SOLVENT EFFECT ON VALENCE VIBRATIONS
OF (O,N)—H BONDS WITH INTRAMOLECULAR HYDROGEN BOND

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Wave numbers of valence vibrations of N—H and O—H bonds of 1-nitrophenoxazine, 5-methoxy--2-nitroaniline and 2-nitrophenol, respectively, have been measured in 21 solvents and correlated with the respective dielectric constants and refractive indices of the solvents using the Buckingham equation.

Quantitative evaluation of solvent effects on position of IR absorption bands is important both from the analytical viewpoint and for investigation of solute solvation in solvents. The dependence of position of the absorption bands on medium was expressed by empirical relations characterizing the solvent by empirical factors or by the equation based on the Onsager theory of electrostatic field[1]. Out of these equations the Buckingham relation[2] (derived from quantum-mechanical evaluation of solvent shifts) has found the broadest application recently. For practical application the relation is used in the form

$$v = A + B\frac{\varepsilon - 1}{2\varepsilon + 1} + C\frac{n^2 - 1}{2n^2 + 1}, \qquad (1)$$

where A, B, C are empirical constants, ε and n are the dielectric constant and refractive index of the solvent used, respectively. Applicability of this equation for the solvent-induced changes in position of IR absorption bands of compounds in solutions was tested in a great number of systems and is considered to be a confirmation of physical nature of collision complexes[3].

The aim of the present paper is to evaluate the influence of medium on wave number of valence vibration of OH and NH groups bound to a nitro group by intramolecular hydrogen bond using the Buckingham equation.

EXPERIMENTAL

The solvents were dried, rectified and kept over molecular sieve. IR spectra were measured with a UR-20 spectrophotometer (Zeiss, Jena) with LiF prism. Calibration of wave number scale

with solution of 2-nitrophenol in tetrachloromethane (3243 cm^{-1}) and phenol in acetonitrile (3409 cm^{-1}) was carried out before and after each measurement (0·1 cm NaCl cells, concentration of solute 20 mmol/l). Accuracy of the measurements was 1 to 2 cm^{-1} depending on the shape of absorption bands. The given wave numbers are mean values of five measurements.

RESULTS AND DISCUSSION

Tables I and II give fundamental vibration frequencies of O—H bond of 2-nitrophenol in 21 solvents and of N—H bond of 1-nitrophenoxazine and 5-methoxy-2-nitro[^{2}H$_1$]aniline in 14 solvents along with deviations between the wave numbers experimentally found and those calculated according to the Buckingham equation.

TABLE I

Dependence of Experimental Fundamental Frequency ν(O—H) of 2-Nitrophenol on Solvent (cm^{-1})

Solvent	$(\varepsilon - 1)/(2\varepsilon + 1)$	$(n^2 - 1)/(2n^2 + 1)$	ν(O—H)	Deviation
n-Hexane	0·1851	0·1853	3 238[a]	−8·3
Cyclohexane	0·2018	0·2038	3 240	−1·9
Tetrachloromethane	0·2251	0·2142	3 243[a]	+1·9
Benzene	0·2296	0·2267	3 240[a]	+3·1
Tetrachloroethylene	0·2321	0·2282	3 240	+3·3
Toluene	0·2395	0·2341	3 239	+3·5
Carbon disulphide	0·2603	0·2610	3 232	+9·3
Trichloroethylene	0·3087	0·2197	3 249	−2·8
Bromoform	0·3449	0·2536	3 248	+3·9
Diethyl ether	0·3416	0·1770	3 277[a]	+3·4
Chloroform	0·3563	0·2094	3 265	+1·8
Diiodomethane	0·3710	0·2869	3 241	+6·0
Bromobenzene	0·3727	0·2477	3 246	−6·3
Chlorobenzene	0·3775	0·2337	3 248	−8·9
Iodomethane	0·3981	0·2356	3 250	−9·3
Tetrahydrofurane	0·4037	0·1971	3 278	+2·7
Tetrachloroethane	0·4138	0·2248	3 260	−6·0
Dichloromethane	0·4202	0·2024	3 266	−9·2
Nitrobenzene	0·4788	0·2418	3 269[a]	−0·4
Acetonitrile	0·4796	0·1740	3 304[a]	+8·1
Nitromethane	0·4798	0·1879	3 288[a]	−2·6

[a] From ref.[9], terms with ε and n^2 taken from ref.[4].

For the studied sets the Buckigham equation has the form:

$$\nu(\text{O—H}) = 3290.5 + 154.1(\varepsilon - 1)/(2\varepsilon + 1) - 392.5(n^2 - 1)/(2n^2 + 1), \quad (2)$$

$$\nu(\text{N—H}) = 3443.8 + 36.0(\varepsilon - 1)/(2\varepsilon + 1) - 103.2(n^2 - 1)/(2n^2 + 1), \quad (3)$$

$$\nu(\text{N—H}) = 3409.5 - 157.0(n^2 - 1)/(2n^2 + 1). \quad (4)$$

The equations (2), (3) and (4) correspond to 2-nitrophenol, 5-methoxy-2-nitro-[²H₁]aniline and 1-nitrophenoxazine, respectively. From the deviations given in Tables I and II it is obvious that agreement between the experimental and calculated values is good in the case of O—H valence vibration of 2-nitrophenol, and it is very good in the case of wave numbers of N—H valence vibrations of 5-methoxy-2-nitro-[²H₁]aniline and 1-nitrophenoxazine.

The correlations of $\nu(\text{O—H})$ with the use of the Buckingham equation were carried out with a number of systems containing either a "free" hydroxyl group or a hydroxyl group involved in an intermolecular donor–acceptor complex on the basis of hydrogen bond[4-8]. The both constants B and C of Eq. (1) were negative in such cases, being higher by about one order of magnitude in the case of the hydroxyl group bound by intermolecular hydrogen bond. Influence of medium on systems with intramolecular hydrogen bond was studied only in the case of $\nu(\text{O—H})$ of 2-methoxybutanol and 2,4-pentandiol[9,10]. In this case the $\nu(\text{O—H})$ values were cor-

TABLE II

Dependence of Experimental Fundamental Frequency $\nu(\text{N—H})$ of 5-Methoxy-2-nitro[²H₁]aniline (*I*) and 1-Nitrophenoxazine (*II*) on Solvent (cm⁻¹)

Solvent	*I*		*II*	
	$\nu(\text{N—H})$	deviation	$\nu(\text{N—H})$	deviation
Tetrachloromethane	3 435	−0.5	3 376	+0.2
Carbon disulphide	3 426	−0.2	3 368	−0.5
Trichloroethylene	3 433	+0.7	3 375	0.0
Bromoform	3 431	+0.9	3 370	+0.3
Diiodomethane	3 427	−0.5	3 364	−0.4
Bromobenzene	3 434	+1.9	3 371	−0.2
Chlorobenzene	3 433	−0.2	3 374	+1.2
Iodomethane	3 432	−1.8	3 372	−0.5
Tetrachloroethane	3 435	−0.5	3 374	−0.2
Dichloromethane	3 436	−2.1	3 376	−1.7
Nitrobenzene	3 437	+0.9	3 372	+0.5
Nitromethane	3 443	+1.3	3 377	−3.0

related with empirical factors G, no relationship being found between these G factors and terms containing ε and n^2 in the Buckingham equation[10]. From Eq. (2) it follows that the constants B and C characterizing the influence of dielectric constant and refractive index on $v(O—H)$ are of comparable magnitude with those of systems with intermolecular hydrogen bond, but the constant B is positive. Similarly positive even though smaller is the constant B in the case of the lower band of NH^2H group of 5-methoxy-2-nitro[$^2H_1$]aniline, whereas it is zero in the case of $v(N—H)$ of 1-nitro-phenoxazine.

IR spectra of substituted 2-nitro[$^2H_1$]anilines contained two bands in the region of N—H valence vibration[11,12] their possition being dependent on the ring substituents in different ways; they were assigned to N—H bond in *cis* and *trans* position with respect to nitro group. Solvent change caused changes in the both bands positions. Increasing refractive index of solvent shifted the both bands towards lower wave numbers, whereas increasing dielectric constant of solvent affected the both bands in different ways. The $v(N—H)$ band at lower wave number (N—H group *cis* to nitro group) shifted to higher wave numbers with increasing dielectric constant of solvent, whereas the band at higher wave number (N—H in *trans* position to nitro group) shifted to lower wave numbers with increasing dielectric constant of solvent, and finally the both bands coalesced in nitromethane solution. Dependence of $v(N—H)$ of the *trans* N—H bond on dielectric constant and refractive index of solvent is expressed in Eq. (5)

$$v(N—H) = 3602{\cdot}0 - 176{\cdot}0(\varepsilon - 1)/(2\varepsilon + 1) - 314{\cdot}1(n^2 - 1)/(2n^2 + 1). \quad (5)$$

The both constants B and C are thus negative as they are in the case of collision complexes of compounds with O—H and N—H bonds. The two bands of 2-nitro-[$^2H_1$]aniline showed similar behaviour as those of 5-methoxy-2-nitro[$^2H_1$]aniline, their coalescence being complete already in dichloromethane solution.

More experimental results are necessary for the decision to what extent the found positive or zero effect of solvent dielectric constant on $v(O,N—H)$ of the groups bound by intramolecular hydrogen bond is peculiar to the systems studied or general for all groups bound by intramolecular hydrogen bond. Thus the sign of this term of the Buckingham equation could become a further criterion of existence of intramolecular hydrogen bond — as it is the case with 2-nitroaniline.

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