

Infrared Studies on the Solvent-Solute Interactions

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possible against Hirschfelder and Linnett's tables¹⁴ and the tables of Kutani, Amemijia, and Simosi.¹⁵ One-electron, three-center integrals were approximated by using Mulligan's method.⁵

One- and two-center Coulomb integrals are taken from Roothaan.¹³ The two-center exchange and hybrid integrals are taken from Hirschfelder¹⁴ or Kotani.¹⁵

¹⁴ J. O. Hirschfelder and J. W. Linnett, *J. Chem. Phys.* **18**, 130 (1950).

¹⁵ Kotani, Amemijia, and Simosi, *Proc. Phys.-Math. Soc. Japan* **20**, extra No. 1 (1938); **22**, extra No. 1 (1940).

The three-center exchange and hybrid integrals are approximated by the method of Mulliken¹⁶ using overlap and Coulomb integrals. In the very few cases where this approximation could be checked, the agreement with directly calculated values is within about 2%. The two- and three-center hybrid and Coulomb integrals which involve different ξ values were approximated according to the method of Mulligan.⁵

¹⁶ R. S. Mulliken, *J. chim. phys.* **46**, 497 (1949); **46**, 675 (1949).

Infrared Studies on the Solvent-Solute Interactions

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The solvent effects on the infrared absorption bands of *trans*-1,4-dichlorocyclohexane in the binary solvent cyclohexane-dioxane were measured. The frequency shifts of band centers are nearly proportional to the mixing ratio of the solvent, while the band widths reach the maxima at the intermediate values of the mixing ratio. These changes of solvent effects agree with the results of computations based on the assumption of the binomial distribution of solvent molecules around the solute molecules. The existence of the maximum of band width is well explained as due to an entropy factor, that is, to the various arrangements of solvent molecules encircling the solute molecules.

WE have seen in the previous paper¹ that in the infrared absorption bands of halogenated hydrocarbons, the frequencies and the peak heights decrease and the band widths and areas increase in the solvents which stabilize the polar form of rotational isomers. It is now of interest to study the nature of the solvent-solute interactions and the mechanisms which explain the observed solvent effects.

In the dilute solution, the solute molecule is surrounded almost exclusively by solvent molecules. The solvent effects may be mainly caused by the solvent molecules which are in contact with the solute molecule. Even in the case of long-range force interaction, such as dipole-dipole coupling, most of the interaction energies come from the interactions with the nearest solvent molecules. The change of the vibrational frequency of a solute molecule by the action of solvent molecules depends, therefore, on the species of the solvent molecules surrounding the solute molecule, as well as on the mutual orientations and the distances between solute and solvent molecules. The solvent molecules which have active groups can largely affect the solute molecules. Then, by the varieties of mutual orientations and distances described above, the solute molecules are placed in many different surroundings. Consequently,

for example, the vibrational frequencies of solute molecules are spread over a wide range. The observed infrared band, then, should be broadened in these solvents as was seen in the previous paper.¹

Now it can be supposed that the use of a mixed solvent will furthermore increase the band width, because the complexity in the area around a solute molecule is believed to increase by the existence of different kinds of solvent molecules. Quantitative studies on such effects may be of use for the study of the mechanisms of the solvent effects and of the interactions between molecules in solution.

For this purpose two C—Cl stretching bands of *trans*-1,4-dichlorocyclohexane, the frequencies of which are about 760 and 785 cm⁻¹ respectively, were observed in mixed solvents. These bands are suitable for the present purpose for the following reasons. (i) The accurate measurement of solvent effects can be made because of the large dispersion of the NaCl prism in this frequency region. (ii) The intensities of the bands are strong enough to be measured in very dilute solutions. (iii) The bands at 760 and 785 cm⁻¹ belong² to the (*a,a*)-³ and (*e,e*)-forms⁴ of inverted isomers respectively

² T. Yoshino, *J. Chem. Soc. Japan* **75**, 592 (1954).

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¹ T. Yoshino, *Bull. Chem. Soc. Japan* **27**, 592 (1954).

³ The notation *p* in^{1,2} and⁴ is changed to *a*, according to the proposal of Barton, Hassel, Pitzel, and Prelog which appeared in *Science* **119**, 49 (1954) and *Nature* **172**, 1096 (1953).

⁴ K. Kozima and T. Yoshino, *J. Am. Chem. Soc.* **75**, 166 (1953).

and the change of abundance ratio of the two forms can be obtained by the measurement of the variation in the intensity ratio of the two bands. (iv) These bands have nearly equal intensities and do not overlap each other appreciably.

Cyclohexane, dioxane, and their mixtures were used as solvents for the following reasons. (i) Both cyclohexane and dioxane are transparent in the frequency region in which the above two bands appear. (ii) The solvent effects of cyclohexane are very much different from those of dioxane¹ and therefore the changes of the solvent effects with the change of mixing ratio of solvent can be observed accurately by use of these mixtures. (iii) As the molecular dimensions of cyclohexane and dioxane are nearly the same, the considerations on the distribution of solvent molecules in the area around a solute molecule are simplified as will be seen later.

EXPERIMENTAL

Spectral data were obtained by use of a Perkin-Elmer Model 112 spectrometer with NaCl prism. The cell thickness and the slit width were 0.2 and 0.33 mm respectively, and the spectral slit widths were 1.4 and 1.6 cm^{-1} at 760 and 785 cm^{-1} respectively. The mole fraction of the solute was about 1/100.

The solvent effects were measured for the changes of the frequencies of band centers, the band widths, and the abundance ratio of two isomers. As the frequency of an absorption maximum is hard to determine accurately from the curve near the peak, the frequency of the band center, that is, the center of the line connecting the two points at which the absorbances are half the apparent maximum absorbance, was used for comparing the band shifts. The frequency shifts of the band center were corrected by use of the carbon dioxide band at 667 cm^{-1} . The change of the abundance ratio of the two inverted isomers was obtained by use of the peak intensities of the two bands. The change of abundance ratio thus obtained was equal within one percent of the

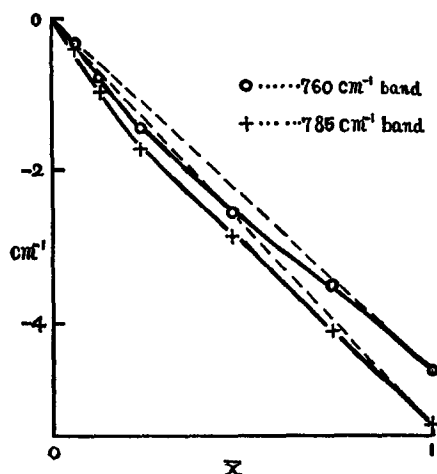


FIG. 1. The frequency shifts of band centers.

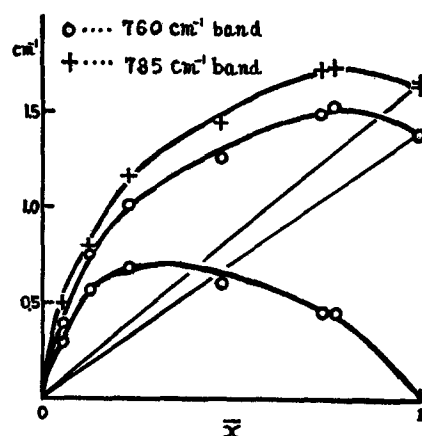


FIG. 2. The changes of apparent band widths and their deviations from the linear interpolation values.

ratio, to that obtained from the changes of the band areas which were estimated by use of the products of the peak heights and the half-intensity widths.

RESULTS OF MEASUREMENTS

The shapes of absorption bands observed are nearly the Lorentzian forms modified by a finite slit width.

The shifts of band centers for various \bar{x} 's are shown in Fig. 1, \bar{x} being the mole fraction of dioxane in the mixed solvent. The limits of uncertainty are $\pm 0.05 \text{ cm}^{-1}$. The shifts are almost the same for the two bands. We see that the decreases of the frequencies are nearly proportional to \bar{x} with small deviations from the straight broken lines drawn through the points which indicate the frequencies of band centers in cyclohexane and in dioxane.

The changes of half-intensity widths are shown in Fig. 2. The range of uncertainty is $\pm 0.05 \text{ cm}^{-1}$. The band widths are 3.7 and 4.5 cm^{-1} for 760 and 785 cm^{-1} bands in cyclohexane. The band widths observed are the apparent half-intensity widths and are larger than the true widths⁵ which would be obtained by an apparatus of infinite resolving power. The larger the differences of the apparent and the true widths are, the narrower the bands concerned are. Therefore the changes of the true widths are larger than those of the apparent ones in Fig. 2.

The curves in Fig. 2 are very much different from those in Fig. 1 and show maximum values at $\bar{x} \approx 0.8$ and maximum deviations at $\bar{x} \approx 0.3 \sim 0.4$ from the straight lines which are drawn through the points indicating the band widths in cyclohexane and in dioxane. The same results were also observed when the mixed solvents of cyclohexane and benzene were used. The deviations from the linear interpolation values are also shown in Fig. 2 for the 760 cm^{-1} band.

The abundance ratio r is expressed by the equation

$$r = kr_0 I_a / I_e,$$

⁵ For example the true widths of the 760 and 785 cm^{-1} band are 3.2 and 4.0 cm^{-1} respectively in cyclohexane solution.

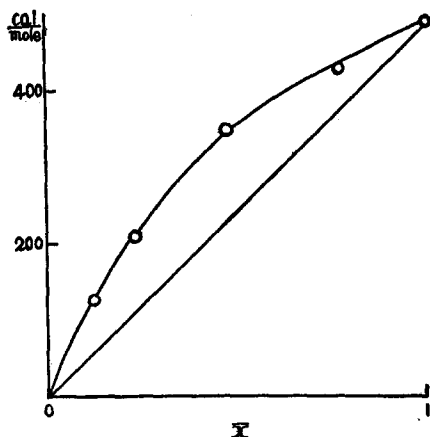


FIG. 3. The changes of free energy difference between two isomers.

where r_0 is the value of r in cyclohexane solution, and I_a and I_e are the peak intensities of the two absorption bands. In this equation it is assumed that k is kept constant for the change of \bar{x} . Even if k changes, serious error will not be introduced into the values obtained for r , because the intensity ratio changes from 1.75 in cyclohexane to 0.75 in dioxane while the difference of k values in cyclohexane and in dioxane will not exceed one tenth of k as is expected from the results in the previous paper.¹ The good agreement between r 's obtained from the peak intensities and the band areas, seems to support the constancy of k .

From r/r_0 , the change of free energy difference between the two isomers in dilute solution $\Delta(\Delta F)$ can be calculated by the following relation

$$\Delta(\Delta F) = RT \ln(r/r_0)$$

and is shown in Fig. 3. The curve of $\Delta(\Delta F)$ shows a departure from the proportionality to \bar{x} , though it is not so remarkable as those of the changes of the band widths in Fig. 2, and the curve has no maximum value.

DISCUSSIONS

The existences of the maximum band widths and the large deviations of the band widths from the linear interpolation values are of interest. We may proceed to elucidate the mechanisms of these solvent effects by quantitative discussions on the surroundings of the solute molecules.

First let us consider the model for the solvent-solute interactions. We approximate by a Lorentzian curve shown below, the curve of absorbance observed for the cyclohexane solution:

$$B/(b^2 + (\nu - \nu_0)^2),$$

where $2b$ is the half-intensity width, B/b^2 the peak height, ν the frequency, and ν_0 the frequency at the peak. This curve expresses the sum of various transitions shifted by the interactions which depend on the mutual orientations and the distances between solute and cyclohexane molecules.

We may consider that each solute molecule is surrounded by n solvent molecules. For a solute molecule which is surrounded by xn dioxane and $(1-x)n$ cyclohexane molecules, there are $n!/((xn)!(1-x)n)!$ ways of distributing solvent molecules in the nearest neighborhood of the solute molecule. For simplicity we assume here that the changes of band width and peak frequency due to the replacement of surrounding cyclohexane molecules by dioxane molecules, depend entirely on the number of dioxane molecules introduced and are proportional to it. Then the curve of absorbance for the solute molecules surrounded by xn dioxane and $(1-x)n$ cyclohexane molecules are given by

$$B'/((b')^2 + (\nu - \nu_0')^2), \quad (1)$$

where $B' = Bb'/b$, $b' = b + \beta x$, $\nu_0' = \nu_0 - \mu x$, and β and μ are the constants. $B' = Bb'/b$ means that the integrated intensity is independent of the band width. Even if the intensity depends on the band width, the intensity change which has been found to be less than 30% in the halogenated hydrocarbon molecules¹ is of no importance for the discussions below.

For simplification we assume here that in the dilute solution the stabilization of a solute molecules is proportional to the number of dioxane molecules surrounding it. Then the probability that the n points in the nearest neighborhood of a solute molecule are occupied by xn dioxane and $(1-x)n$ cyclohexane molecules in the solution in which the concentration of dioxane is \bar{x} , is represented by the formula

$$NQ \exp(x\Delta E/RT) = Q, \quad (2)$$

where

$$Q = \bar{x}^{xn} (1-\bar{x})^{(1-x)n} n! / (xn)! ((1-x)n)!,$$

$$1/N = \sum_{x=0}^1 [Q \exp(x\Delta E/RT)],$$

and $\Delta E = E(\text{cyclohexane}) - E(\text{dioxane})$, $E(\text{cyclohexane})$ being the internal energy change when one mole of solute is dissolved in an infinitely large volume of cyclohexane, and similarly $E(\text{dioxane})$ being that of dioxane.

From (1) and (2), the curve of absorbance to be observed for a given \bar{x} is obtained as follows⁶:

$$A(\nu) \equiv N$$

$$\times \sum_{x=0}^1 \left[\frac{B(b+\beta x)/b}{(b+\beta x)^2 + (\nu - \nu_0 + \mu x)^2} Q \exp(x\Delta E/RT) \right]. \quad (3)$$

The values of \bar{x} 's at which the deviations of the band width and the frequency shift from their linear interpolation values are maximum, can be obtained⁷ from

⁶ As the absorption bands were observed in such condition as the minimum transmissions were about 1/2 and the spectral slit widths were smaller than halves of the true widths, the apparent absorbance can be regarded to be additive. Therefore the addition of the absorbances for different \bar{x} 's in (3) is allowed.

⁷ The obtained values are not strictly correct when β is different from zero, but the effects of β on these values are very small.

TABLE I. The changes of half-intensity width of the 760 cm⁻¹ band and their deviations from the linear interpolation values (cm⁻¹).

\bar{x}	$\Delta E=0$ kcal/mole		Calculated $\Delta E=2.3$ kcal/mole		$\Delta E=2.8$ kcal/mole		Observed	
	Changes	Deviations	Changes	Deviations	Changes	Deviations	Changes	Deviations
1/4			0.92	0.57	0.95	0.60	1.02	0.67
1/2	1.25 ^a	0.56 ^a	1.31	0.61	1.33	0.63	1.35	0.65
3/4			1.45	0.41	1.46	0.42	1.50	0.46
1			1.39	0	1.39	0	1.39	0

^a The corresponding values calculated for $n=14$ is 1.18 and 0.49.

(2) and (3) as follows. The function (3) shows that the deviations of band width from the linear interpolation values depend on the distributions of the solute molecules in various states of different \bar{x} 'es. When ΔE is zero, the numbers of the solute molecules for different \bar{x} 'es are expressed by the binomidal distribution. Hence the solute molecules are most widely spread over the abscissa x , when \bar{x} is 0.5, and tend to concentrate in the region near $x=\bar{x}$, as \bar{x} increases or decreases from 0.5. Therefore the maximum deviation of the band width appears at $\bar{x}=0.5$.

\bar{Q} in (2) can be expressed in the same form as Q :

$$\bar{Q} = \bar{x}^n (1-\bar{x})^{(1-x)n} n! / (xn)! ((1-x)n)!,$$

where

$$\bar{x}/(1-\bar{x}) = \exp(\Delta E/nRT) \bar{x}/(1-\bar{x}). \quad (4)$$

The deviation of the band width becomes maximum at

$$\bar{x} = 1/(1 + \exp(\Delta E/nRT)) \leq 0.5, \quad (5)$$

which is obtained by setting \bar{x} in (4) to be 0.5. The position of the maximum deviation of the frequency shift is obtained to be

$$\bar{x} = 1/(1 + \exp(\Delta E/2nRT)) \leq 0.5 \quad (6)$$

by setting

$$d(\bar{x} - \bar{x})/d\bar{x} = 0.$$

Therefore the positions of the maximum deviations of the band width and the frequency shift from their

 TABLE II. The deviations of frequency shifts of the 760 cm⁻¹ band from the linear interpolation values (cm⁻¹).

\bar{x}	Calculated $\Delta E=2.3$ kcal/mole		$\Delta E=2.8$ kcal/mole		Observed
	Changes	Deviations	Changes	Deviations	
1/4			0.28	0.35	0.32
1/2			0.35	0.42	0.32
3/4			0.25	0.30	0.13

linear interpolation values, shift to smaller \bar{x} 'es with the increase of ΔE .

For the numerical calculations of the band widths and the frequency shifts by (3), the values of n and ΔE are required. n may be taken to be 12 by assuming the closest packing of molecules. It is thought to be reasonable to take ΔE to be a few kcal/mole.⁸ The uncertainty of ΔE has rather small effect on the results of calculations of the band widths.

The changes of half-intensity width, their deviations from the linear interpolation values, and also the deviations of frequency shifts from linearity are calculated for the 760 cm⁻¹ band and listed in Table I and II together with the corresponding experimental values taken from Figs. 1 and 2. The positions of maximum deviations of the band width and the frequency shift given by (5) and (6), are also calculated for $\Delta E=2.8$ kcal/mole to be 0.4 and 0.45 respectively.

By the discussions above described, we come to the conclusions that the simple model used is suitable for considerations on the solvent-solute interactions, and that an entropy factor represented by the binomial terms in (3) plays important rôles in the mechanisms of the solvent effects.

The author wishes to express his appreciation to Professor K. Kozima for his encouragement and advice during the pursuit of this work.

⁸ [$E(\text{benzene})-E(\text{cyclohexane})$] of ethylene dibromide is 1 kcal/mole according to the International Critical Tables, Vol. V. That of *trans*-1,4-dichlorocyclohexane is considered to be the same order of magnitude. For the latter compound [$E(\text{dioxane})-E(\text{cyclohexane})$] may be approximately estimated to be twice [$E(\text{benzene})-E(\text{cyclohexane})$], because $\Delta(\Delta F)$ in dioxane is observed to be nearly twice that in benzene.