STUDIES OF SOLUTE–SOLVENT INTERACTIONS. V.*

THE SOLVENT INDUCED FREQUENCY SHIFTS OF THE ν(C=O) AND ν(C≡N) INFRARED BANDS

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Buckingham equation was found suitable to describe the solvent induced frequency shifts of ν(C=O) and ν(C≡N) vibrations of the chosen carbonyl and nitrile solutes.

In the preceding papers of this series solvent shifts of the infrared O—H stretching frequencies were measured for donor–acceptor complexes[2] and collision complexes[3] of some phenols and methanol in media of widely varying dielectric constants and refractive indices. It was found that the experimentally observed solvent shifts of the band frequencies due to the complexes can be satisfactorily accounted for with the aid of the Buckingham relation[4] written to the first order

$$\nu = \nu_0 - C_1[(\varepsilon - 1)/(2\varepsilon + 1)] - C_2[(n^2 - 1)/(2n^2 + 1)] \qquad (1)$$

provided the conditions used for the derivation of this relation are satisfied.

In order to check criteria put forward in our previous work[1-3] on a wider range of chemical compounds, the characteristic C=O and C≡N stretching frequencies of donor–acceptor complexes formed by some carbonyl compounds and by nitriles, respectively, were correlated in the present paper with macroscopic properties of the solvents using the Buckingham relation *(1)*.

EXPERIMENTAL

All compounds used were analytically pure and carefully dried. The solvents were redistilled and dried over a molecular sieve before use.

Infrared spectra in the ν(C=O) region ($\sim 1\,700$ cm^{-1}) were measured by using the spectro-photometers Zeiss (Jena) model UR-10 (NaCl prism) and/or Unicam model SP-100 with an

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*   Part IV: This Journal *36*, 544 (1971); see ref.[1].

SP-130 grating accessory. For measurements in the $\nu(C≡N)$ region (~ 2200 cm^{-1}), the spectro-photometer Perkin-Elmer, model 225, was employed.

Due to a careful calibration of the wavenumber scales of all instruments used, the accuracy of wavenumbers achieved was about ± 1.5 cm^{-1} for regular band shapes.

The mathematical separation of overlapped $\nu(C≡N)$ bands was carried out by using National Elliott 503 computer and a program written by Vítek[5]. Also least squares reductions of the results were performed by using this computer.

RESULTS

The solvent induced $\nu(C=O)$ frequency shifts were studied in a rather wide scale of carbonyl solutes and solvents. Some results published in the literature were used for correlation, too. Table I refers to solvent shifts of the $\nu(C=O)$ of carboxylic acid dimers and Table II refers to shifts of the $\nu(C=O)$ in chloral, bromal, ethyl trifluoroacetate and of acetyl chloride. In Table III, the constants ν_0, C_1 and C_2 of the Buckingham relation (1) are summarized for all carbonyl solutes studied.

The $\nu(C≡N)$ frequency shifts were studied in the spectra of ternary mixtures composed of acetonitrile-d_3, phenol and a third organic liquid component. Experimental and calculated $\nu(C≡N)$ frequencies of the system studied are given in Table IV. Table V brings information on the change in $\nu(N≡C)$ frequencies of solvated isonitrile complexes. Parameters ν_0, C_1 and C_2 of the Buckingham relation (1) applied to the $\nu(C≡N)$ and $\nu(N≡C)$ frequency shifts are presented in Table VI.

DISCUSSION

The $\nu(C=O)$ frequency shifts. The $\nu(C=O)$ frequencies are in general less sensitive to the influence of complex-forming solvents than the $\nu(O—H)$ frequencies studied in preceding papers of this series[1]. It is therefore more difficult to follow their solvent induced shifts in the spectra of various species of solute molecules in mixed solvents by using techniques applied to the $\nu(O—H)$ frequency shifts[2,3].

The $\nu(C=O)$ frequencies manifest themselves in the infrared spectrum of solutions of carbonyl solutes in mixed polar and nonpolar solvents rather often in the form of a doublet. The low-wavenumber component of the doublet represents the strong "chemical" complex* in almost all cases;** the second component was usually described as being connected with the presence of "free" solute molecules in the mixture[7-9]. It seems that this solute form can be described as a "collision complex", as defined in paper[3], formed from molecules of the solute and of appropriate non-

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* The spectra reproduce effects of hydrogen-bond formation[6-9], charge transfer[11,12] and coordination[13] in a similar way.
** In systems with H-bonded carbonyl groups, the variations in stoichiometry (1 : 1, 1 : 2 *etc.*) make the situation more complex[6-9]. There are also inconsistencies in the interpretation of the $\nu(C=O)$ (ref.[6-9]) and of the $\nu(O—H)$ region[10] of these complexes.

polar liquid. This idea is supported by the presence of a $\nu(C{=}O)$ doublet band in the spectra of solutions of carbonyl solutes in binary mixtures of nonpolar liquids (cyclohexanone in the mixture cyclohexane–tetrachloromethane[8], tertiary amides in solutions of tetrabromomethane in tetrachloromethane[14] etc.). Individual bands also occur in the spectra of complexes of carbonyl solutes with nitriles[15], aromatic hydrocarbons[16,17] etc.

For the solutions of acetic, caproic and benzoic acid dimers, the C=O stretching frequencies measured by Lascombe and coworkers[18] were correlated with dielectric constants and refractive indices of the solvents by using Eq. (1). The results given in Table I show a relatively good fit of experimental and calculated frequencies. The C_1 and C_2 constants obtained by the least squares fits are summarized in Table III. It should be noted that in these cases the coefficient C_2 of the refractive index term is considerably greater than the coefficient C_1 of the dielectric constant term in contrast to the case of the complexes of phenols with polar liquids, where the two terms were found to be of a comparable magnitude[2]. This is the reason of a quite succesful attempt of Lascombe and coworkers[18] to correlate the carboxylic acid dimer carbonyl frequency shifts with the refractive indices of solvents only.

For the donor–acceptor complexes of hydroxyl solutes studied previously[2], the

TABLE I

Frequency Differences $\Delta\nu$ (cm^{-1}) between the $\nu(C{=}O)$ Frequencies of the Carboxylic Acid Dimers in Various Solvents, Observed and Calculated According to the Eq. (1)

Solvent	$f(\varepsilon)^a$	$f(n^2)^b$	Acetic acid		Caproic acid		Benzoic acid	
			$\nu_{obs.}{}^c$	$\Delta\nu$	$\nu_{obs.}{}^c$	$\Delta\nu$	$\nu_{obs.}{}^c$	$\Delta\nu$
n-Hexane	0·1851	0·1853	1 717·0	−0·5	1 714·0	−0·1	1 700·0	+0·8
Cyclohexane	0·2018	0·2030	1 716·5	+0·8	1 712·5	+0·3	1 697·5	+0·0₅
Acetonitrile	0·4798	0·1739	1 715·0	+0·2	1 711·0	+0·2	1 697·0	+0·3
Tetrachloromethane	0·2251	0·2142	1 714·0	−0·3	1 710·5	−0·3	1 696·0	−0·2
Chloroform	0·3563	0·2094	1 713·0	−0·1	1 708·5	−0·8	1 694·5	−0·6
Methylene chloride	0·4202	0·2024	1 713·0	+0·0₅	1 709·0	+0·4	1 694·5	−0·4
Benzene	0·2296	0·2267	1 712·5	−0·6	1 709·0	−0·6	1 693·5	−1·6
Carbon disulphide	0·2603	0·2610	1 711·0	+1·4	1 708·0	+2·1	1 693·0	+1·2
Methyl iodide	0·3981	0·2356	1 711·0	+0·8	1 707·5	+1·3	1 693·0	+0·6
Bromoform	0·3449	0·2536	1 708·0	−1·2	1 703·5	−1·8	1 691·5	+0·0₅
Methylene bromide	0·4028	0·2393	1 709·5	−0·3	1 706·0	+0·3	1 692·0	+0·0
Methylene iodide	0·3710	0·2869	1 705·5	−0·3	1 701·0	−0·7	1 688·0	−0·3

$^a f(\varepsilon) = (\varepsilon - 1)/(2\varepsilon + 1)$; values of ε (at 25°C) taken from ref.[26-28]; $^b f(n^2) = (n^2 - 1)/(2n^2 + 1)$; values of n (at 25°C) taken from ref.[26-28]; ^{c} experimental values taken from ref.[18].

Table II

The $\Delta\nu$ Frequency Differences (cm^{-1}) between the ν(C=O) Frequencies of Chloral, Bromal, Ethyl Trifluoroacetate and Acetyl Chloride in Various Solvents, Observed and Calculated According to the Eq. (1)

Solvent	$f(\varepsilon)^a$	$f(n^2)^a$	Chloral		Bromal		Ethyl Trifluoroacetate		Acetyl Chloride	
			$\nu_{obs.}$	$\Delta\nu$	$\nu_{obs.}$	$\Delta\nu$	$\nu_{obs.}^{\ b}$	$\Delta\nu$	$\nu_{obs.}^{\ c}$	$\Delta\nu$
	—	—	1 778·0^d	−0·9	1 764·0^d	−0·4	1 801·4^d	−0·2	1 821^d	−1·3
n-Hexane	0·1851	0·1853	—	—	—	—	1 791·6	+1·0	1 810	+1·3
Diethyl ether	0·3416	0·1770	—	—	—	—	1 788·3	0·0	1 810	+3·0
Methanol	0·4774	0·1681	—	—	—	—	1 787·5	+1·0	—	—
Cyclohexane	0·2018	0·2030	1 768·0	+1·3	1 751·5	+0·7	—	—	1 809	+1·5
Tetrachloromethane	0·2251	0·2142	1 766·5	+0·8	1 749·5	−0·1	1 788·0	−0·7	1 806	−0·5
Carbon disulphide	0·2603	0·2610	1 763·0	−0·2	1 747·0	+0·2	1 786·5	+0·4	1 805	+1·8
Chloroform	0·3563	0·2094	1 763·0	+0·9	1 746·5	+0·9	—	—	1 800	−4·9
Methylene chloride	0·4202	0·2024	1 761·0	+0·5	1 744·5	+0·5	1 784·0	−1·9	1 804	−0·4
Acetonitrile	0·4798	0·1739	1 759·5	−0·2	1 742·5	−0·5	1 786·5	+0·3	1 807	+1·7
Methylene iodide	0·3710	0·2869	1 757·0	−2·2	17 41·0	−1·4	—	—	1 798	−2·1

^{a} cf. Table 1; ^{b} experimental values taken from ref.[9]; ^{c} experimental values taken from ref.[19]; ^{d} vapours.

Table III

The ν_0, C_1 and C_2 Constants of the Buckingham Eq. (1) for the ν(C=O) Shifts (cm^{-1}) of the Carbonyl Solutes Studied

Carbonylsolute	$\nu_{vap.}^{\ a}$	ν_0	C_1	C_2	ϱ^b
Acetic acid dimer	1 732^c	1 736·9	−12·7	−92·1	0·62
Caproid acid dimer	1 728^c	1 734·5	−15·2	−94·5	1·26
Benzoic acid dimer	—	1 717·2	−11·7	−85·4	0·63
Chloral	1 778	1 778·9	−28·5	−31·6	1·82
Bromal	1 764	1 764·4	−31·7	−35·8	0·82
Ethyl trifluoroacetate	1 801·4^d	1 801·6	−16·7	−43·0	1·28
Acetyl chloride	1 821^e	1 822·3	−14·0	−59·1	7·08

^{a} Values obtained experimentally for carbonyl stretching frequency in vapours; ^{b} mean square root error, $\varrho = [(\Sigma\,\Delta\nu^2)/(n-m)]^{1/2}$, where n is the number of equations, m the number of unknowns and $\Delta\nu$ is the frequency difference; ^{c} ref.[18]; ^{d} ref.[9]; ^{e} ref.[19].

TABLE IV

The Frequency Differences (cm^{-1}) between the $\nu(C\equiv N)$ Frequencies of the Complex Phenol–Acetonitrile-d_3 in Various Solvents, Observed and Calculated According to the Eq. (1)

Solvent	$f(\varepsilon)^a$	$f(n^2)^a$	Observed $\nu(C\equiv N)$	$\Delta\nu$
n-Hexane	0·2311	0·1858	2 274·7	−0·3
Chloroform	0·3775	0·2132	2 274·4	+0·1
Tetrachloromethane	0·2636	0·2146	2 274·1	+0·9
Benzene	0·2834	0·2272	2 271·7	−0·7
Bromoform	0·3871	0·2504	2 271·6	−0·1
Iodoform	0·3852	0·2829	2 269·3	+0·1

^{a} The dielectric constants and the refractive indices used are those of solution mixtures.

TABLE V

The $\Delta\nu$ Frequency Differences (cm^{-1}) between the $\nu(N\equiv C)$ Frequencies of Isonitrile Complexes in Various Solvents, Observed and Calculated According to Eq. (1)

Solvent	$f(\varepsilon)^a$	$f(n^2)^a$	Complex $(CH_3C_6H_4NC)_2Co(NO)(CO)^b$				Complex $[(CH_3)_3CNC]_2Co(NO)(CO)^b$			
			ν_{obs}	$\Delta\nu$	ν_{obs}	$\Delta\nu$	ν_{obs}	$\Delta\nu$	ν_{obs}	$\Delta\nu$
Carbon disulphide	0·2603	0·2610	2 087·8	−3·6	—	—	2 111·8	−3·0	—	—
n-Hexane	0·1851	0·1853	2 085·9	−1·7	2 135·4	−0·7	2 108·4	−0·8	2 141·8	−2·4
Toluene	0·2395	0·2341	2 096·1	+5·7	2 140·5	+2·7	2 117·7	+4·5	2 151·6	+3·4
Diethyl ether	0·3416	0·1770	2 095·2	−2·1	2 139·6	−2·1	2 115·9	−3·4	2 151·6	−0·4
Tetrachloro-methane	0·2251	0·2142	2 090·1	+0·4	2 136·8	−0·6	2 111·9	−0·2	2 146·3	−0·7
Methylene iodide	0·3710	0·2869	2 097·2	−0·7	2 141·1	−1·0	2 120·6	−1·6	2 153·5	−2·9
Acetone	0·4646	0·1794	2 103·5	−1·4	2 145·6	−0·4	2 125·1	−2·2	2 155·2	−3·2
Methylene bromide	0·4028	0·2393	2 099·8	−0·6	2 142·6	−0·9	2 123·7	−0·1	2 156·9	+0·1
Acetonitrile	0·4798	0·1739	2 107·2	+1·3	2 147·4	+0·8	2 129·8	+1·5	2 160·7	+1·7
Bromoform	0·3449	0·2536	2 097·1	+0·4	2 141·0	−0·4	2 121·2	+1·0	2 155·1	+0·9
Methylene chloride	0·4202	0·2024	2 103·5	+1·6	2 145·5	+1·2	2 126·4	+1·8	2 158·0	+1·3
Chloroform	0·3563	0·2094	2 098·6	+0·7	2 143·3	+1·3	3 123·2	+2·6	2 155·8	+2·2

^{a} cf. Table I; ^{b} both complexes show two $\nu(N\equiv C)$ bands each, see ref.[25].

determination of the "free" complex frequency v_0 involved a rather long extrapolation[1,2]; on the other hand, the frequency in vapours v_{vap} for the dimers of acetic and caproic acids is available experimentally. This makes it possible to check the accuracy of the extrapolation (carried out on the basis of data obtained from solutions only) by comparing the extrapolated frequency v_0 with the frequency in vapours v_{vap}. The deviations of v_0 from v_{vap} do not seem to be too serious.

The effect of vicinal halogen atoms on the C=O bond is well known. The electron-withdrawing effect of halogen atoms affects its bond order and in this way increases the $v(C=O)$ frequency; this effect becomes more important when more halogen atoms are situated in the vicinity of a carbonyl. Some polyhalogenocarbonyl derivatives like chloral, bromal and ethyl trifluoroacetate and also acetyl chloride show rather high values of $v(C=O)$. Carbonyl stretching frequencies found in the spectra of solutions of these compounds obey rather well* the Buckingham relation (1) (see Tables II and III).

The carboxylic acid dimers of general formula I existing as stable donor–acceptor complexes even in the gas phase will not form complexes with other polar or non-polar compounds and the effect of solvents on their vibrational frequencies can be attributed completely to the solvation of their molecules in the secondary solvation shell (see ref.[17]).

$$R-C \begin{array}{c} O-H...O \\ \diagdown \quad\quad\quad \diagup \\ \diagup \quad\quad\quad \diagdown \\ O...H-O \end{array} C-R$$

I
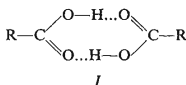
The behaviour of carboxylic acid dimers is rather exceptional when compared with the behaviour of common carbonyl solutes[19] (aldehydes, ketones, derivatives of carboxylic acids,** etc.). The exceptional character of carboxylic acid dimers results from the fact that their molecules are strong solutions. However, there exist some other exceptions, *e.g.* in molecules of the polyhalogenocarbonyl derivatives. These molecules (chloral, bromal, ethyl trifluoroacetate *etc.*) are very weak electron donors and do not form strong "chemical" complexes when dissolved in complex-forming solvents, but only weak "collision" complexes. These are conditions where the Buckingham equation (1) can also be used for expressing the solvent induced frequency shift (see ref.[3]).

The $v(C≡N)$ frequency shifts. The frequency shifts induced by solvents in C≡N group are very tiny. On the other hand, there is a pronounced effect of solvents in changes of $v(C≡N)$ band intensity[20].

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*   The poorest correlation was found for acetyl chloride.

**   Solvent induced frequency shifts in carboxylic acid monomers also differ from that of dimers.

TABLE VI

The ν_0, C_1 and C_2 Constants of the Buckingham Eq. (1) for the $\nu(C\equiv N)$ and the $\nu(N\equiv C)$ Shifts (cm^{-1}) of the Nitrile and Isonitrile Complexes

Complex	ν_0	C_1	C_2	ϱ^a
Acetonitrile-d_3–phenol	2 286·5	9·4	— 74·0	0·47
$(CH_3C_6H_4NC)_2Co(NO)(CO)$				
(low frequency)	2 078·2	61·9	—11·3	6·73
(high frequency)	2 130·6	35·2	— 5·4	2·31
$[(CH_3)_3CNC]_2Co(NO)(CO)$				
(low frequency)	2 095·6	64·9	9·0	6·90
(high frequency)	2 129·8	51·5	26·0	5·86

^{a} ϱ see Table III.

In spectra of strong complexes of nitriles with *e.g.* Lewis acids, a higher $\nu(C\equiv N)$ frequency was always found in comparison with that of the parent nitrile component[21,22]. Attempts were made to explain this effect by taking into consideration the changes in hybrid character of N in the $C\equiv N$ bond due to the complex formation[23]. This is in contradiction with the situation in carbonyl solutes where complexation with Lewis acids causes a decrease in the $\nu(C=O)$ frequency.

The effect of complexation with phenol causes an increase in the $\nu(C\equiv N)$ frequency, too. This effect was studied in mixtures of acetonitrile-d_3 (CD_3CN^*) with phenol in organic liquids. When the concentrations of all components were properly chosen, doublets with nearly the same intensity of both branches were found in the infrared spectra.** The component with higher frequency belongs to the hydrogen-bonded complex CD_3CN–phenol; its frequency varies slightly in dependence on the third solution component (see Table IV).

Considering that small shifts*** of $\nu(C\equiv N)$ of the complex (due to the bulk effect of the solution mixtures†) obey the Buckingham equation (1), the effect of solvents on the complex can be discussed in terms of Onsager reaction field theory[17] (see Table IV).

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* CD_3CN was used for a simple shape of its $\nu(C\equiv N)$ absorption band; CH_3CN shows a doublet in this region, the origin of which is in Fermi resonance.

** Both components of the doublet are rather close to each other. For further purposes they were mathematically separated into individual components.

*** Due to a careful calibration of the spectrophotometer wavenumber scale, the accuracy of wavenumbers is ± 0.4 cm^{-1}.

†   The dielectric constants and the refractive indices used are those of solution mixtures.

There is a basic difference when the $\nu(C\equiv N)$ solvent induced frequency shifts are compared with those of $\nu(OH)$ and $\nu(C=O)$. In the latter case, the effect of complex formation causes a decrease in the $\nu(OH)$ and $\nu(C=O)$ frequencies and the bulk effect of solvents also acts in the same direction. On the other hand, the complex formation with nitriles results in an increase of $\nu(C\equiv N)$ frequency and hence it acts against the direction of the bulk effect. There exist four ways in which the frequency shift of any solute vibration can be affected by the simultaneous action of complex formation and solvent bulk effect: the individual effects can increase or decrease the particular frequency and act in the same or opposite directions. Two of these four possibilities were found by us; it seems that another one is described and explained by Lascombe and coworkers[24].

For carbonyl solutes, both the C_1 and the C_2 constants of the Buckingham equation (1) were found negative (see Table III). The same is valid when correlations of the OH group are considered[2]. On the other hand, correlation of the data for $\nu(C\equiv N)$ gives the C_1 constant positive (Table VI). On correlating the $\nu(N\equiv C)$ solvent induced frequency shift of solutions of the $(RN\equiv C)_2Co(NO)(CO)$ complexes (Table V) by using Eq. (1) the C_1 constant was always found positive; for $[(CH_3)_3CN\equiv C]_2$.$Co(NO)(CO)$ both C_1 and C_2 showed the sign $+$ (Table IV). Unfortunately, these few experiments caried out until now with nitriles and isonitriles as solutes do not allow to decide whether the variations in signs of C_1 and C_2 constants of Eq.(1) are characteristic for these cases or accidental.

CONCLUSIONS

The Buckingham equation (1) can be used for correlating the solvent induced $\nu(C=O)$, $\nu(C\equiv N)$ and $\nu(N\equiv C)$ frequency shifts in solution systems described by the model based on the Onsager's reaction field theory. These systems are realized:

1. By molecules of a particular, strong complex dissolved in various solvents or solvent mixtures (*e.g.* molecules of carboxylic acid dimers, molecules of phenol–-CD$_3$CN complex, molecules of isonitrile-complexes *etc.*).

2. By molecules not forming strong complexes in polar solvents (carbonyl solutes possessing very low basicity of the carbonyl oxygen atom).

In other cases the frequency shifts cannot be described in this way. For example the frequencies of a polar solute in various solvents or solvent mixtures belonging to various complexes (furthermore solvated by molecules of solvents left over by the complex formation) cannot be simply compared and treated by the procedure described above.

REFERENCES

1. Horák M., Moravec J.: This Journal *36*, 544 (1971).
2. Horák M., Poláková J., Jakoubková M., Moravec J., Plíva J.: This Journal *31*, 622 (1966).
3. Horák M., Moravec J., Plíva J.: Spectrochim. Acta *21*, 919 (1965).
4. Buckingham A. D.: Proc. Roy. Soc. London *248A*, 169 (1958).
5. Vítek A.: *Program FA-450*. Program Library, Inst. of Organic Chemistry and Biochemistry, Prague 1968.
6. Lascombe J.: *Thesis*. Bordeaux 1960.
7. Whetsel K. B., Kagarise R. E.: Spectrochim. Acta *18*, 315 (1962).
8. Whetsel K. B., Kagarise R. E.: Spectrochim. Acta *18*, 329 (1962).
9. Kagarise R. E., Whetsel K. B.: Spectrochim. Acta *18*, 341 (1962).
10. Fritzsche H.: Acta Chim. Acad. Sci. Hung. *40*, 31 (1964).
11. Augdahl E., Klaeboe P.: Acta Chem. Scand. *16*, 1637 (1962).
12. Middaugh R. L., Drago R. S., Niedzielski R. J.: J. Am. Chem. Soc. *86*, 388 (1964).
13. Lappart M. F.: J. Chem. Soc. *1961*, 817.
14. Heald C., Thompson H. W.: Proc. Roy. Soc. London *268A*, 89 (1962).
15. Becker R. S.: J. Mol. Spectry *3*, 1 (1959).
16. Weimer R. F., Prausnitz J. M.: Spectrochim. Acta *22*, 77 (1966).
17. Horák M., Plíva J.: Spectrochim. Acta *21*, 911 (1965).
18. Lascombe J., Haurie M., Josien M. L.: J. Chim. Phys. *1962*, 1233.
19. Bellamy L. J., Williams R. L.: Trans. Faraday Soc. *55*, 14 (1959).
20. Jesson J. P., Thompson H. W.: Spectrochim. Acta *13*, 217 (1958).
21. Coerver H. J., Curran C.: J. Am. Chem. Soc. *80*, 3522 (1958).
22. Evans J. C., S. Lo G. Y.: Spectrochim. Acta *21*, 1033 (1965).
23. Brune H. A., Zeil W.: Z. Naturforsch. *16a*, 1251 (1961).
24. Devaure J., Pham van Huong, Lascombe J.: J. Chim. Phys. *65*, 1686 (1968).
25. Horrocks W. D., Mann R. H.: Spectrochim. Acta *19*, 1375 (1963).
26. Weissberger A., Proskauer E. S., Riddick J. A., Toops E. E. in the book: *Organic Solvents, Technique of Organic Chemistry*, Vol. VII. (A. Weissberger, Ed.). Interscience, New York, 1955.
27. Timmermans J.: *Physico-Chemical Constants of Pure Organic Compounds*. Elsevier, New York 1950.
28. Maryott A. A., Smith E. A.: *Tables of Dielectric Constants of Pure Liquids*. National Bureau of Standards Circular No 514, Washington 1951.

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