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Infrared Study of Solvent-Solute Interactions of 1-Substituted 2-Pyrrolidinones and Related Compounds

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Summary. The wavenumbers of the carbonyl stretching vibrations of 2-pyrrolidinone (*P*), 1-methyl-2-pyrrolidinone (*MP*), 1-isopropyl-2-pyrrolidinone (*IPP*), 1-(2-hydroxyethyl)-2-pyrrolidinone (*HEP*), 2-oxobenzothiazole (*OBT*), and 3-octyl-2-oxobenzothiazole (*OOBT*) were measured in *n*-hexane/$CDCl_3$, acetonitrile/D_2O, methanol/D_2O, and 2-butoxyethanol/D_2O mixtures and compared with similar data for 1-cyclohexyl-2-pyrrolidinone (*CHP*) and dimethylacetamide (*DMA*). The dependencies of the wavenumbers on the mole fraction of the less polar cosolvent in binary mixtures allow a distinction and assignment of all species resulting from weak solute-solvent and solute-solute interactions. The slopes of the dependencies of the wavenumbers on the mole fraction for similar intermolecular species in *n*-hexane/$CDCl_3$ mixtures correlate well with the relative hydrogen bond basicities (*i.e.* hydrogen bonding abilities with phenol) and reveal that the solvent sensitivities significantly depend on the steric requirements in the vicinity of the C=O group. On the other hand, the slopes of similar dependencies in acetonitrile/D_2O mixtures are proportional to the electron donating effects of alkyl groups attached to the nitrogen atom of the pyrrolidinone ring. In the case of mixtures formed by two strongly hydrogen bonding cosolvents (alcohols/D_2O), a competitive equilibrium occurs between the hydrogen bonding tendency of both cosolvents and 1-substituted 2-pyrrolidinones. In solutions of 1-substituted 2-pyrrolidinones in water-rich 2-butoxyethanol/D_2O mixtures, microheterogeneous domains occur before classic mixtures of two polar liquids are formed.

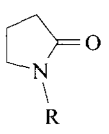
Keywords. 1-Substituted 2-pyrrolidinones; Carbonyl stretching vibration wavenumbers; Hexane/$CDCl_3$; Acetonitrile/D_2O; Methanol/D_2O; 2-Butoxyethanol/D_2O; Solute-solvent interactions.

Infrarotuntersuchungen über Wechselwirkungen von 1-substituierten 2-Pyrrolidinonen und verwandten Verbindungen mit Lösungsmitteln

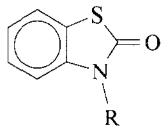
Zusammenfassung. Die Wellenzahlen der Carbonylstreckschwingungen von 2-Pyrrolidinon (*P*), 1-Methyl-2-pyrrolidinon (*MP*), 1-Isopropyl-2-pyrrolidinon (*IPP*), 1-(2-Hydroxyethyl)-2-pyrrolidinon (*HEP*), 2-Oxobenzothiazol (*OBT*) und 3-Octyl-2-oxobenzothiazol (*OOBT*) wurden in *n*-Hexan/$CDCl_3$, Acetonitril/D_2O, methanol/D_2O und 2-Butoxyethanol/D_2O gemessen und mit den entsprechenden Daten für 1-Cyclohexyl-2-pyrrolidinon (*CHP*) und Dimethylacetamid (*DMA*) verglichen. Die Abhängigkeit der Wellenzahlen vom Molenbruch des weniger polaren Lösungsmittels in binären Mischungen erlaubt eine Unterscheidung und Zuordnung aller durch schwache Wechselwirkungen zwischen gelöster Substanz und Lösungsmittel bzw. durch Wechselwirkungen der gelösten Moleküle untereinander entstehenden Spezies. Für ähnliche Moleküle in *n*-Hexan/$CDCl_3$ – Mischungen korrelieren die Steigungen der Abhängigkeiten der Wellenzahlen vom Molenbruch gut mit den relativen Basizitäten der Wasserstoffbrückenbindungen (d.h. mit der Fähigkeit zur Ausbildung von Wasserstoffbrückenbindungen mit Phenol) und beweisen, daß die Lösungsmittelabhängigkeiten wesentlich von sterischen Faktoren in der Umgebung der Carbonylgruppe abhängen. Andererseits sind die Steigungen entsprechender Korrelationen in Acetonitril/D_2O – Mischungen zur Elektronendonatorfähigkeit von an das Stickstoffatom des Pyrrolidinonrings gebundenen Alkylgruppen proportional. Im Fall von Mischungen aus zwei stark wasserstoffbrückenbildenden Lösungsmitteln (Alkohole/D_2O) stellt sich ein kompetitives Gleichgewicht zwischen der Tendenz zur Wasserstoffbrückenbindungsbildung beider Lösungsmittel und den 1-substituierten 2-Pyrrolidinonen ein. In Lösungen von 1-substituierten 2-Pyrrolidinonen in 2-Butoxyethanol/D_2O – Mischungen mit hohem Wasseranteil treten vor der Ausbildung klassischer Mischungen zweier polarer Flüssigkeiten mikroheterogene Domänen auf.

Introduction

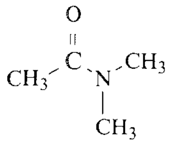
Recently it has been observed that the wavenumbers of the carbonyl stretching vibration of 1-cyclohexyl-2-pyrrolidinone in both aqueous and organic solvent mixtures are rather sensitive to the composition of the mixture [1, 2]. In a subsequent study, the wavenumbers of the carbonyl stretching vibration of 1-cyclohexyl-2-pyrrolidinone, measured in hexane/$CDCl_3$ mixtures, were successfully interpreted using the AM1 semiempirical approach [3]. *Laurence et al.* [4], but also *Nolte* and coworkers [5] have shown that in the case of carbonyl compounds interacting with alcohols or phenols two stereochemically different types of intermolecular hydrogen bonds can be observed. The first type is the conventional angular hydrogen bond formed by the lone electron pairs of the carbonyl group oxygen atom. This hydrogen bond exhibits an O–H stretching vibration in the lower wavenumber region. If, however, bulky groups adjacent to the C=O group destabilize the above interaction, the second type of linear (or axial) hydrogen bond is favoured, resulting from an electrical attraction between the π-electrons of the C=O group and the hydroxy group. The $\tilde{\nu}$(O–H) wavenumbers of these species are substantially higher than those of angular hydrogen bonds. The above observations as well as our previous results [1, 2] provided a stimulus to use the marked solvent sensitivity of the carbonyl stretching vibration to study the stereochemistry of hydrogen bonds in the context of solvent-solute interactions. As 1-cyclohexyl-2-pyrrolidinone appears to be a suitable model for simple cyclopeptides, we decided to extend the above investigation to further 1-substituted 2-pyrrolidinones and related compounds bearing substituents with different steric requirements and alkyl group effects in *n*-hexane/$CDCl_3$, acetonitrile/D_2O, methanol/D_2O, and 2-butoxyethanol/D_2O mixtures and to compare the results with those obtained previously with 1-cyclohexyl-2-pyrrolidinone and dimethylacetamide [2].



R = H (*P*)
R = CH_3 (*MP*)
R = $CH(CH_3)_2$ (*IPP*)
R = *cyclo*-C_6H_{13} (*CHP*)
R = CH_2–CH_2–OH (*HEP*)



R = H (*OBT*)
R = C_8H_{17} (*OOBT*)



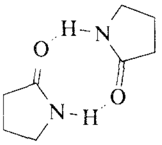
$CH_3C(=O)N(CH_3)_2$ (*DMA*)

Results and Discussion

Organic Mixtures

The wavenumbers of the carbonyl stretching vibrations of 1-substituted 2-pyrrolidinones measured in mixtures of hexane and deuteriotrichloromethane are listed in Table 1.

2-Pyrrolidinone (*P*) in pure *n*-hexane (dilute solution) exhibits two well-resolved absorption bands in the $\tilde{\nu}$(C=O) region. The less intensive band at higher wavenumber (1734.0 cm^{-1}) belongs to molecules in the free monomeric state (*FM*), whereas the more intense lower wavenumber one (1712.4 cm^{-1}) can be assigned to two molecules bonded together by intermolecular hydrogen bonds, *i.e.* "cyclic dimers", or free dimers (*FD*).



The higher wavenumber band becomes gradually less intensive as the concentration of solute in C_6H_{14} increases; this means that at higher concentrations the *FD* species are favoured. This spectroscopic behavior is typical also for other five-membered heterocycles bearing C=O and N–H groups in vicinal position [11]. When $CDCl_3$ is added to a solution of *P* in *n*-hexane, the $\tilde{\nu}$(C=O) band belonging to *FD* is shifted to lower wavenumbers (1703.4 cm^{-1}); its position is significantly dependent on the mole fraction of *n*-hexane in the binary mixture (Fig. 1). The species belonging to the above absorption band can be assigned to monomeric pyrrolidinone, the carbonyl group of which is angularly hydrogen bonded with a $CDCl_3$ molecule (*AM*). Evidently, the species bearing linear hydrogen bonds between the C=O group and $CDCl_3$ molecules are missing in this case because of an easier steric accessibility of the carbonyl group in 2-pyrrolidinone.

Table 1. Wavenumbers $\tilde{\nu}$(C=O) for the carbonyl stretching mode of *P*, *MP*, *IPP*, and *HEP* as a function of the mole fraction of *n*-hexane in *n*-hexane/$CDCl_3$ mixtures

$x(C_6H_{14})$	$\tilde{\nu}$(C=O) (cm^{-1})											
	P			*MP*			*IPP*			*HEP*		
	AM	*FD*	*FM*	*AM*	*LM*	*FM*	*AM*	*LM*	*FM*	*LI*	*MI*	*FM*
0.000	1689.4			1674.5			1666.0			1662.2		
0.064	1691.6			1676.2			1666.6			1665.8		
0.133	1693.0			1675.2			1666.4			1667.5		
0.208	1692.8			1679.0			1669.2			1669.0		
0.290	1694.0			1679.8			1669.2			1670.0		
0.380	1696.6			1680.4			1671.0			1670.0		
0.479	1699.2			1680.6			1670.0	1686.0		1671.0		
0.533	1697.6			1680.6	1695.0		1672.6	1687.0		1673.6		
0.590	1699.0			1683.5	1696.0		1672.6	1687.0		1675.4		
0.648	1699.0			1683.0	1697.0		1673.2	1687.2		1674.8		
0.710	1700.0			1683.4	1697.0		1673.4	1687.6		1676.2		
0.777	1701.0			1682.8	1696.6		1674.0	1687.6		1676.0		
0.847	1702.8			1683.0	1696.6		1674.0	1689.2	1702.8	1676.8		
0.921	1703.4	1712.4	1734.0		1696.6	1711.0	1674.0	1690.0	1704.0	1680.0		
1.000					1697.4	1712.2			1704.0		1691.2	1705.6

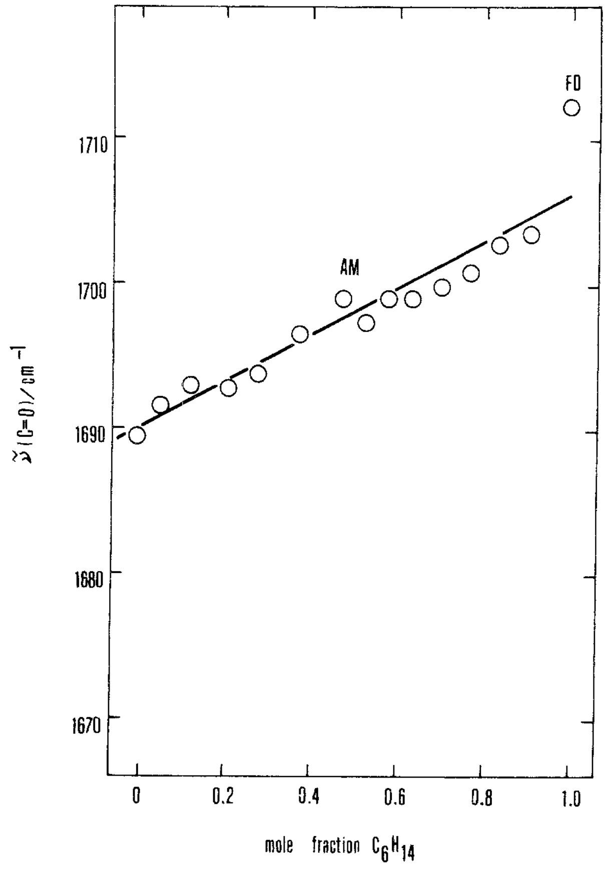


Fig. 1. Dependence of $\tilde{\nu}$(C=O) on the mole fraction of *n*-hexane in mixtures of *n*-hexane and $CDCl_3$ for 2-pyrrolidinone

1-Methyl-2-pyrrolidinone (*MP*) in *n*-hexane is passing from the free monomeric state (*FM*; $\tilde{\nu}$(C=O) = 1712.2 cm^{-1}) to species linearly bonded with a $CDCl_3$ molecule (*LM*; 1697.6–1695.0 cm^{-1}) upon addition of $CDCl_3$. This is evidently caused by a partial destabilization of the angular hydrogen bonding interaction due to the higher steric bulk of the methyl group. However, after increasing the concentration of $CDCl_3$ in the mixture, the angularly hydrogen bonded species (*AM*; $\tilde{\nu}$(C=O) = 1683.0–1674.5 cm^{-1}) is finally observed. The wavenumbers of both the *LM* and *AM* species are remarkably dependent upon the mole fraction of *n*-hexane in the solvent mixture. This behavior is very similar to that observed recently with 1-cyclohexyl-2-pyrrolidinone (*CHP*) [2].

The similarity between the dependencies of the $\tilde{\nu}$(C=O) wavenumbers upon the mole fraction of *n*-hexane for 1-isopropyl-2-pyrrolidinone (*IPP*) and both *MP* and *CHP* is illustrated in Fig. 2. However, in $x(C_6H_{14})$ ranges characteristic for the presence of *FM* and *LM* species in all three 1-substituted 2-pyrrolidinones, a significant difference can be observed. As it is evident from Table 1 and the former results [2, 3], the above ranges increase in the order $CH < MP < IPP$, *i.e.* in the same order in which the steric requirements in the surroundings of the C=O group increase.

1-(2-Hydroxyethyl)-2-pyrrolidinone (*HEP*) in *n*-hexane exhibits two sharp and well resolved $\tilde{\nu}$(C=O) absorption bands ($\Delta\nu_{1/2} \approx 1$ cm^{-1}) at 1691.2 cm^{-1} and 1705.6 cm^{-1}, the intensity ratio of which is practically independent of concentration.

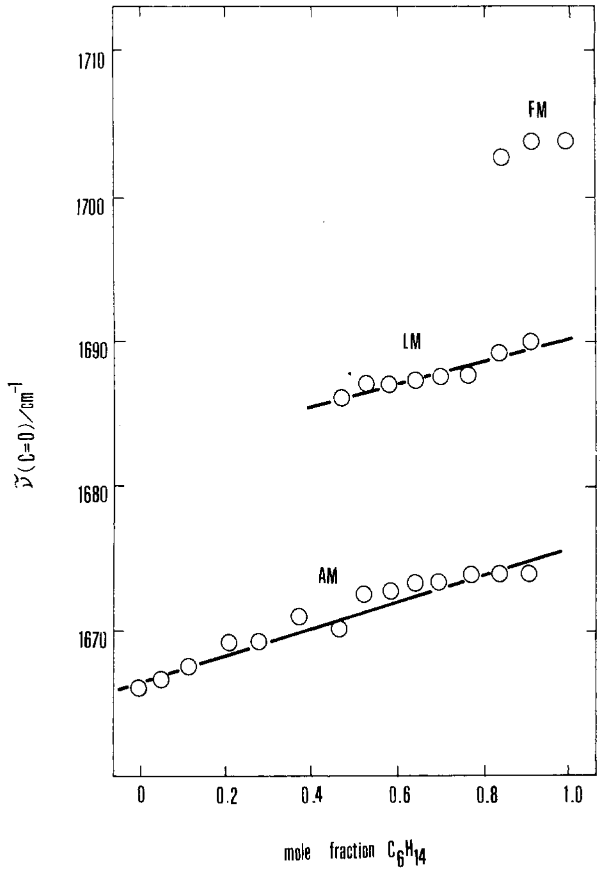
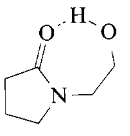


Fig. 2. Dependence of $\tilde{\nu}$(C=O) on the mole fraction of *n*-hexane in mixtures of *n*-hexane and $CHCl_3$ for 1-isopropyl-2-pyrrolidinone

This provides evidence that the absorption band at higher wavenumbers belongs to the free monomeric species (*FM*), whereas the lower-wavenumber band must be assigned to intramolecularly hydrogen bonded molecules of *HEP* (*MI*).

When $CDCl_3$ is added to the solution, $\tilde{\nu}$(C=O) is shifted to lower wavenumbers and the position of the absorption band decreases as the mole fraction of *n*-hexane in the mixture is lowered (Fig. 3). The corresponding species can be most probably assigned to intramolecularly hydrogen bonded *HEP* interacting by a linear hydrogen bond with the cosolvent $CDCl_3$ (*LI*).



2-Oxobenzothiazole derivatives can be regarded as aromatic thia-analogues of 2-pyrrolidinones. The wavenumbers of their carbonyl stretching vibrations were measured in binary mixtures of hexane and deuteriotrichloromethane and listed in Table 2.

The behaviour of 2-oxobenzothiazole (*OBT*) in *n*-hexane is similar to that of 2-pyrrolidinone. passing from concentrated to diluted solutions, the intensity of the higher wavenumber $\tilde{\nu}$(C=O) band (at 1728.0 cm^{-1}) raises, whereas the intensity

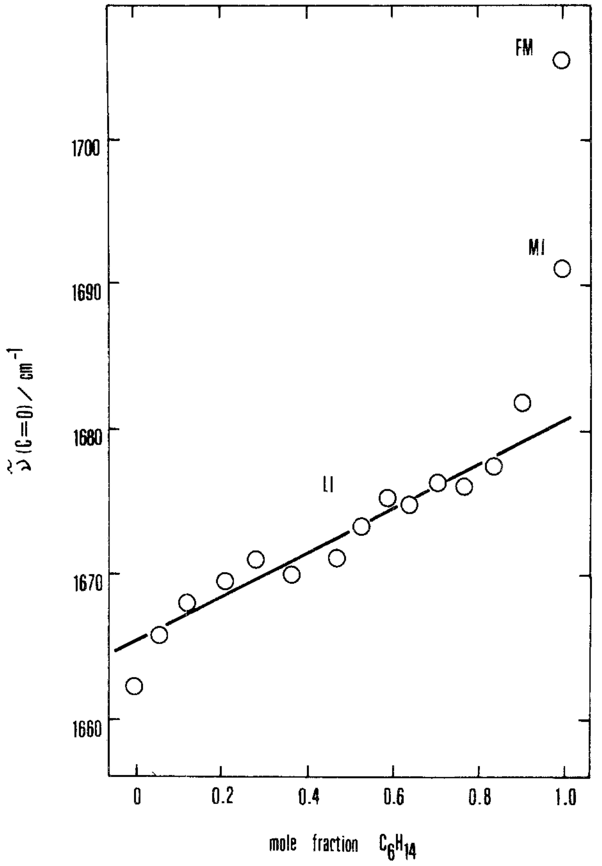


Fig. 3. Dependence of $\tilde{\nu}$(C=O) on the mole fraction of *n*-hexane in mixtures of *n*-hexane and $CDCl_3$ for 1-(2-hydroxyethyl)-2-pyrrolidinone

Table 2. Wavenumbers $\tilde{\nu}$(C=O) for the carbonyl strecthing mode of *OBT* and *OOBT* as a function of the mole fraction of *n*-hexane in *n*-hexane/$CDCl_3$ mixtures

$x(C_6H_{14})$	$\tilde{\nu}$(C=O) (cm^{-1})							
	OBT				*OOBT*			
	FD	*LD*	*LM*	*FM*	*BAM*	*AM*	*LM*	*FM*
0.000		1685.0	1708.8		1665.6			
0.064		1685.2	1708.2		1664.6			
0.133		1686.4	1708.0		1667.0			
0.208		1686.0	1709.2			1678.6		
0.290	1673.6		1710.0			1678.4		
0.380	1674.4		1711.2			1680.0		
0.479	1675.6		1712.0			1681.0		
0.533	1676.0		1711.8			1681.4		
0.590	1676.8		1712.0			1681.0		
0.648	1677.4		1712.1			1680.6	1695.0	
0.710	1678.0		1712.0			1681.6	1695.0	
0.777	1679.0		1712.4			1683.8	1696.4	
0.847	1680.0		1712.8			1683.6	1697.0	
0.921	1680.3		1712.4			1682.4	1697.2	
1.000	1680.8		1712.4	1728.0				1699.6

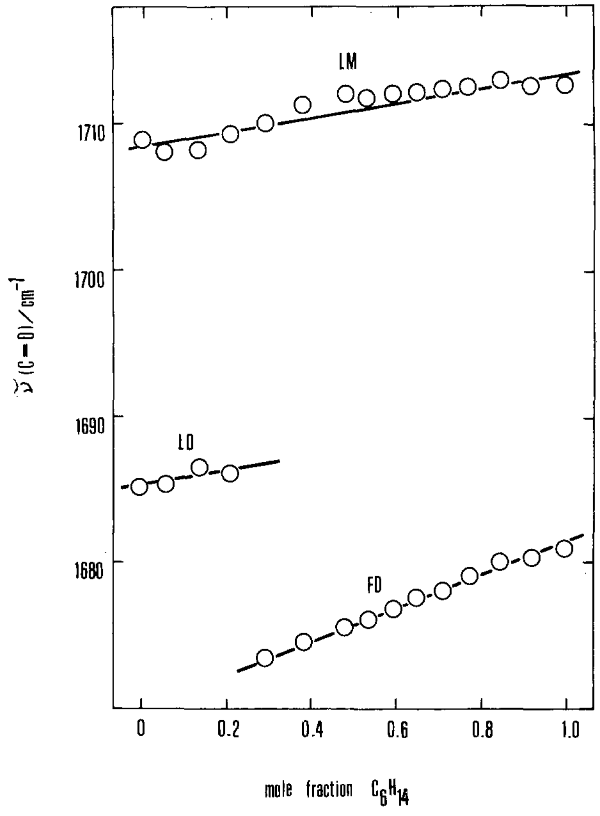
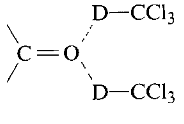


Fig. 4. Dependence of $\tilde{\nu}$(C=O) on the mole fraction of *n*-hexane in mixtures of *n*-hexane and $CDCl_3$ for 2-oxobenzothiazole

of the lower wavenumber one (at 1680.8 cm^{-1}) decreases. We suppose that the former band can be assigned to the free monomeric species (*FM*), whereas the latter one belongs to the intermolecularly hydrogen bonded "cyclic dimers" (*FD*). The *FD* species are also present in the media of binary mixtures (Fig. 4), and their $\tilde{\nu}$(C=O) wavenumbers depend on the mole fraction of *n*-hexane. The addition of $CDCl_3$ to a solution of *OBT* in *n*-hexane causes the appearance of a new absorption band at 1721.4 cm^{-1} which exhibits a dependency upon the mole fraction of *n*-hexane and can be assigned to the monomeric *OBT* linearly bonded with a $CDCl_3$ molecule (*LM*). At higher concentrations of $CDCl_3$ in the mixture, the "cyclic dimers" of *OBT* are interacting by forming linear hydrogen bonds with $CDCl_3$ molecules (*LD*) in a relatively narrow range of $x(C_6H_{14})$ values.

Figure 5 illustrates that 3-octyl-2-oxobenzothiazole (*OOBT*) in binary mixtures of hexane and $CDCl_3$, similarly to *MP*, *IPP*, and *CHP*, exists in three structural domains: *FM*, *LM*, and *AM*. However, in $CDCl_3$-rich mixtures an additional absorption band is observed at relatively low wavenumbers (1686.0–1685.0 cm^{-1}). This absorption is probably connected with one *OOBT* molecule angularly hydrogen bonded to two molecules of $CDCl_3$ (*BAM*). This situation is possible in the case of 3-substituted 2-oxobenzothiazoles, in which the C=O group is sterically less hindered than in 1-substituted 2-pyrrolidinones.



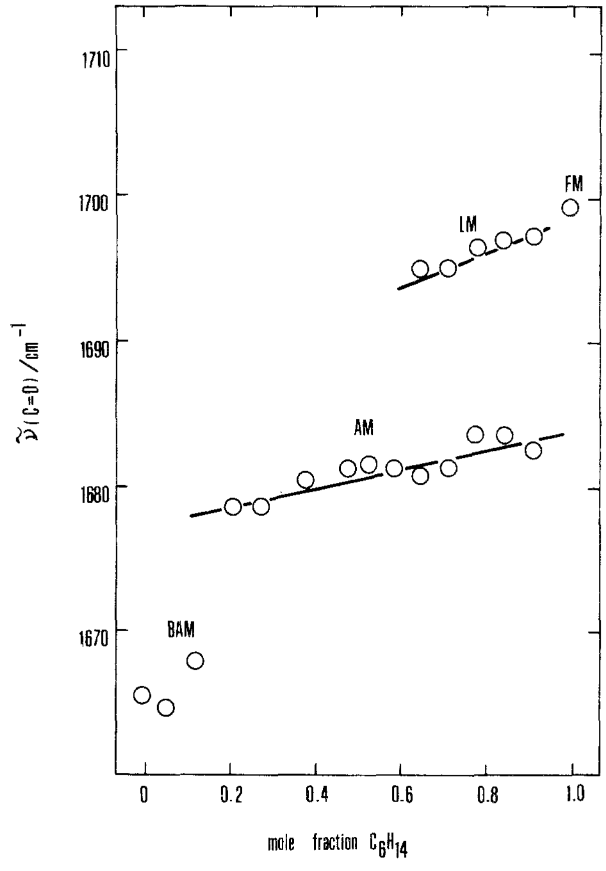


Fig. 5. Dependence of $\tilde{\nu}$(C=O) on the mole fraction of *n*-hexane in mixtures of *n*-hexane and $CDCl_3$ for 3-octyl-2-oxobenzothiazole

The statistical parameters of the correlation of $\tilde{\nu}$(C=O) with the mole fraction of *n*-hexane in *n*-hexane/$CDCl_3$ mixtures for different species of 1-substituted pyrrolidinones and related compounds are listed in Table 3. Table 4 contains the relative hydrogen bond basicities $\Delta\tilde{\nu}$(OH) and corresponding hydrogen bond enthalpies for all investigated compounds determined on the basis of the interaction between the C=O group and the hydroxy group of phenol. For the *AM* species of most of the compounds, a linear correlation exists between the slopes ϱ of $\tilde{\nu}$(C=O) *vs.* $x(C_6H_{14})$ and the $\Delta\tilde{\nu}$(OH) values (Fig. 6). It is evident that the sensitivity of the carbonyl stretching vibration to the composition of the solvent mixture (expressed by ϱ) depends remarkably on the steric effects in the proximity of the C=O group. In the series of 1-substituted 2-pyrrolidinones, the sterically most hindered *IPP* forms the weakest hydrogen bond with phenol ($\Delta H = 23.6\,\mathrm{kJ\cdot mol^{-1}}$), and its $\tilde{\nu}$(C=O) sensitivity to the solvent mixture is also small. On the other hand, the sterically less crowded C=O group of *P* is bonded stronger to the phenol molecule ($\Delta H = 29.7\,\mathrm{kJ\cdot mol^{-1}}$) and is more sensitive to changes in the composition of the solvent mixture. Nevertheless, it follows from Fig. 6 that a general relationship between the ϱ and $\Delta\tilde{\nu}$(OH) values complies well even with structurally different compounds: 2-pyrrolidinones, 2-oxobenzothiazoles, and dimethylacetamide. However, there are exceptions for *HEP* and *OBT* which exhibit other than the *AM* species.

Table 3. Statistical parameters for $\tilde{\nu}$(C=O) *vs.* $x(C_6H_{14})$ correlations for *P*, *MP*, *IPP*, *HEP*, *CHP*, *OBT*, *OOBT*, and *DMA* in *n*-hexane/$CDCl_3$ mixtures

Compound	Species	n^a	ϱ^b	q^c	r^d	s^e
P	*AM*	14	14.24±0.75	1690.4	0.984	0.81
MP	*AM*	13	10.55±1.20	1675.6	0.936	0.12
LM	*LM*	8	3.29±1.41	1694.1	0.689	0.58
IPP	*AM*	14	9.35±0.69	1666.6	0.969	0.74
	LM	8	7.88±1.14	1682.3	0.942	0.47
HEP	*LI*	14	16.11±1.06	1664.5	0.975	0.11
CHP^f	*AM*	15	11.05±0.85	1664.0	0.962	0.93
	LM	7	9.16±2.07	1649.7	0.893	0.71
OBT	*FD*	11	10.75±0.32	1670.4	0.996	0.22
	LD	4	5.98±3.06	1685.0	0.810	0.47
	LM	15	4.47±0.48	1708.9	0.933	0.57
OOBT	*AM*	11	6.73±1.14	1677.3	0.892	0.82
	LM	5	12.36±1.98	1686.6	0.952	0.58
	LM	5	12.36±1.98	1686.6	0.952	0.58
DMA^f	*AM*	14	9.64±0.61	1636.2	0.977	0.59
	LM	7	9.16±2.07	1649.7	0.893	0.71

[a] Number of points in the correlation; [b] slope of the $\tilde{\nu}$(C=O) *vs.* $x(C_6H_{14})$ plot; [c] intercept; [d] correlation coefficient; [e] standard deviation; [f] taken from Ref. [2]

Table 4. Relative basicities $\Delta\tilde{\nu}$(OH) and enthalpies for hydrogen bonding between phenol and the carbonyl group of *P*, *MP*, *IPP*, *HEP*, *CHP*, *OBT*, *OOBT*, and *DMA*

Compound	$\Delta\tilde{\nu}(OH)^a (cm^{-1})$	$\Delta H^b (kJ\cdot mol^{-1})$
P	404.0	29.7
MP	342.4	25.5
IPP	314.0	23.6
HEP	244.0	18.9
CHP^c	346.8	25.8
OBT	457.5	33.2
OOBT	241.8	18.8
DMA^c	333.0	24.9

[a] Determined as $\Delta\tilde{\nu}(OH) = \tilde{\nu}(OH)_{free} - \tilde{\nu}(OH)_{bonded}$ in CCl_4; [b] calculated using the *Badger* empirical equation $\Delta H = 0.0669\,\Delta\tilde{\nu}(OH) + 2.63$; [c] taken from Ref. [2]

It is anticipated that the observations regarding the geometry and steric requirements for solute-solvent interactions can serve as a suitable model for further investigation of simple cyclic peptides and proteins.

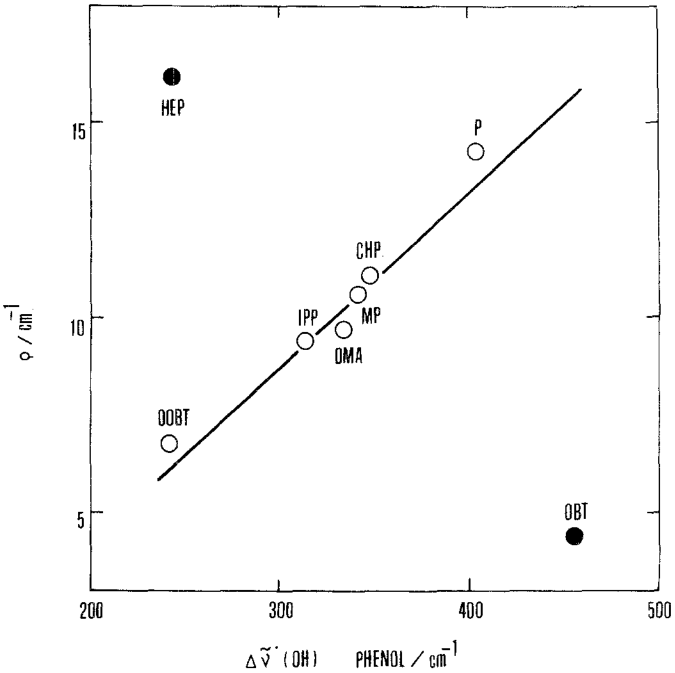


Fig. 6. Correlation between the slopes ϱ of $\tilde{\nu}$(C=O) *vs.* $x(C_6H_{14})$ and the relative hydrogen bond basicities ($\Delta\tilde{\nu}$(OH)) for 1-substituted 2-pyrrolidinones and related compounds

Aqueous Mixtures

The wavenumbers measured for *P*, *MP*, *IPP*, and *CHP* in acetonitrile/D_2O mixtures are listed in Table 5. In agreement with previous results for all compounds, four clearly separated regions of wavenumbers can be observed. In pure MeCN, the highest wavenumber band corresponds to the free monomeric molecules (*FM*). At wavenumbers approximately 20 cm^{-1} lower, the absorption bands belonging to species in which the C=O group is linearly hydrogen bonded to one molecule of D_2O (*LM*) is observed. Below the above region, the absorption bands characterizing the species in which the C=O group is angularly hydrogen bonded to one molecule of D_2O (*AM*) occur over a wide range of MeCN mole fractions. Finally, at the lowest wavenumbers the absorption bands connected with the existence of species in which the C=O group is angularly hydrogen bonded to two molecules of D_2O (*BAM*) are observed. For all 1-substituted 2-pyrrolidinones the wavenumbers of *AM* species are significantly dependent upon the composition of the mixture (Fig. 7). A statistical treatment of corresponding linear correlations is given in Table 6.

Similarly to *AM* species of 1-substituted 2-pyrrolidinones formed by the interaction with hexane/$CDCl_3$ mixtures, a correlation can be found between the slopes ϱ of $\tilde{\nu}$(C=O) *vs.* x(MeCN) and the relative basicities $\Delta\nu$(OH) determined by hydrogen bonding with phenol (Fig. 8). However, a comparison of the above correlation with that reported for hexane/$CDCl_3$ mixtures (Fig. 6) shows that the slope has a negative sign in the case of MeCN/D_2O mixtures. This suggests that the sensitivity of $\tilde{\nu}$(C=O) wavenumbers to the mole fraction of the solvent mixture

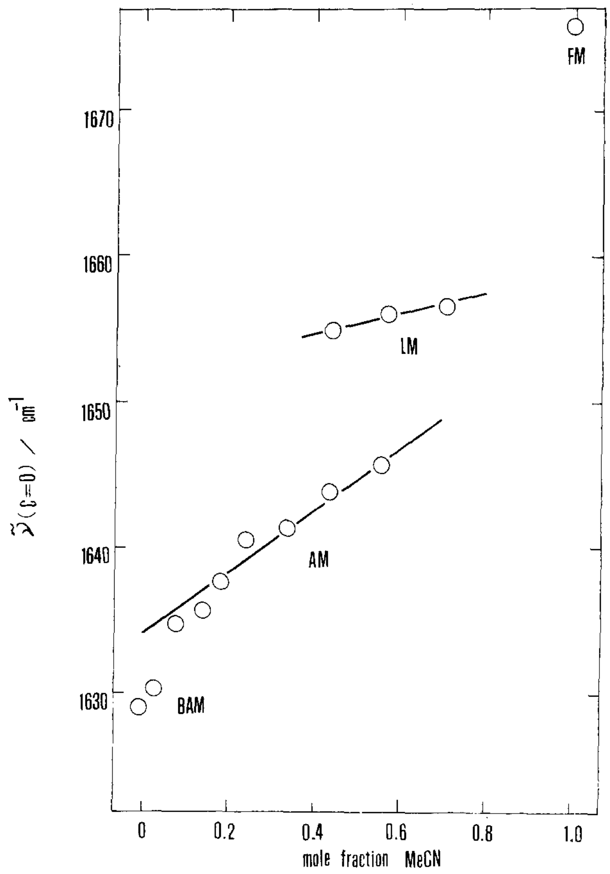


Fig. 7. Dependence of $\tilde{\nu}$(C=O) on the mole fraction of acetonitrile in mixtures of acetonitrile and D_2O for 1-isopyropyl-2-pyrrolidinone

is proportional to alkyl group effects as expected from *Taft* substituent constants, whereas in the case of hexane/$CDCl_3$ mixtures the steric requirements of substituents in position 1 are determinant. The above distinct behaviour of solvent-solute interactions in MeCN/D_2O and C_6H_{14}/$CDCl_3$ mixtures can be reasonably explained by the difference in the size of small D_2O and bulky $CDCl_3$ molecules interacting with sterically hindered C=O groups.

The $\tilde{\nu}$(C=O) wavenumbers for *P*, *MP*, *IPP*, and *CHP* in methanol/D_2O mixtures are listed in Table 7; a typical dependence of $\tilde{\nu}$(C=O) wavenumbers upon the mole fraction of methanol in the case of *CHP* is illustrated in Fig. 9. It is evident that in all cases the absorption bands belonging to the free monomeric molecules (*FM*) can be clearly distinguished, whereas the wave-numbers characterizing the species bonded by hydrogen bonds to the solvent molecules (*BM*) coherently change over the wide range of *x*(MeOH) values. This behaviour is most likely caused by the presence of two strongly polar and hydrogen bonding cosolvents (MeOH and D_2O). When the 2-pyrrolidinone derivative is dissolved in the mixture, probably a competitive equilibrium occurs between the hydrogen bonding tendency of both cosolvents with the pyrrolidinone carbonyl group; the equilibrium continuously alters as the composition of the mixture changes.

Table 5. Wavenumbers $\tilde{\nu}$(C=O) characterizing the carbonyl stretching mode of *P*, *MP*, *IPP*, and *CHP* as a function of the mole fraction of MeCN in MeCN/D_2O mixtures

	$\tilde{\nu}$(C=O) (cm^{-1})							
x(MeCN)	*P*				*MP*			
	BAM	*AM*	*LM*	*FM*	*BAM*	*AM*	*LM*	*FM*
0.000	1645.0				1641.8			
0.037	1645.2					1644.9		
0.079		1650.0				1645.0		
0.141		1650.4				1648.0		
0.187		1650.8				1650.5		
0.265		1650.8	1654.8			1651.4		
0.349		1651.5	1658.0			1651.2		
0.445		1651.8	1659.8			1653.2		
0.579			1663.6			1657.0	1663.0	
0.775			1668.8				1667.4	
1.000				1693.2				1684.6

	$\tilde{\nu}$(C=O) (cm^{-1})							
x(MeCN)	*IPP*				*CHP*			
	BAM	*AM*	*LM*	*FM*	*BAM*	*AM*	*LM*	*FM*
0.000	1629.2				1621.8			
0.037	1630.4					1630.0		
0.079		1634.8				1630.0		
0.141		1635.8				1633.2		
0.187		1637.6				1635.0		
0.265		1640.5				1636.4		
0.349		1641.4				1637.5		
0.445		1644.0	1655.0			1639.6		
0.579		1646.0	1656.0			1641.5	1650.0	
0.775			1656.4			1643.0	1650.8	
1.000				1675.8				1674.6

Table 8 shows the $\tilde{\nu}$(C=O) wavenumbers for *P*, *MP*, *IPP*, and *CHP* in 2-butoxyethanol/D_2O mixtures; the corresponding $\tilde{\nu}$(C=O) *vs.* *x*(BuOEtOH) dependence in the case of *IPP* is graphically presented in Fig. 10. Similarly to the case of the methanol/D_2O mixtures, only the absorption bands belonging to the free monomeric molecuels (*FM*) can be clearly recognized. The $\tilde{\nu}$(C=O) wavenumbers connected with the hydrogen bonded species (*BM*) exhibit a coherent dependence upon the mole fraction of 2-butoxyethanol. There is, however, a clear difference between the BuOEtOH/D_2O and MeOH/D_2O mixtures. In the case of BuOEtOH/D_2O, the $\tilde{\nu}$(C=O) *vs.* *x*(BeOEtOH) dependencies exhibit an extremely

Table 6. Statistical parameters of the linear correlations between the $\tilde{\nu}$(C=O) wavenumbers of *AM* species formed by 1-substituted 2-pyrrolidinones and the mole fraction of acetonitrile in binary mixtures with D_2O

Compound	n^a	ϱ^b	q^c	r^d	s^e
P	6	4.87±0.49	1649.7	0.980	0.15
MP	8	21.19±2.28	1644.7	0.967	1.12
IPP	7	23.23±1.71	1633.3	0.987	0.74
CHP	9	17.39±1.52	1631.0	0.974	1.06

[a] Number of points used in the correlation; [b] slope of the $\tilde{\nu}$(C=O) *vs.* x(MeCN) plots; [c] intercept; [d] correlation coefficient; [e] standard deviation

steep slope in the small region of mole fractions close to zero. This provides evidence that the water-rich mixtures of BuOEtOH ($0 \leqslant x$(BuOEtOH)$\leqslant 0.1$) contain in all cases a high proportion of apolar domains formed from 2-butoxyethanol molecules. This is in accordance with the known existence of microheterogenities in BuOEtOH/D_2O mixtures before switching into a more homogenous mixture of two polar liquids [1, 2].

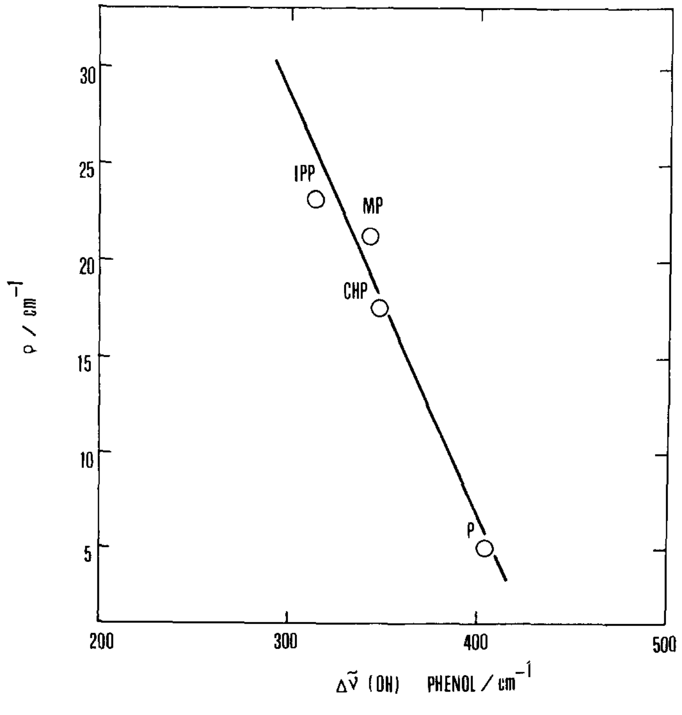


Fig. 8. Correlation between the slopes ϱ of $\tilde{\nu}$(C=O) *vs.* x(MeCN) and the relative hydrogen bond basicities for 1-substituted 2-pyrrolidinones

Table 7. Wavenumbers $\tilde{\nu}(C{=}O)$ characterizing the carbonyl stretching mode of *P*, *MP*, *IPP*, and *CHP* as a function of the mole fraction of MeOH in MeOH/D_2O mixtures

	$\tilde{\nu}(C{=}O)$ (cm^{-1})							
x(MeOH)	*P*		*MP*		*IPP*		*CHP*	
	BM	*FM*	*BM*	*FM*	*BM*	*FM*	*BM*	*FM*
0.000	1645.0		1641.8		1629.2		1621.8	
0.047	1646.0		1643.0		1631.0		1628.8	
0.100	1650.4		1645.2		1633.2		1631.8	
0.161	1651.4		1645.6		1635.1		1632.0	
0.229	1653.5		1647.8		1636.0		1634.3	
0.308	1655.0		1648.8		1637.6		1635.5	
0.401	1657.1		1651.0		1638.0		1637.7	
0.510	1660.0		1651.2		1641.4		1638.0	
0.641	1664.1		1651.4		1642.6		1639.0	
0.800	1667.0		1651.2		1644.0		1639.8	
1.000		1683.5	1653.6	1669.6	1644.8	1662.2	1640.0	1660.0

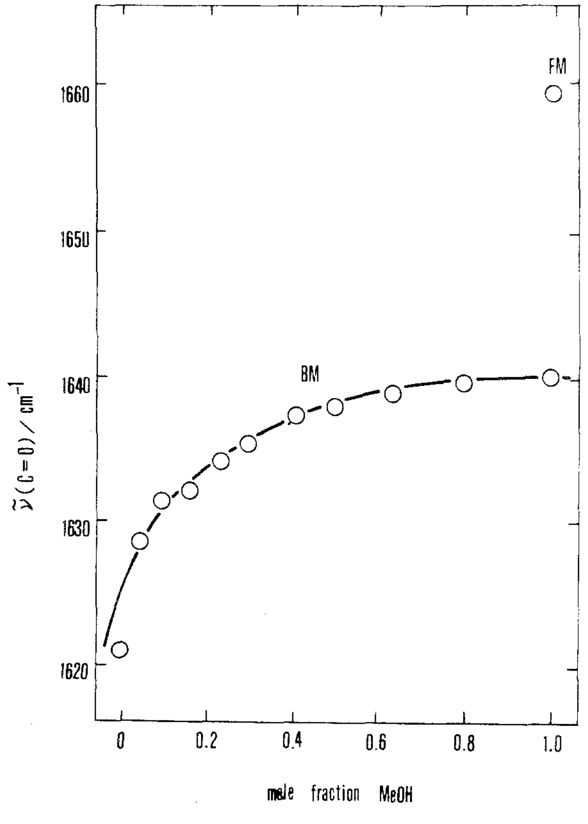


Fig. 9. Dependence of $\tilde{\nu}(C{=}O)$ on the mole fraction of methanol in mixtures of methanol and D_2O for 1-cyclohexyl-2-pyrrolidinone

Table 8. Wavenumbers $\tilde{\nu}(C{=}O)$ characterizing the carbonyl stretching mode of *P*, *MP*, *IPP*, and *CHP* as a function of the mole fraction of BuOEtOH in BuOEtOH/D_2O mixtures

x(BuOEtOH)	$\tilde{\nu}(C{=}O)$ (cm^{-1})							
	P		*MP*		*IPP*		*CHP*	
	BM	*FM*	*BM*	*FM*	*BM*	*FM*	*BM*	*FM*
0.000	1645.0		1641.8		1629.2		1621.8	
0.015	1650.0		1644.0		1632.0		1632.8	
0.033	1650.5		1645.0		1635.1		1636.2	
0.056	1652.5		1644.2		1636.0		1638.0	
0.084	1654.0		1646.6		1639.0		1639.7	
0.121	1655.5		1648.0		1640.7		1640.3	
0.172	1656.2		1649.7		1641.8		1641.8	
0.244	1658.2		1650.8		1642.8		1643.8	
0.356	1662.0		1653.8		1644.0		1645.2	
0.544	1666.0		1655.8		1645.0		1645.5	
1.000		1684.0		1672.0		1663.4		1661.8

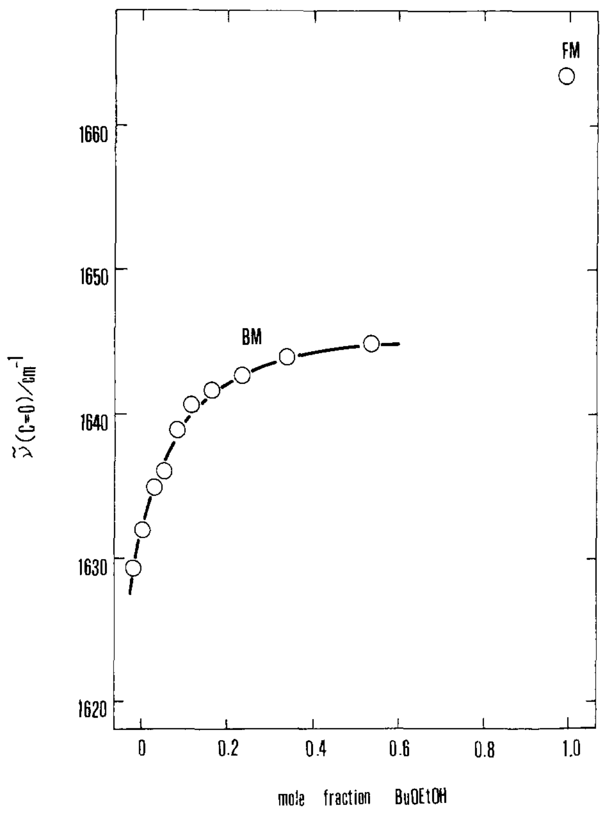


Fig. 10. Dependence of $\tilde{\nu}(C{=}O)$ on the mole fraction of 2-butoxyethanol in mixtures of 2-butoxyethanol and D_2O for 1-isopyropyl-2-pyrrolidinone

Experimental

Materials

2-Pyrrolidinone (*P*) and 1-methyl-2-pyrrolidinone (*MP*) were purchased from Jansen Chimica, 1-isopropyl-1-pyrrolidinone (*IPP*) and 1-(2-hydroxyethyl)-2-pyrrolidinone (*HEP*) from GAF Corp. Their purities were confirmed by gas chromatography. The refractive indexes of above substances corresponded with literature values [6, 7].

2-Oxobenzothiazole (*OBT*) was synthesized according to Ref. [8] and its purity was checked by m.p., elemental analysis, and ^{1}H NMR spectroscopy. 3-Octyl-2-oxobenzothiazole (*OOBT*) was prepared according to a general procedure [9]. The product was purified by column chromatography over silica gel with $CHCl_3$ as the eluent. The fraction with $R_f = 0.54$ was distilled at 170°C and 0.05 mm Hg. A colourless liquid was obtained. $R_f = 0.09$; $n_D^{20} = 1.5520$; $C_{15}H_{19}NOS$ (261.39); calculated: 68.44 C, 7.98 H, 5.32 N; found: 67.94 C, 8.25 H, 5.11 N. Structure and purity of the compound were confirmed by ^{1}H NMR spectroscopy.

Deuteriotrichloromethane, *n*-hexane, tetrachloromethane, deuteriumoxide (99.8 atom %), acetonitrile, methanol, and 2-butoxyethanol were spectroscopically or analytically pure (Uvasol, Merck). The organic liquids were dried over molecular sieves prior to use. Phenol, used for determination or relative hydrogen-bond basicities was of analytical purity and was freshly sublimed prior to application. Solutions were prepared by volume using Exmire microsyringes.

Spectroscopy

Infrared spectra were recorded at room temperature using Perkin-Elmer 841 and Zeis Specord M 80 spectrophotometers. For the measurement of $\tilde{\nu}$(C=O) wavenumbers in $C_6H_{14}/CDCl_3$ mixtures, NaCl cells with 0.5 mm path lengths were used and the concentrations of solutes in the mixtures were between 10^{-3} and $3{\cdot}10^{-3}$ mol·dm^{-3}. The $\tilde{\nu}$(C=O) absorption bands of 2-pyrrolidinone, 1-(2-hydroxyethyl)-2-pyrrolidinone, and 2-oxobenzothiazole were examined in *n*-hexane in the range of concentrations of 10^{-1}–10^{-4} mol·dm^{-3} using NaCl cells of 0.1, 0.4, 1.0, and 2.6 mm thickness. The relative basicities of carbonyl compounds interacting with phenol were determined in tetrachloromethane using NaCl cells of 1 cm thickness according to expermental conditions described earlier [10]. For aqueous mixtures, CaF_2 cells having 0.02 mm path lengths were used and the concentrations of solutes in the mixtures were 3.10^{-2}–$6{\cdot}10^{-2}$ mol·dm^{-3}. It has been demonstrated that it is not necessary to perform the infrared spectral measurements under a nitrogen atmosphere [1]. The maxima in absorption bands corresponding to $\tilde{\nu}$(C=O) were measured within ± 0.5 cm^{-1} and those corresponding to ν(O–H) were determined with an accuracy of ± 2 cm^{-1}.

The ^{1}H NMR spectra were measured on a Tesla BS 487 A (80 MHz) spectrometer in deuteriotrichloromethane solutions using tetramethylsilane as an internal standard.

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