

STUDIES OF SOLUTE-SOLVENT INTERACTIONS. IV.*
SOLVENT EFFECTS ON HALF-WIDTHS AND INTENSITIES
OF $\nu(\text{OH})$ BAND IN INFRARED SPECTRA

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The half-width and the integrated intensity of the $\nu(\text{OH})$ infrared band of the hydrogen-bonded phenol-acetonitrile complex was shown to depend on the properties of the liquid medium surrounding the complex molecules. On the other hand, the absorptivity in the band maximum was found to be quite insensitive to the effect of the medium.

Vibrational spectra of polar compounds show rather different patterns if measured under varied experimental conditions (*e.g.* ref.²). Although the spectra may differ even in the number of bands, more often only frequency, half-width, integrated intensity, or absorptivity in band maxima change due to the effects of intermolecular forces.

In previous papers of this series^{3,4}, the solutions of polar compounds in binary solvent mixtures were used for studying the solvent-induced band frequency shifts. In the present paper all band parameters of the $\nu(\text{OH})$ infrared band of the H-bonded complex phenol-acetonitrile are investigated in the spectra of phenol solutions in the acetonitrile-tetrachloromethane mixture.

EXPERIMENTAL

All solvents and compounds used in this work were carefully purified and dried over a molecular sieve.

Infrared spectra of solutions were measured with a double-beam spectrophotometer Zeiss (Jena) model UR-10 using LiF prism. The spectral slit width of the spectrophotometer in the region $3700-3200\text{ cm}^{-1}$ is assumed to be about $5-6\text{ cm}^{-1}$. The linearity of the wave-number as well as of the transmittance scales was carefully rechecked before and after each measurement. Samples were prepared by weighing all components into tempered and calibrated bottles of 5 ml volume. The NaCl cells of the thicknesses of 0.06 and 0.25 cm were used.

* Part III: This Journal 31, 622 (1966), see ref.¹.

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Except of solutions Nos 1 and 9 (phenol in neat acetonitrile and tetrachloromethane resp.) all solutions consisted of three components. The analytical phenol concentration was kept roughly constant in experiments Nos 1-9 ($\sim 0.03 \text{ mol l}^{-1}$) and 10-13 ($\sim 0.02 \text{ mol l}^{-1}$) (Table I). Concentrations of both the phenol complexes (of donor-acceptor and collision types) were obtained from absorbance values measured in appropriate band maxima; the absorptivity $\epsilon_{\text{max}}^{\text{a}}$ in band maximum of the collision complex was estimated to $189.1 \text{ [l mol}^{-1} \text{ cm}^{-1}]$, the analogous value of the band of the hydrogen-bonded complex is $167.8 \text{ [l mol}^{-1} \text{ cm}^{-1}]$. The band frequency $\nu \text{ [cm}^{-1}]$ and the band half-width $\Delta\nu_{1/2} \text{ [cm}^{-1}]$ were determined by direct reading or by computer calculations. The integrated intensity, $B \text{ [l mol}^{-1} \text{ cm}^{-1}]$, was calculated by using the analytical formula

$$B = \pi/2 \cdot \Delta\nu_{1/2} \cdot \epsilon_{\text{max}}^{\text{a}} \quad (1)$$

Both the $\epsilon_{\text{max}}^{\text{a}}$ and B are apparent values. Considering the rather large value of band half-widths in relation to the spectral slit-width the corrections for the finite slit-width were neglected. Bands of both the hydrogen-bonded and collision complexes appeared in the spectra in a close vicinity. A computer program was used for separation of these bands as formulated and written by Vitek⁵. The input data for the computer operation consisted of parameter estimates of both bands and of transmittance values from spectral records in the range $3\,700\text{--}3\,300 \text{ cm}^{-1}$ (read off in intervals of 3 cm^{-1}). The band parameters were computed by iteration methods and showed no further changes when treated in approximately 10 cycles.

RESULTS AND DISCUSSION

By changing properties of the liquid medium, surrounding the complex phenol-acetonitrile molecules, changes in solute structure and thus also in spectra were called up. Experimental results may bring information about the strength of intermolecular forces; the extrapolation to "zero" effects would bring even an evidence about properties of the complex molecule not affected by external forces. The knowledge of the system studied and of its spectra is based on the experience obtained earlier^{1,4}.

Table II brings direct readings of $\nu(\text{OH})$ band frequencies and of half-widths of both complexes. On the other hand, Table III contains values of band parameters of the hydrogen-bonded complex only as estimated by computer. Resolution of both bands has been carried out successfully in experiments Nos 2-7 (cf. parameter tolerances in Table III). The data computed for experiment No 8 were out of tolerances; in this case the intensity of the hydrogen-bonded complex was too low. For experiments Nos 1 and 10-13 the computation procedure was adapted to a one-band system. The difference in both procedures introduced a systematic deviation in computed band parameters; in order to correlate the B values in the full range of experiments, those from experiments Nos 10-13 were multiplied by a factor 1.0696 (this factor represents the ratio of both the computed values of $\epsilon_{\text{max}}^{\text{a}}$ for experiments Nos 2-7 and 10-13). Very high tolerances, found for computed parameters of the collision complex band in experiments 2-5, make any discussion of these parameter changes useless.

In the solutions of phenol in the acetonitrile-tetrachloromethane mixture three processes can be considered: 1. formation of strong (hydrogen-bonded) complex phenol-acetonitrile¹; 2. formation of weak collision complex phenol-tetrachloromethane⁴ and 3. nonspecific interactions due to electrostatic effects. According to the Onsager reaction field theory⁶ the solute molecules are subjects of a reaction field induced in the continuum (composed of molecules left over at the complex formation) by the solute dipole. In this work attempts are made to show how far the molecular structure and consequently the parameters of the $\nu(\text{OH})$ band of phenol are affected by the complex formation itself and by the effect of external fields.

In a rather good approximation, the "free" phenol molecules can be realized to exist in phenol vapours under a low partial pressure⁷. Under these conditions, the $\nu(\text{OH})$ band lies at 3655 cm^{-1} , the integrated intensity of the band was estimated to be $0.18 \cdot 10^4 \text{ [l mol}^{-1} \text{ cm}^{-2}]$. The band frequency of the complex phenol-acetonitrile varies with the composition of the liquid medium surrounding its molecu-

TABLE I
Mixtures Phenol-Acetonitrile-Tetrachloromethane; Component Concentrations

No ^a	CH ₃ CN in CCl ₄ mol %	Concentrations, mol l ⁻¹ · 10 ²			Error ^e %
		phenol ^b	phenol-CH ₃ CN ^c	phenol-CCl ₄ ^d	
1	100.00	3.004	3.035	—	-1.0
2	38.17	3.060	2.975	0.018	+2.2
3	24.95	3.062	2.925	0.071	+2.2
4	17.21	3.003	2.844	0.133	+0.8
5	10.48	2.989	2.644	0.347	-0.05
6	3.560	2.974	1.943	0.995	+1.2
7	1.846	3.098	1.412	1.591	+3.1
8	0.341	3.007	0.461	2.613	-2.2
9	0.000	3.075	—	3.083	-0.3
10	1.713	1.990	1.073	0.918	—
11	0.779	2.025	0.648	1.337	—
12	0.388	2.009	0.410	1.599	—
13	0.191	2.038	0.238	1.799	—

^a The solutions Nos 1-9 were studied in cells of 0.06 cm thickness, the solutions Nos 10-13 (characterized also by lower phenol concentrations) in cells of 0.25 cm thickness. ^b analytical concentration of phenol; ^c the concentration of hydrogen-bonded complex phenol-acetonitrile calculated from experimental absorbance values of the appropriate $\nu(\text{OH})$ band; ^d the concentration of the collision complex phenol-tetrachloromethane calculated from experimental absorbance values of appropriate $\nu(\text{OH})$ band; ^e the differences between the values of analytical phenol concentration (100%) and of the sum of concentrations of both complexes.

les^{1,3,4}. The frequencies follow rather well the Buckingham equation⁸, *i.e.* they are functions of dielectric constants and of refractive indices of appropriate solution mixtures¹. An extrapolation to the "zero" effect of liquid medium gives the value of the $\nu(\text{OH})$ "free complex" band frequency of about 3540 cm^{-1} (ref.¹). On comparing the $\nu(\text{OH})$ band frequencies of "free" phenol (3655 cm^{-1}), the extrapolated value of "free complex" phenol-acetonitrile (3540 cm^{-1}) and the value of "solvated complex" (3409 cm^{-1} , found in the spectrum of phenol in neat acetonitrile) it is seen that the effect of complex formation as well as the effect of nonspecific solvation are roughly of the same magnitude considering the frequency shifts.

The Band Half-Width $\Delta\nu_{1/2}$

As seen from Table II also values of $\Delta\nu_{1/2}$ are sensitive to the bulk effect of solvent mixtures. The greatest value of $\Delta\nu_{1/2}$ (138 cm^{-1}) of the hydrogen-bonded complex band (phenol-acetonitrile) was found in the spectrum of acetonitrile solution of phenol; the smallest value (90 cm^{-1}) was estimated from the spectrum of phenol solution in a mixture containing only very small concentration of acetonitrile in tetrachloromethane (the acetonitrile concentration was $\sim 1 \cdot 10^{-5} \text{ mol l}^{-1}$; cell thickness 1 cm). The spectra of both extreme cases are introduced in Fig. 1.

TABLE II

Mixtures Phenol-Acetonitrile-Tetrachloromethane; Direct Reading of Experimental Band Frequencies and Half-Widths of Phenol Complexes [cm^{-1}] with Acetonitrile and Tetrachloromethane

No ^a	Acetonitrile		Tetrachloromethane	
	$\nu(\text{OH})$	$\Delta\nu_{1/2}$	$\nu(\text{OH})$	$\Delta\nu_{1/2}$
1	3 409	138	—	—
2	3 422	121	3 608	24 ^b
3	3 428	117	3 609	22
4	3 431	116	3 609	22
5	3 437	109	3 610	23
6	3 450	106	3 611	22
7	3 456	100	3 611	20
8	3 460	99 ^b	3 611	20
9	—	—	3 611	20
10	3 454	98	3 611	20
11	3 454	93	3 611	20
12	3 460	90	3 611	20
13	3 460	90	3 611	20

^a The numbers agree with those used in Table I; ^b inaccurate estimates (from very weak bands).

In most cases it was rather easy to obtain experimental values of half-width by direct reading. Further, there is not necessary to know the concentration of the species for which the band width is established. A good agreement of experimental values in Table II and calculated values in Table III shows that the model used for calculations is rather valid. In these calculations the validity of the Lorentzian function for the description of the band shape is introduced. Table III (especially the tolerances introduced) shows that this approximation is accurate enough and that the band shape does not change seriously from one experiment to the other (the deviations are within an experimental error).

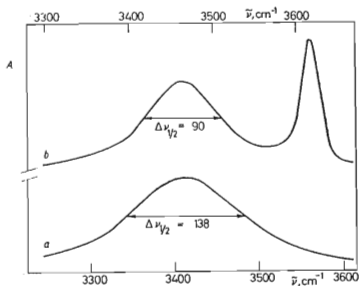


FIG. 1

Phenol in Neat Acetonitrile (*a*) and in a Mixture of Acetonitrile ($1 \cdot 10^{-5}$) with Tetrachloromethane (*b*)

Cell thickness 1 cm.

TABLE III

Mixtures Phenol-Acetonitrile-Tetrachloromethane; Calculated $\nu(\text{OH})$ Band Parameters of the Hydrogen-Bonded Complex Phenol-Acetonitrile

No ^a	ν^b [cm ⁻¹]	$\Delta\nu_{1/2}^b$ [cm ⁻¹]	ϵ_{max}^a [l mol ⁻¹ cm ⁻¹]	$B \cdot 10^2$ [l mol ⁻¹ cm ⁻²]
1	3 409 (0.8)	143.4 (4.1)	178.5 (2.6)	402
2	3 422 (0.8)	125.2 (2.8)	182.2 (1.9)	358
3	3 426 (0.7)	123.4 (3.6)	181.0 (2.5)	351
4	3 429 (0.8)	118.2 (3.0)	180.5 (2.0)	335
5	3 436 (0.8)	117.7 (4.7)	181.6 (3.4)	336
6	3 447 (0.8)	109.8 (5.3)	182.4 (4.8)	314
7	3 453 (0.9)	102.6 (4.3)	176.2 (3.5)	284
8	3 460 (11.6)	113.9 (72.2)	175.0 (66.4)	313
10	3 453 (1.5)	97.9 (3.7)	167.7 (2.6)	276 ^c
11	3 454 (0.7)	93.1 (3.7)	169.0 (3.1)	264 ^c
12	3 460 (1.5)	90.1 (7.5)	169.8 (6.4)	257 ^c
13	3 460 (3.1)	90.2 (16.4)	167.9 (14.4)	255 ^c

^a The numbers agree with those used in Table I; ^b the numbers in parentheses are the tolerances calculated with regard to 95% confidence limits; ^c the corrected values *cf.* text.

With (increasing) solution polarity (expressed in terms of dielectric constant) the magnitude of $\Delta\nu_{1/2}$ also increases. Comparing the extreme values of $\Delta\nu_{1/2}$, it does 36%. It is interesting to note that an analogous relationship was found between frequency shifts or changes in $\Delta\nu_{1/2}$ on one side and parameters characterizing the solution mixture on the other. This results in a linear relationship between the values of frequencies and of $\Delta\nu_{1/2}$. Without attempts to look for physical explanation of this fact, the relation obtained by least square fit can be written:

$$\Delta\nu_{1/2} = -0.959\nu_{\max} + 3411.1. \quad (2)$$

In ref.¹, the extrapolated value of the band frequency was given of the complex phenol-acetonitrile. This value, 3540 cm^{-1} , seems to be characterizing molecules of the complex phenol-acetonitrile not affected by any external forces. By use of Eq. (2) and this value of frequency, the extrapolated $\Delta\nu_{1/2}$ value of $\approx 15 \text{ cm}^{-1}$ was estimated, which can be considered the half-width of the $\nu(\text{OH})$ band of the complex phenol-acetonitrile in condensed phase not affected by external field.

Integrated Intensity

Computed values of integrated intensity B also show a dependence on the composition of the solution mixture. They increase with increasing relative concentration of acetonitrile in the mixture and is maximal in the spectrum of phenol in neat acetonitrile. In the full range, the B values increase by $\approx 35\%$.

This statement is made under an assumption of the invariance of absorptivities in band maxima. In the mixtures studied, phenol is distributed between two complex species; the concentration of these species is ascertained from experimental absorbance values in appropriate band maxima by using the value of ϵ_{3409}^a ($167.8 \text{ [l mol}^{-1} \text{ cm}^{-1}]$) and ϵ_{3611}^a ($189.1 \text{ [l mol}^{-1} \text{ cm}^{-1}]$) (absorptivity values of $\nu(\text{OH})$ band of phenol from solutions in neat acetonitrile and tetrachloromethane, respectively).

The supposition of the constancy of both the ϵ_{\max}^a values with respect to the composition of solution mixtures can be tested only in an indirect way. The sum of both calculated concentrations fits for every experiment rather well with the appropriate analytical phenol concentration. The bands of both, rather different species of phenol complexes (hydrogen-bonded in acetonitrile and collision complex in tetrachloromethane) differ only slightly in absorbancy (the value of ϵ_{3409}^a is by 11.3% smaller than the value of ϵ_{3611}^a). It does not seem very probable that the electrostatic effect itself in the solution produces changes in absorptivity three times greater than both the electrostatic effect and the effect of complex formation. In other words, if the integrated intensity should not depend on the solvent effect and, on the contrary, the absorptivities in band maxima should depend on it, then the increase in half-width

ought to be compensated by the decrease in the ϵ_{\max}^a by 35% which is three times higher than that of experimental finding (11.3%). Also any formation *e.g.* of hydrogen-bonded complexes with nonequivalent stoichiometry (phenol-acetonitrile 1 : 1, 1 : 2, 1 : 3 ... *etc.*) is not much probable. Rather good correlations of band frequencies¹ obtained in these experiments by using Buckingham Eq.⁹ *etc.* are a strong support above mentioned assumption.

Similarly to half-widths and frequencies, also the values of integrated intensity correlate with dielectric constants and refractive indices of the solution mixtures used. The form of these correlations is not solved here but their similarity can be demonstrated by the linear plot (a second order correlation) between frequencies and integrated intensities:

$$B \cdot 10^2 = -2.719\nu_{\max} + 9669. \quad (3)$$

This plot was used for estimating the "extrapolated" value of B at the "extrapolated frequency" (see ref.¹); this is $0.6 \cdot 10^4$ [$1 \text{ mol}^{-1} \text{ cm}^{-2}$] which is approximately a 3-times greater value than that of "free phenol" in vapours ($0.18 \cdot 10^4$ [$1 \text{ mol}^{-1} \cdot \text{cm}^{-2}$]).

From experiments and correlations of this work and from ref.¹ these parameters of the $\nu(\text{OH})$ band of hydrogen-bonded complex phenol-acetonitrile were estimated: $\nu \dots 3540$ [cm^{-1}], $\Delta\nu_{1/2} \dots 15$ [cm^{-1}], $B \dots 0.6 \cdot 10^4$ [$1 \text{ mol}^{-1} \text{ cm}^{-2}$]. We assume these are approximate band parameters of phenol-acetonitrile complex molecules not affected by external forces.

It was not possible to obtain useful values of band parameters for the phenol-tetrachloromethane collision complex. The band is too weak and too narrow to be sufficiently separated by the methods used.

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