensity as the temperature changed. In the present paper, the Raman spectra of acetaldehyde and its solutions in light and heavy water are studied. At the same time, those of dimethylacetal, chloral and chloral hydrate are recorded as related compounds useful for the sake of comparison.

Experimental

Materials.—Pure acetaldehyde was obtained from its trimer compound, which was depolimerized with a drop of concentrated sulfuric acid. The fraction below 27°C of the distillate was redistilled to get acetaldehyde, boiling at 20∼20.5°C. The dimethylacetal synthesized[4] was purified by distillation over metallic sodium. Fractional distillation was repeated until the boiling point was constant at 64.3°C. Chloral and the chloral hydrate of E. P. grade (Tokyo Kasei) were used without further purification. Water purified through ion exchange resins was used as a solvent. The isotope content in the deuterium oxide used was 99%.

Measurements.—*The Raman Spectra of Liquids.*—A Cary Raman spectrophotometer, model 81, was used to measure the Raman spectra of pure liquids and solutions. Measurements were usually carried out at ordinary temperatures in a mercury lamp compartment (35∼40°C), a sealed glass cell (O. D. 7 mm.) 4.5 ml. in volume being used. For the purpose of recording a spectrum at various points of equilibrium, the temperature of the Raman cell was kept almost constant by circulating water of a desired temperature through the tube jacket. The jacket was specially fitted to the space between the filter cylinder and the cell, as is illustrated in Fig. 1.

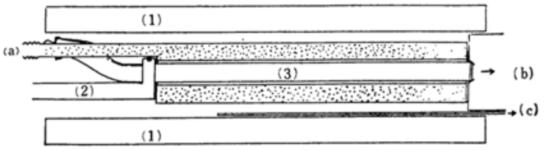

Fig. 1. Illustration of the tube jacket for adjusting temperature in a Raman tube.
- (a) To a thermostat and a pump for circulating water
- (b) To a monochrometer
- (c) To a reference beam entrance
- (1) Filter cylinder
- (2) Cell holder
- (3) Raman tube

The Raman Spectra of Solids.—The Raman spectrum of chloral hydrate, (m. p. 58°C) was

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[1] R. P. Bell and W. C. E. Higginson, *Proc. Roy. Soc.* **A197**, 141 (1949).

[2] R. P. Bell and D. B. Darwent, *Trans. Faraday Soc.*, **46**, 34 (1950).

[3] J. H. Hibben, "The Raman Effect and Its Chemical Applications", Reinhold Publishing Corp., New York (1939), p. 187.

[4] K. Nukada, *Reports of the Government Chemical Research Institute, Tokyo*, **55**, 99 (1960).

recorded at 60°C in the melted phase by using the tube jacket mentioned above.

The Irradiation of Polarized Lights.—The exciting light was polarized by surrounding a Raman tube with a polaroid cylinder, the transmitted electric vector of which was either parallel or perpendicular to the axis of the Raman tube. Baffles were not used to get a parallel exciting light, nor were the observed depolarization ratios corrected for the convergence error, so the results should be treated only as a measure of the true ratios.

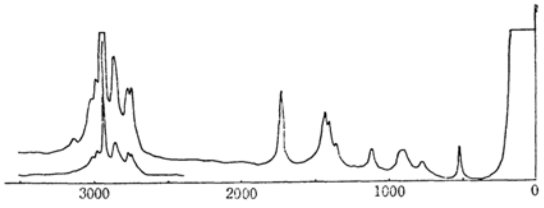
Results (Part I)

The Raman Spectra of Acetaldehyde and Its Solutions in Light and Heavy Water. — The results obtained are summarized in Table I, together with the relative intensities. The spectra shown in Figs. 2, 3, and 4 were recorded at ordinary temperatures; Fig. 5 shows the spectrum of pure water. In a heavy water solution, the exchange reaction of deuterium with hydrogen in aldehyde might occur following the instantaneous hydration process. It was, however, observed that there are no visible changes in intensity for the lines arising from C–H vibrations, and no visible new lines corresponding to C–D vibrations either. Since the rate of the exchange reaction is much less than that of the hydration process, it is not necessary to take account of the effect of the former reaction within the period of time employed for recording the Raman spectra.

TABLE I. OBSERVED FREQUENCIES (cm⁻¹)

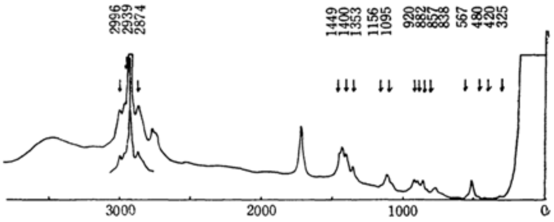
Acetaldehyde	Aqueous solution (equimolar)	Heavy water solution (equimolar)
	325 W	322 W
	420 w	410 w
	480 w	473 w
513 m	516 m	520 m
	567 w	
770 m (D)	772 m (D)	770 m (D)
	838 w	
	857 s (P)	845 s (P)
895 m (b)	882 m	
916 m (b)	920 m	918 m (b)
	1095 m	
1113 m	1116 m	1118 m
	1156 w	1198 W
1353 m (D)	1353 m (D)	1358 m (D)
1398 s	1400 s	1400 s
1429 S	1430 s	1430 s
	1449 S	1449 S
1720 S	1715 s	1715 s
2696 sh	2688 W	2688 W
2732 m	2741 m (P)	2738 sh
2754 m	2765 m (P)	2766 m
2844 s		
	2874 m	2873 m
2919 S (P)	2919 S (P)	2919 S
	2939 S	2941 S
2962 m		
	2996 s	2995 s
3000 W	3115 w	3118 w

The order of intensities: S, s, m, W and w relatively.



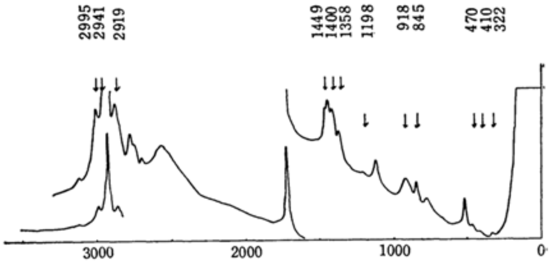
← cm⁻¹

Fig. 2. Raman spectrum of acetaldehyde.



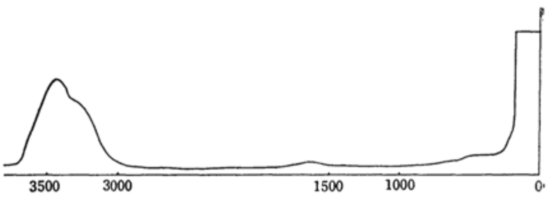
← cm⁻¹

Fig. 3. Raman spectra of acetaldehyde in aqueous solution at ordinary temperature (equimolar solution).



← cm⁻¹

Fig. 4. Raman spectra of acetaldehyde in heavy water solution at ordinary temperature (equimolar solution).



← cm⁻¹

Fig. 5. Raman spectrum of pure water.

In practice, the spectra of solutions are different from that of pure aldehyde, although in Figs. 3 and 4 the difference is not clearly shown. Arrows are given to show the position of each new line as it was acertained from observations at various temperatures and concentrations. (See Results, Part II.)

The spectra shown below, in Figs. 7 and 8, obviously indicate the effect of the temperature and concentration on the intensities of certain new lines; these factors cause at the same time compensative changes in the intensities of lines for aldehyde. Spectral lines corresponding to the new species may be distinguished from those for the original aldehyde when the lines of the latter are subtracted from all those observed in solution, at least with the exception of some overlapping lines. Generally, lines for aldehyde itself are not substantially shifted, even in solution, nor do they change their shapes except for the line around 900 cm^{-1}. This line is very broad, and its center shifts to a higher frequency in the case of a solution. It seems, however, very reasonable to interpret this change by regarding the broad line as the superposition of a couple of lines which might have their peaks within this range. The decrease in intensity of the lower frequency peak resulted in showing the higher frequency peak to be stronger. The change about 900 cm^{-1} can be interpreted thus, and not as the result of solvent shift of the broad line.

Concerning C–H vibrations, one of the noticeable changes is the appearance of a strong new line at 1449 cm^{-1} with the decrease in intensity of the line at 1430 cm^{-1} for aldehyde. The line at 2919 cm^{-1} (aldehyde) produces a strong line at 2939 cm^{-1} as it decreases. A similar change is observed on the new lines at 2874 and 2996 cm^{-1}.

For the O–H stretching region, it is obvious that the stronger of the two broad peaks, around 3275 and 3425 cm^{-1} in pure water, shifts towards a frequency higher by 50 in the unit of cm^{-1} and that the separation becomes unclear. There may be a new broad line centered about 3400 cm^{-1} which would lead to the general broadening in this region.

The Raman Spectra of Related Compounds.—The results obtained with chloral, chloral hydrate and dimethylacetal are listed in Table II. The difficulty in the purification of chloral hydrate caused the superposing on the spectrum of a main impurity, chloral. The lines showing the same frequencies as Raman lines belonging to chloral are marked with (?) in the Table. The spectrum for dimethylacetal is shown in Fig. 6.

TABLE II. OBSERVED FREQUENCIES (cm^{-1})

Chloral	Chloral hydrate	Dimethyl-acetal
200 s	194 m	292 W
242 S	242 ?	396 W
266 s	269 S	537 s
313 s	300 m	631 W
	340 w	808 S (P)
	414 S	829 m (P)
444 S (P)	444 ?	869 W
	570 s	988 m
614 s	623 s	1045 W
	686 W	1061 W
728 s (D)	728 ?	1087 W
846 m (D)	830 s	1125 m
983 W (D)	984 ?	1140 m
1018 W (D)	1015 w	1190 m
	1070 W	1362 m (D)
	1105 W	1448 S (D)
	1275 w	
1348 W	1358 m	
1454 w (P)	1388 w	2674 W
1757 S	1757 ?	2768 W
2685 w		2833 m
2860 S	2870 ?	2910 s
	2940 S	2944 S
3110 w	3550 vb	2994 s

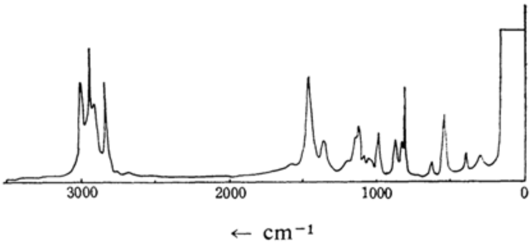


Fig. 6. Raman spectrum of dimethylacetal.

TABLE III. THE NUMBER OF THE NORMAL MODES FOR THE HYDRATE

	A′	A″		A′	A″
C–H stretching	1	0	C–C stretching	1	0
C–H deformation	1	1	$\mathrm{O}{\diagup}^{\mathrm{C}}{\diagdown}\mathrm{O}$ stretching	1	1
CH_3 stretching			(sym. & asym.)		
symmetric	1	0	$\mathrm{O}{\diagup}^{\mathrm{C}}{\diagdown}\mathrm{O}$ scissoring	1	0
degenerate	1	1	$\mathrm{O}{\diagup}^{\mathrm{C}}{\diagdown}\mathrm{O}$ skeletal		
CH_3 sym. def.	1	0	deformation	1	1
deg. def.	1	1	O–H stretching	2	0
CH_3 rocking	1	1	O–H deformation	2	2
CH_3 torsion	0	1	(in- and out-of-plane)		

An Analysis of the Spectrum for the Hydrated Molecule.—Since $CH_3CH(OH)_2$ involves ten atoms, twenty-four normal vibrations are expected. Assuming that the hydrate molecule takes a symmetric configuration belonging to the point group C_s, all the modes of normal vibrations expected are listed in Table III.

As both A′ and A″ species of vibrations are active in the Raman effect, all of those modes of vibration are observable. Six of them, such as the C–H and O–H stretching modes, are expected in the region above 2500 cm^{-1}; another six, including skeletal deformation, $\mathrm{CH_3}$ torsion and O–H out-of-plane deformation, are below 700 cm^{-1}, and the remaining twelve are between 700 and 1500 cm^{-1}.

Tentative Assignments.—First, in the region below 700 cm^{-1}, all the lines except 420 cm^{-1} are assigned as follows. The line at 325 cm^{-1} in an aqueous solution is remarkable among new lines. This could be most reliably assigned to the skeletal deformation vibration (A′) in the $\mathrm{C{-}C}\langle^{\mathrm{O}}_{\mathrm{O}}$ structure. Also, the line at 322 cm^{-1} in a heavy water solution seems to correspond to the mode in its lower frequency and sharpness. This assignment is supported by the fact that the line at 292 cm^{-1} for dimethylacetal is due to the skeletal deformation vibration, which shows a similar property in its shape. Those wave numbers are reasonable, considering their mass difference. The out-of-plane vibrations of O–H are also expected in this region. The line at 567 cm^{-1} in an aqueous solution is attributed to it because no line is observed in a heavy water solution near the frequency and because the line at 410 cm^{-1} in the heavy water solution could be regarded as the corresponding one from the product rule. The rather higher frequency of this vibration is explained by the fact that the hydrogen bonding in water could shift a frequency of this mode to a higher frequency than usual. The line at 480 cm^{-1} in the aqueous solution is assigned to $_{\mathrm{O}}\diagup^{\mathrm{C}}\diagdown_{\mathrm{O}}$ scissoring (A′), the line at 473 cm^{-1} in the heavy water solution corresponding to it. This scissoring mode (A′) is more reasonable than that other skeletal deformation vibration (A″) which is the only mode left among the skeletal deformation vibrations. Since a mode belonging to the A″ species can not usually show a stronger intensity than that for A′ species in a Raman spectrum, we can not attribute the observed line in question to a mode belonging to the A″ species when no suitable line for the remaining mode is observed.

Moreover, such an assignment is unacceptable because the scissoring mode is probable for the frequencies left in this region. All the assignments stated above being relatively consistent with each other, the broad band at 420 cm^{-1} in an aqueous solution is the only line in this region on which no comment can be made at present.

In the region between 700 and 1500 cm^{-1}, skeletal stretching vibrations and $\mathrm{C{-}H}_n$ and O–H (in-plane) deformation vibrations are expected. No clear conclusion on some of them can be obtained at present, mainly because couplings between similar modes should be considered, especially in the region between 700 and 1200 cm^{-1}. The following attempt is focused on the modes of vibration related to the O–H group. The most distinguishable line, at 857 cm^{-1}, was assigned to the symmetric stretching vibration of $\mathrm{C}\langle^{\mathrm{O}}_{\mathrm{O}}$ in the structure of $\mathrm{C{-}C}\langle^{\mathrm{O}}_{\mathrm{O}}$. At the same time, it was observed that the new line at 845 cm^{-1} in the heavy water solution is also sharp, equivalent in its intensity and with the same order of depolarization ratio. The assignment is decisively supported by the existence of the line at 808 cm^{-1} in dimethylacetal, which has features similar to those mentioned above and has been attributed to the symmetric skeletal stretching vibration. The asymmetric stretching vibration seems to be at 920 cm^{-1} in the aqueous solution and around 918 cm^{-1} in the heavy water solution.

The features of the broad line centered at 918 cm^{-1} imply the superposing of another line, which line may well be assigned to O–D (in-plane) deformation since it is a reasonable position evaluated from the product rule if we suppose either the line at 1095 cm^{-1} or the line at 1156 cm^{-1} to be an O–H (in-plane) deformation vibration. It might be one coupled with a $\mathrm{CH_3}$ rocking vibration. The reasons why we should suppose either of those lines to be an O–H deformation vibration are, one, that no lines are observed in the same frequency region in heavy water, which implies a large frequency shift due to the change of mass from H to D, and, two, that those frequencies are probable for O–H (in-plane) deformations. This assignment, as well as those for such vibrations as C–C stretching, C–H deformation (A′) and $\mathrm{CH_3}$ rocking (A′ and A″), will be discussed elsewhere with extensive further data.

The lines at 1353, 1400 and 1449 cm^{-1} are due to C–H deformation (A″), $\mathrm{CH_3}$ symmetric deformation, and $\mathrm{CH_3}$ degenerate deformation respectively. The assignment for the first one, (A″), is supported by the value of its depolarization ratio and by the existence of the line at 1348 cm^{-1} in the chloral hydrate. The new line at 1449 cm^{-1} changes in intensity in compensation for the intensity at 1430 cm^{-1} for aldehyde. Moreover, it keeps the same frequency in a heavy water solution. The depolarization ratio implies the superposition of the A′ and A″ species of vibration. In the spectrum of dimethylacetal, the equivalent line is found at 1448 cm^{-1}.

In the region of C–H stretching vibrations, one C–H stretching (A′), one CH_3 symmetric, and one CH_3 degenerate stretching vibration are to be expected. As a result of the investigation of their relative intensities and degrees of depolarization, the line at 2995 cm^{-1} is attributed to the CH_3 degenerate stretching mode, the one at 2940 cm^{-1} to the CH_3 symmetric stretching mode, and the other, at 2874 cm^{-1}, to the C–H stretching vibration. This conclusion is not consistent with that obtained for the CH_3 symmetric stretching frequencies of formals, acetals and related compounds.[4] For these, however, it has been suggested that the CH_3 symmetric stretching frequencies of OCH_3 groups split into two frequencies as a result of the Fermi resonance, with overtones of the CH_3 asymmetric deformation frequencies of OCH_3 groups. The splitting of the symmetric stretching frequency under the influence of an overtone frequency was not introduced here. Those frequencies remain in deuterated compounds, also. The fact that the frequency for a tertiary C–H stretching mode varies rather widely from hydrates to acetals may indicate a strong dependency of this frequency upon the groups attached to the tertiary carbon atom.

Thus, assignments have been carried out tentatively for as many observed lines as possible on the basis of the data presented here. The assignments described above are shown in Table IV.

As has been discussed above, reliable lines characteristic of hydrated molecules which exist only in solution can be used for spectroscopic investigation of reactive intermediates having two hydroxy groups on one and the same carbon atom.

Since changes in an aqueous solution are closely connected with a skeletal structure, further precise analysis of the relative intensities for new and original lines and a complete knowledge of acetaldehyde would provide us with assignments in more detail, especially for the region where complicated lines are produced out of couplings with skeletal vibrations.

TABLE IV. THE ASSIGNMENT OF THE RAMAN LINES FOR THE HYDRATE AND DEUTERATE OF ACETALDEHYDE

$CH_3CH(OH)_2$	$CH_3CH(OD)_2$	Mode
325	322	Skeletal deformation (A′)
480	473	$\mathrm{O}\diagup^{\mathrm{C}}\diagdown\mathrm{O}$ scissoring
567	410	O–H or O–D out-of-plane deformation
857	845	$\mathrm{O}\diagup^{\mathrm{C}}\diagdown\mathrm{O}$ sym. stretching
920	918	$\mathrm{O}\diagup^{\mathrm{C}}\diagdown\mathrm{O}$ asym. stretching
1095 1156 or	918～	O–H or O–D in-plane deformation
1353	1358	C–H deformation (A″)
1400	1400	CH_3 sym. deformation
1449	1449	CH_3 deg. deformation
2874	2873	C–H stretching
2939	2941	CH_3 sym. stretching
2996	2996	CH_3 deg. stretching

Results (Part II)

Observation of the Spectra at Various Temperatures and in Various Concentrations.—The spectra for solutions were recorded at various temperatures from 0 through 60°C, some of which are shown in Figs. 7 and 8. The ratios of the intensities for new lines to those of original lines increase as the temperature and

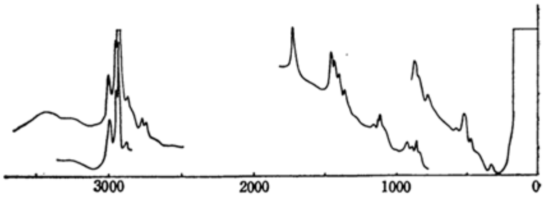


Fig. 7(a). Raman spectra of acetaldehyde in aqueous solution at 0°C (equimolar solution).

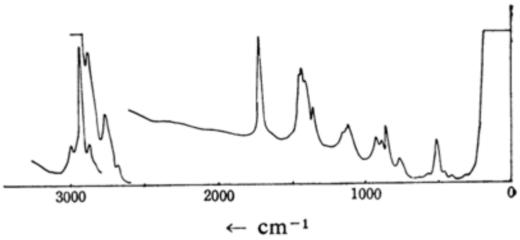


Fig. 7(b). Raman spectra of acetaldehyde in aqueous solution at ordinary temperature (molar ratio, 1 : 2 H_2O).

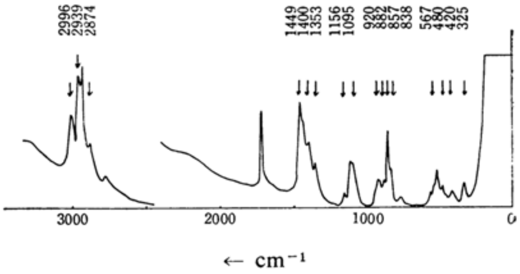


Fig. 7(c). Raman spectra of acetaldehyde in aqueous solution at 0°C (molar ratio, 1 : 2 H_2O).

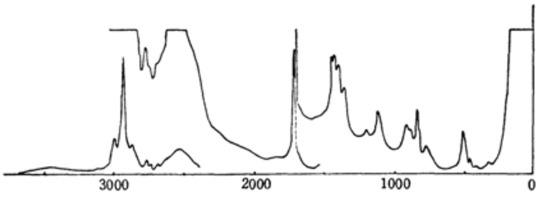


Fig. 8(a). Raman spectra of acetaldehyde in heavy water solution at ordinary temperature (molar ratio, 1 : 2 D_2O).

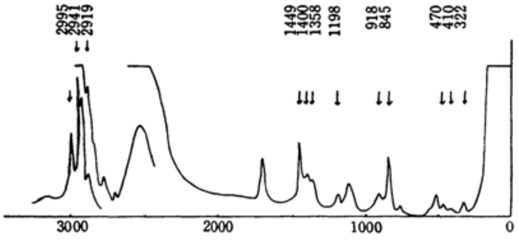


Fig. 8(b). Raman spectra of acetaldehyde in heavy water solution at 0°C (molar ratio, 1 : 2 D_2O).

the concentration of aldehyde decrease. At 60°C only a few stronger lines are observable. Their compensative changes with the lines for aldehyde have been described in Results (Part I) of this paper. This observation was quite helpful in attributing the observed lines to the species present in a solution.

The reproducibility of their intensities upon a change in temperature is good enough to prove this hydration process to be reversible.

Evaluation of Raman Intensities.—For the purpose of quantitative measurements, working curves were drawn for various temperatures by using mixtures of acetaldehyde and *n*-hexane. The carbonyl frequency, 1720 cm^{-1}, in this solution does not undergo any significant changes due to intermolecular interaction, but retains the same shape as in a pure liquid. We have, therefore, used the peak height of this line as a measure of the concentration of acetaldehyde in order to obtain each working curve at different temperatures. Using these working curves, we can eliminate several basic factors which must be taken into account in intensity measurement[5,6]. We, however, have still had trouble in an aqueous solution in estimating the peak heights of a carbonyl frequency at a lower temperature, trouble such as a lifting-up of a base line and a variation in the shape. The specific causes of these phenomena have not yet been elucidated. Therefore, the values calculated of the basis on this observation could give only a measure of the true values. One of the working curves is shown in Fig. 9.

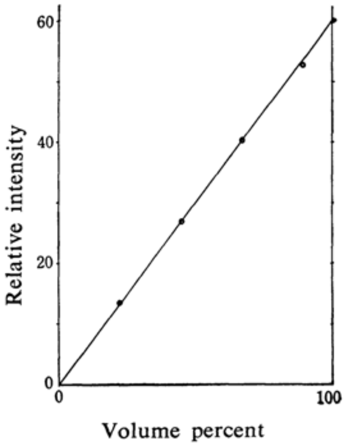


Fig. 9. The working curve for carbonyl band in solution.
$\nu_{C=O}$: 1720 cm^{-1}
at 0°C, in *n*-hexane solution

Equilibrium Constants and Calculation of the Hydration Energy. — The equilibrium constant is written as

$$K=\frac{(X)}{(a-X)(b-X)}$$

where *a* and *b* denote the initial concentrations of aldehyde and water respectively and *X*, the concentration of the hydrated species. The concentration of aldehyde remaining at an equilibrium point was determined from the spectrum recorded after keeping the sample tube at a desired temperature for more than one hour[7]. *K*'s were obtained since the values of *a* and *b* were known.

The hydration energy can be determined from a plot of log *K* against $1/T$, as is obvious in the following equation:

$$K=A\exp(-\Delta H^{\text{h}}/\boldsymbol{RT})$$

The equilibrium constants and the calculated hydration energy are: $K^{273}=0.029$, $K^{313}=0.0040$ (mol^{-1}), and $\Delta H^{\text{h}}=-8.7$ kcal./mol., and the initial concentrations: $a=12.1$, and $b=18.5$ mol./l. Fig. 10 shows the experimental results from which the value of the hydration energy was calculated.

Bell and Clunie[7] made an attempt to separate the instantaneous heat of solution from that of the subsequent hydration process, and

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[5] H. J. Bernstein and G. Allen, *J. Opt. Soc. Amer.*, **45**, 237 (1955).

[6] R. Rea, ibid., **50**, 90 (1960).

[7] R. P. Bell and J. C. Clunie, *Trans. Faraday Soc.*, **48**, 439 (1952).

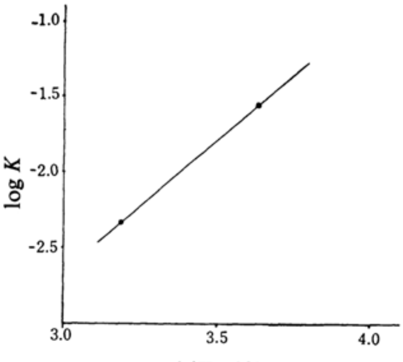

Fig. 10. The plot of $\log K$ against $1/T$.

reported, by combining calorimetric and ultraviolet absorption measurements, that the heat of hydration in question is -5.10 kcal./mol. for a very dilute solution. The value obtained here seems to be a little larger than those given by others. We have to notice, however, that there is confusion in the literature regarding the equilibrium constants and the heat of hydration. Our experiments concerned a very concentrated solution. Most others have investigated rather dilute solutions, and no consideration has been paid to the form of the equation for equilibrium constants. Since water molecules are apt to associate with each other, they are also at an equilibrium between aggregate water and isolated water, in which we should mention various extents of aggregation. Moreover, the isolated form might be a reactive form. Therefore, the effective concentration of water, for instance, must be varied according to the initial concentration as well as to the temperature range investigated. This could be introduced as a correction for use in determining the actual equation for this hydration equilibrium in an effort to obtain constant values. Generally speaking, a very delicate balance between the hydration process and the dissociation of aggregate water molecules might be shown in changes of the value of K depending on the initial concentration of components. This will be discussed elsewhere[8] through the precise measurement of the proton magnetic resonance.

Summary

The Raman spectra of acetaldehyde, its aqueous solution and its heavy water solution have been recorded at various temperatures and in various concentrations in order to find the Raman frequencies characteristic of the hydrated species and in order to investigate the reversible hydration process. Almost all the lines have been assigned tentatively on the assumption that the hydrate molecule has C_s symmetry. The lines at 325, 480, 567, 1353, 1440, 1449, 2874, 2939 and 2996 cm^{-1} can be referred to as the lines characteristic of the hydrate. Supporting data have also been obtained for the related compounds for the sake of comparison. Moreover, through the intensity measurements, equilibrium constants, as well as the heat of hydration, have been evaluated as the basis for a discussion of the hydration process.

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[8] M. Matsushima, Hydration Studies, II, to be published.