INTERACTION OF PHENOL
WITH NITROBENZENE IN DILUTED SOLUTIONS'

J.Hejtmánková, M.Hejtmánek and P.Adámek

Department of Physical Chemistry and
Department of Analytical Chemistry,
Institute of Chemical Technology, Prague 6

The work deals with interaction between phenol and nitrobenzene in diluted solutions in tetra-chloromethane. It was found that the compounds form the 1 : 1 complex. On the basis of quantitative spectroscopic measurements in the $\nu(OH)$ region, the equilibrium constant for the formation of this complex was determined.

Recently one of the authors[1] studied the extraction of cesium from its aqueous solutions by alkylphenols in nitrobenzene from the analytical point of view. A more detailed analysis of the dependence of extraction ability of the organic phase on the initial and equilibrium compositions of both phases[2] revealed that it would be desirable to estimate quantitatively the possibility of formation of complexes between individual components of these systems. As the first part of this problem we studied the interaction between phenol and nitrobenzene in diluted solutions.

A high reactivity of hydroxyl group of phenol as a proton donor has been shown in a number of studies. This reactivity frequently exhibits itself in the formation of stoichiometric complexes with an appropriate proton acceptor, in which the two components are hydrogen-bonded. This was proved both by examination of shifts of $\nu(OH)_{free}$ band brought about by proton acceptors[3-6] and by theoretical calculations of intermolecular interactions between these components which lead to the change in corresponding energy levels[7-10].

The formation of intermolecular hydrogen bond between phenol and nitrobenzene was suggested already in the earlier work of Josien and Fuson[11] which was devoted to the study of solvent effects on the position of absorption band of phenol O—H stretching vibration. The interaction between alcohols or some phenols and nitro compounds was recently studied by Smith and de Maine[12]. Baitinger and coworkers[13] employed IR spectroscopy in the examination of proton-acceptor ability of the nitro group. On the basis of extensive experimental material these authors arrived at general conclusion that the nitro group is capable of forming definite, but rather weak hydrogen bonds with proton donors. All the studies cited above are in harmony with the assumption that the formation of the complex between phenol and nitrobenzene might occur. The only work which disagrees with this idea is that of Kaveeshvar and Dwivedi[14], who measured

parachor of solutions of nitro compounds in alcohols. The authors did not observe decrease in parachor of solutions of phenol in nitrobenzene, in contrast to the behaviour of alcohols. This finding was taken as indicative of the absence of the hydrogen-bonding in the former case. Compared to spectral method, the physical method used in that study was however less sensitive. It is thus uncertain if in the case of weak hydrogen bonds it can provide unambigueous information.

In the present study we employed infrared spectroscopy in studying interaction between phenol and nitrobenzene, regarding it as the most suitable method for this purpose on the basis of analysis of the above mentioned studies. To avoid eventual distortion of data by common solvent effect, we used three-component systems consisting of diluted solutions of both interacting compounds in tetrachloromethane. The IR measurements were made in the region of O—H stretching vibrations, as is usual in such a case[15].

EXPERIMENTAL

Chemicals

Nitrobenzene (analytical purity grade) was purified in the usual manner[16] and dried over a molecular sieve Nalsit, type 4 A. Phenol (analytical purity grade) was freshly distilled under reduced pressure before use. Tetrachloromethane (analytical purity grade) was rectified and then dried over Nalsit 4 A.

Infrared Measurements

The infrared spectra were measured on a Zeiss UR 10 spectrophotometer (Zeiss, Jena) over the range of 3800 to 3000 cm^{-1}; LiF prism, scanning speed 32 cm^{-1}/min, slit program 4. The intensity scale of the instrument was calibrated with rotating sector, the wavenumber scale by means of ammonia vapors with the aid of reported data[17]. Temperature of the solutions was maintained at 28 ± 1°C.

The measurements of diluted solutions were carried out in the two cells made in this laboratory (cell thickness 1 cm). Distance ring of the cells was made of brass (9.8 mm thickness), the surface of the ring subjected to the action of solvents was protected by a teflon film. The ring was connected with NaCl plates by amalgamated plumbum foils (0·1 mm thickness). Into cell room was inserted a termocouple (copper–constantan) through the distance ring. The filling part of the cell was also located at the distance ring.

In quantitative measurements of binary mixtures phenol–tetrachloromethane the reference cell contained tetrachloromethane, in the measurement of ternary solutions phenol–nitrobenzene–tetrachloromethane the reference cell contained the corresponding solution of nitrobenzene in tetrachloromethane to ensure the compensation of absorbance of nitrobenzene.

RESULTS AND DISCUSSION

Nature of the Bond between Nitrobenzene and Phenol

According to general scheme of the interaction of phenol with substituted aromatic compounds, suggested *e.g.* by Osawa and coworkers[5], these compounds can partici-

pate in the formation of hydrogen bonds in general as multifunctional proton acceptors, if they possess more then one center of basic character. In such a case, this is reflected in the infrared spectrum by multiple splitting of the absorption band of corresponding phenol OH stretching vibration. So, for instance, the authors[5] found quadruplet splitting of the absorption band in the case of tetrachloromethane solutions of phenol and methoxyazobenzene.

In analogy with this idea the two basic centers must be considered in the case of nitrobenzene, namely the nitro group and the π-electron system of the aromatic ring. The frequency of the band corresponding to hydrogen bond between the hydroxyl and the nitro group should be, for aliphatic compounds according to Baitinger and coworkers[13], approximately $3\,520\ cm^{-1}$. The frequency of the absorption band corresponding to the hydrogen bond between hydroxyl group and the aromatic ring is reported[5] to be $3\,560—3\,520\ cm^{-1}$.

We have thus measured at first the spectrum of ternary mixtures phenol–nitrobenzene–tetrachloromethane over wide range of concentrations and mutual ratios of the two components in the region of $3\,800$ to $3\,200\ cm^{-1}$. We found that in the presence of nitrobenzene the spectrum of phenol, when compared with that of phenol itself, exhibits only one additional, relatively diffuse absorption band at $3\,540\ cm^{-1}$. The form of the spectra just mentioned is represented in Fig. 1. According to literature, the formation of very strong hydrogen bond can result in the almost total dissappearance of the absorption band of the free hydroxyl group. This is not however the case here. The absorption band of $\nu(OH)_{free}$ at $3\,611\ cm^{-1}$ appears even on using very

FIG. 1
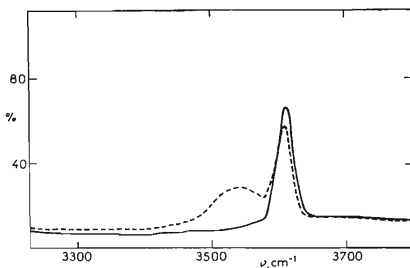
Infrared Spectrum of Binary and Ternary Solutions of Phenol in the Region of $\nu(O—H)$

ν Wavenumber, % absorption; ———— $3 . 10^{-3}$M phenol in tetrachloromethane (compensation — pure tetrachloromethane), – – – $3 . 10^{-3}$M phenol $+0\cdot3$M nitrobenzene in tetrachloromethane (compensation 0.3M nitrobenzene in tetrachloromethane).

large excess of nitrobenzene (of about three orders of magnitude), and also frequency difference between the free and associated OH group (71 cm^{-1}) is relatively small, which indicates the formation of a relatively weak bond[13,18,19].

The appearance of only one new absorption band, the frequency of which is lower than that of the absorption band of the free hydroxyl group of phenol, indicates that only one type of new bond is being formed between the two components. The assumption that we deal here with the interaction between the hydroxyl and the nitro group is supported above all by satisfactory agreement between the wavenumber of the new absorption band and that of the band of hydroxyl group of phenol associated with the nitro group of nitroalkanes (3520 $\pm$ 10 cm^{-1})[12]. The difference between our and reported values is likely due to the aromatic character of the compound studied here. Baitinger and coworkers[13] extrapolated the value 3521 cm^{-1} for the system phenol–nitrobenzene, did not however reported the extrapolation procedure used. In addition, the wavenumbers recorded by the above authors[13] are in general somewhat lower than those commonly reported. So for instance they report the wavenumber of $\nu(OH)_{free}$ equaling to 3606 cm^{-1} while other authors prefer the values ranging between 3610 and 3614 cm^{-1} (cf. refs[4,6,20,21]), in agreement with our results. Anyway, the frequency shift determined by us is substantially greater than that obtained with the system phenol–benzene (49 cm^{-1}) (ref.[5]), which may be regarded as further support for the assumption that it is the nitro group which participates in association. Recent theoretical calculations of energy levels in a series of organic compounds provide further support for the assumption of the hydrogen bond formation between the hydroxyl and the nitro group[7-10,22].

Type of the Complex

Most of the studies dealing with the quantitative measurements of the equilibria of similar type (cf.[4,23-25]) presuppose a *priori*, sometimes without statement, the formation of a sole, usually an 1 : 1 complex. Since this condition may not be generally fulfilled[26-28] it seemed to be desirable to verify the validity of this presumption in our case.

The verification of only one complex can be made on the basis of the occurence of the isosbestic point in a series of measurements in which total analytical concentration of phenol is kept constant, while the concentration of nitrobenzene and thus also the ratio of the concentrations of the free and associated phenol are changed. The isosbestic point was found in our case at about 3594 cm^{-1} (Fig. 2). As an evidence for the formation of the 1 : 1 complex may be regarded the results of logarithmic treatment of the dependence of the absorbance in the region of free OH group on concentration.

The formation of the complex can be described by equation (*A*)

$$nC_6H_5OH + C_6H_5NO_2 = C_6H_5NO_2.nC_6H_5OH. \qquad (A)$$
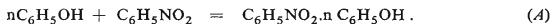
The equilibrium constant of this reaction is defined as

$$K_n = \frac{c_1^0 - c_1}{n \, c_1^n (c_2^0 - c_1^0 + c_1)},$$ (1)

where c_1^0 and c_1 are the initial analytical and the equilibrium concentration of phenol, resp. and c_2^0 is the initial analytical concentration of nitrobenzene. The use of concentrations in place of activities is justified with respect to low concentrations used in the measurements. If the concentrations are expressed by absorbances of the solutions, A, for unit thickness of the cell, at the frequency at which Beer's law is obeyed and phenol is the only absorbing component, one obtains $A_1 = \varepsilon_1 c_1$, $A_1^0 = \varepsilon_1 c_1^0$, where ε_1 is the corresponding absorptivity. If $c_2^0 \gg c_1^0$, Eq. (1) can be transformed to the form

$$K_n = \varepsilon_1^{n-1} (A_1^0 - A_1)/(n A_1^n c_2^0),$$ (2)

or

$$\log \left(\frac{A_1^0 - A_1}{c_2^0} \right) = n \log A_1 + \log \left(\frac{n K_n}{\varepsilon_1^{n-1}} \right).$$ (3)

The value of n for equation (A) can be thus obtained as the slope of the plot of the left side of Eq. (3) against $\log A_1$.

This dependence for a series of measurements with varying concentrations c_1^0 and c_2^0 is represented in Fig. 3. The projected straight line with the slope $n = 1$ indicates that the experimental data correspond to formation of the only complex with the ratio of the components 1 : 1.

Equilibrium Constant

The equilibrium constant of reaction (A) $(n = 1)$, after neglecting activity coefficients, is defined as

$$K = \frac{c_3}{(c_1^0 - c_3)(c_2^0 - c_3)} = \frac{c_1^0 - c_1}{c_1(c_2^0 - c_1^0 + c_1)},$$ (4)

where c_3 is the equilibrium concentration of the complex of phenol with nitrobenzene. In order to determine the accurate value of K the knowledge of the only one of these variables, *i.e.* either c_1 or c_3, is needed.

In fact, either of these ways can be employed: to determine c_1, to follow the sharp absorption band of free OH stretching frequency of phenol; to determine c_3, to follow the diffuse absorption band of associated OH group. The problem, which of these methods is more suitable, was studied in detail by Heinen in the case of association of phenol with acetone[6]. In agreement with his results we have reached conclusion that also here the determination of changes in the region of free OH stretching frequencies (maximum at 3611 cm^{-1}) would be more accurate. The results obtained during measurements in the region of absorbance of associated OH group (maximum at 3540 cm^{-1}) are reported as well.

The determination of equilibrium constant K from Eq. (4) from the set of measurements of the absorbance of free OH group can be performed in two ways. In the first one, the total concentration of a proton acceptor is kept constant and that of a proton donor is changed $(cf.^{29,30})$. The second one is the inverse procedure[6]. The calculation of K can be then carried out either graphically or numericaly with sufficient precision.

The first way, using varying concentration of a proton donor, did not seem to us convenient. The complex between the components studied is a relatively weak one, and a large excess of the compounds the concentration of which is changed is needed to observe appreciable change in concentration of the other component of constant concentration. We were unable to vary widely the concentration of phenol because of its self-association[6,21,31].

From this reasons we have used the second procedure which allows to work with an excess of the proton acceptor. In this case, providing that very large excess of the proton acceptor is used, that the absorbances of free OH group obey Beer law and that the measurements are carried out in the same cell, Eq. (4) can be re-written to the form
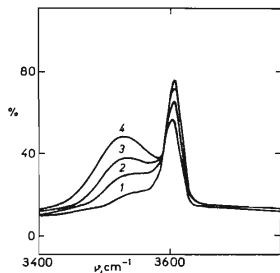

Fig. 2

Isosbestic Point for Ternary Solutions of Phenol in Tetrachloromethane

ν Wavenumber, % absorption; phenol conc. $4 \cdot 10^{-3}$ mol/l, compensation by solutions of nitrobenzene in tetrachloromethane, nitrobenzene conc. *1* 0·08 mol/l, *2* 0·20 mol/l, *3* 0·40 mol/l, *4* 0·80 mol/l.
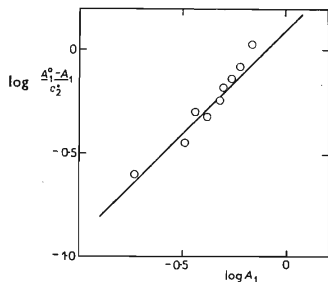
Fig. 3

Logarithmic Analysis for Ternary Solutions of Phenol

For meaning of symbols see Eq. (3).

$$K = \frac{A_1^0 - A_1}{A_1} \cdot \frac{1}{c_2^0} \cdot \qquad (5)$$

The equilibrium constant K can be easily obtained graphically from the relation

$$1/A_1 = \left(K/A_1^0\right) c_2^0 + 1/A_1^0 \, . \qquad (6)$$

The calculation of K from single points according to Eq. (5) is laden with greater error in particular when proton acceptor concentration is low and thus the difference between A_1 and A_1^0 is small.

Preliminary experiments showed that the most convenient concentration of phenol for equilibrium constant determination is $4 \cdot 10^{-3}$ mol/l. At this concentration the amount of selfassociated phenol molecules is lesser than 1% of the total concentration[6]. For the complex to be formed in sufficient amount, the concentration of nitrobenzene of one to two orders of magnitude higher than that of phenol is necessary. By this also condition $c_2^0 \gg c_1^0$ was met.

Slit width. The $\nu(OH)$ absorption band is relative very sharp. As in expressing absorbances we used exclusively transmittance in the band maximum it was necessary to make sure that the slit width used does not affect the calculation. The form of the absorption bands of hydroxyl group of phenols is of Lorentz type[4]. For such absorption bands Ramsay reported[32] correction factors for absorbance as a function

TABLE I

Absorbance of the Free OH Group of Phenol in Tetrachloromethane at 3611 cm^{-1}

Analytical concentration of phenol in all the solutions was $3 \cdot 999 \cdot 10^{-3}$ mol l^{-1}; c_2^0 is the analytical concentration of nitrobenzene, A_1 is the absorbance of the free OH group corrected to water. Cell thickness 1 cm, temperature $28 \pm 1°C$.

c_2^0 mol l^{-1}	Transmittance % at 3611 cm^{-1}		Absorbance			
	maximum	null line[a]	at 3611 cm^{-1}	at 3710 cm^{-1} (water)	A_1	$\frac{1}{A_1}$
0	15·0	90·5	0·780	0·025	0·774	1·29
0	15·5	90·5	0·766	0·025	0·760	1·31
0·0803	18·0	86·0	0·679	0·020	0·674	1·48
0·1997	21·0	83·5	0·599	0·024	0·593	1·69
0·3000	23·5	83·0	0·546	0·021	0·541	1·85
0·3994	26·0	82·5	0·501	0·020	0·496	2·02
0·7988	34·5	80·0	0·365	0·025	0·359	2·79

[a] After correction on the band of the complex.

of the ratio of spectral slit-width to the half-width of the band. For the values of this ratio smaller than 0·4 the relative error in absorbance is independent of its absolute magnitude. In the opposite case the relative error increases with observed absorbance, resulting in some cases in the error of equilibrium constant determination[6] as much as 20%. In the latter case Beer law is not obeyed.

Without knowing the value of mentioned ratio we therefore verified the validity of Beer law for phenol at 3611 cm^{-1}. The results obtained are given in Table I and Fig. 4. It is evident that in concentration range referred to Beer law is obeyed with satisfactory precision. The molar absorptivity $\varepsilon_1 = 196 \text{ cm}^{-1} \text{ l mol}^{-1}$ determined graphically agrees well with the data of Goddu[33] for slit-width 8 cm^{-1}. From the graphical dependence of experimental extinction coefficients on slit-width reported by Heinen[6], the slit-width in our case can be estimated as being 11 cm^{-1}.

Interferring components. The calculation of K according to Eq. (5) is fully justified only on condition that the value of A_1 truly represents the absorbance corresponding to the free hydroxyl group only. To the absorbance at 3611 cm^{-1} can also contribute the absorption band of associated OH group, which is relatively diffuse and located in the vicinity of the free OH absorption band, along with the absorbance of free water molecules incidentally present in the solution.
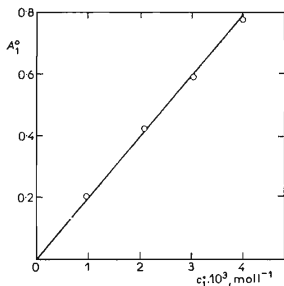

Fig. 4

Verification of the Validity of Beer Law for Solutions of Phenol in Tetrachloromethane (3611 cm^{-1})

c_1^0 Analytical concentration of phenol, A_1^0 absorbance. Cell thickness 1 cm, compensation tetrachloromethane, correction on water (see text).
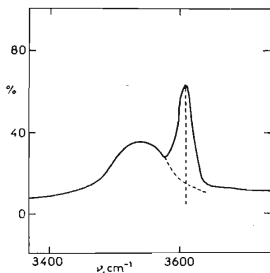
Fig. 5

Example of Correction for the Overlap of the Free OH Band with the Associated OH Absorption Band

v Wavenumber; % absorption; phenol conc. $4 \cdot 10^{-3}$ mol/l, nitrobenzene conc. 0·4 mol/l.

We therefore made correction for overlap of the absorption band of associated phenol, by extrapolating graphically the band of the associated OH group symmetrically with respect to the long-wave side of the band. As null line for the determination of absorbance of the free OH groups we took the point of intersection of the drawn shape of the absorption band of the associated group with the value of 3611 cm^{-1} on the wavenumber scale (see Fig. 5).

Interferring absorbance of water molecules exhibits itself to substantially lesser degree, above all due to the fact that after careful drying the components as well as the solvent only trace amounts of water may be present. According to the work[34] the spectrum of water dissolved in tetrachloromethane exhibits two absorption bands of different intensity, which are located in the region of $\nu(OH)$ bands. The first, more intense band has its maximum at 3710 cm^{-1}, the other at 3620 cm^{-1}. The latter, relatively diffuse band might interfere with the band located in the 3611 cm^{-1} region. Correction for this source of errors was performed in the way suggested by Heinen[6], which is based on the known ratio of the absorptivity of water at the wavenumber of the absorption band of phenolic OH$_{free}$ stretching vibration and that at 3710 cm^{-1}. The value of this ratio is $0·25$.

Equilibrium constant. The final results used in plotting the dependence of $1/A_1$ on c_2^0 for the determination of K according to Eq. (6) are summarized in Table I. The absorbances of the free OH group at 3611 cm^{-1} were obtained after correction for interferring band of the complex, as described above.
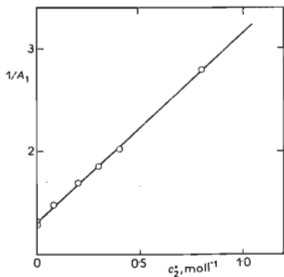

FIG. 6

Dependence of Reciprocal Value of Absorbance of Free Hydroxyl Group $1/A_1$ on Nitrobenzene Concentration c_2^0

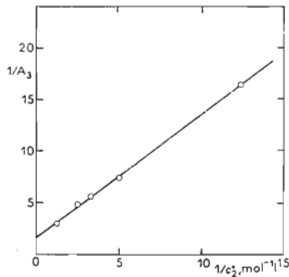The corresponding data are given in Table I.

FIG. 7

Dependence of Reciprocal Value of Absorbance of Associated Hydroxyl Group, $1/A_3$, on Reciprocal Value of Nitrobenzene Concentration $1/c_2^0$

The corresponding data are given in Table II.

TABLE II

Absorbance of the Associated OH Group of Phenol in Tetrachloromethane at $3540\ cm^{-1}$

c_2^0 Analytical concentration of nitrobenzene, A_3 absorbance of the associated OH group. For experimental conditions see Table I.

c_2^0 mol l^{-1}	Transmittance % at $3540\ cm^{-1}$		A_3	$1/c_2^0$	$1/A_3$
	maximum	null line[a]			
0·0803	76·5	88·0	0·061	12·45	16·39
0·1997	65·0	88·5	0·135	5·01	7·41
0·3000	59·0	89·0	0·178	3·33	5·61
0·3994	55·5	89·5	0·207	2·50	4·83
0·7988	43·5	89·5	0·337	1·25	2·97

[a] Read from the spectrum of phenol in tetrachloromethane.

The dependence of $1/A_1$ on c_2^0 is represented graphically in Fig. 6. Under the given experimental conditions this dependence is linear. The value of K determined at $28 \pm 1°C$ by least squares method amounts to $1·41 \pm 0·07\ l\ mol^{-1}$.

To confirm the correctness of the obtained value of equilibrium constant we calculated this quantity also from absorbances of the absorption bands of the complex at $3540\ cm^{-1}$.

If the absorbance in the maxima of the absorption bands of the complex fulfill presumptions put forward in deriving Eq. (5), Eq. (4) can be re-written to the form

$$1/A_3 = 1/(c_1^0 \varepsilon_3 d) + 1/(K c_1^0 \varepsilon_3 d c_2^0),\qquad(7)$$

where A_3 is the absorbance of the associated OH groups, d is the cell thickness, ε_3 is the molar absorptivity of the associated OH groups, the other symbols having the same meaning as in Eq. (4) and (6). Graphical representation of this equation can be advantageously made by plotting $1/A_3$ against $1/c_2^0$. This dependence for the set of measurements given in Table I is shown in Fig. 7. The corresponding data are presented in Table II.

The resulting value of K $1·38\ l\ mol^{-1}$ obtained by least squares method agrees well with the value obtained by the former method. With respect to the fact that the two independent procedures were used, this result shows that the procedure and corrections used in plotting the graph in Fig. 6 were adequate.

REFERENCES

1. Hejtmánek M.: Dissertation. Institute of Chemical Technology, Prague 1967.
2. Hejtmánek M.: A paper presented at the Conference of the *Verein Österreichischer Chemiker*, Wien, Sept. 1968.
3. Baba H., Suzuki S.: J. Chem. Phys. *35*, 1118 (1961).
4. Boroďko Ju. G., Krylova A. E.: Izv. Akad. Nauk SSSR, Ser. Chim. *10*, 1747 (1966).
5. Osawa E., Kato T., Yoshida Z.: J. Org. Chem. *32*, 2803 (1967).
6. Heinen W.: *Thesis*. Univ. Utrecht, Utrecht 1964.
7. Filippova L. G., Terpugova A. F.: Izv. Vyš. Učeb. Zaved. Fiz. *2*, 92 (1963).
8. Filippova L. G., Terpugova A. F.: Izv. Vyš. Učeb. Zaved. Fiz. *2*, 105 (1963).
9. Danilova V. I., Belomytcev S. Ja.: Izv. Vyš. Učeb. Zaved. Fiz. *9*, 162 (1966).
10. Filippova L. G.: *Spektroskopija, Metody i Primenenie*, p. 147. Akad. Nauk SSSR, Sib. Otd. 1964.
11. Josien M. L., Fuson N.: J. Chem. Phys. *22*, 1169 (1954).
12. Smith M. S., de Maine P. A. D.: J. Miss. Acad. Sci. *12*, 109 (1966).
13. Baitinger W. F., Schleyer P. R., Murty T. S. S. R., Robinson L.: Tetrahedron *20*, 1635 (1964).
14. Kaveeshvar S. N., Dwivedi J. K.: Agra Univ. J. Research *6*, 39 (1957).
15. Pimentel G. C., Mc Clellan A. L.: *The Hydrogen Bond*. Freeman, San Francisco 1960.
16. Weissberger A., Proskauer E.: *Technique of Organic Chemistry*, Vol. VII. Interscience, New York 1955.
17. König R., Malewski G.: Jenaer Rundschau *12*, 132 (1967).
18. Purcell K. F., Drago R. S.: J. Am. Chem. Soc. *89*, 2874 (1967).
19. Sellier G., Wojtkowiak B.: J. Chim. Phys. Physicochim. Biol. *65*, 936 (1968).
20. Fritzsche H.: Spectrochim. Acta *21*, 799 (1965).
21. Adámek P.: *Thesis*. Institute of Chemical Technology, Prague 1969.
22. Zubkova L. B., Danilova V. I.: Izv. Vyš. Učeb. Zaved. Fiz. *10*, 152 (1967).
23. Yoshida Z., Ishibe N.: Spectrochim. Acta *24A*, 893 (1968).
24. De Maine P. A. D., Goble A. G., Maddock A. G.: Spectrochim. Acta *12*, 1054 (1959).
25. Takahashi F., Karoly W. J., Greenshields J. B., Li N. C.: Can. J. Chem. *45*, 2033 (1967).
26. Liptay W.: Z. Electrochem. *65*, 375 (1961).
27. Ramaswamy K., Pichai R., Gnanadesikan S. G.: J. Mol. Spectry *23*, 416 (1967).
28. Clotman D., Lichtfus G., Zeegers-Huyskens T.: Bull. Soc. Chim. Belges *77*, 115 (1968).
29. Tsuboi M.: Bull. Chem. Soc. Japan *25*, 60 (1952).
30. Widom J. M., Philippe R. J., Hobbs M. E.: J. Am. Chem. Soc. *79*, 1383 (1957).
31. Fletcher A. N., Heller C. A.: J. Phys. Chem. *71*, 3742 (1967).
32. Ramsay D. A.: J. Am. Chem. Soc. *74*, 72 (1952).
33. Goddu R. F.: J. Am. Chem. Soc. *82*, 4533 (1960).
34. *Advances in Analytical Chemistry and Instrumentation*, Vol. I. (C. N. Reilley, Ed.). Interscience, New York 1960.