

INFRARED STUDY ON THE INFLUENCE OF STERIC EFFECTS ON
THE HYDROGEN BOND IN SOME ALCOHOLS

BY R. KONOPKA, B. PĘDZISZ AND M. JUREWICZ

Institute of Physics, Silesian University, Katowice*

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Infrared spectroscopy was applied in investigations on the influence of steric effects on the hydrogen bond in primary, secondary and tertiary butyl alcohols, amyl alcohol, hexyl alcohol and heptyl alcohols. Determinations were made of the vibrational frequencies of the hydroxyl group in the alcohol molecule ν_0 , the half-widths of the absorption bands of this group $\Delta\nu_{1/2}$, the maximum extinction coefficients ϵ_{\max} , and the integrated absorption intensities A , as a function of alcohol concentration in CCl_4 , C_6H_{14} and $\text{C}_4\text{H}_8\text{O}_2$. The obtained results are arranged in tables. A discussion of results of measurements is given.

1. Introduction

The interaction of molecules *via* a hydrogen bond appears in an enormous number of organic and inorganic compounds. Hydrogen bond properties depend on, apart from the mode of interaction of the proton with groups of the same or other molecules, to a large extent on the geometry of the molecules [1, 2].

The aim of this work was to acquire information about the influence of steric effects on the hydrogen bond in some alcohols. The object of research was the valence vibration of the hydroxyl group (3000 to 3700 cm^{-1}) of butyl (primary, secondary and tertiary), amyl, hexyl and heptyl alcohols in active and inactive solvents.

The measurements were performed on a double-beam UR-20 spectrophotometer of Zeiss-Jena manufacture, employing an LiF prism. The temperature of the samples was 35°C . In the measurements use was made of NaCl trays whose thicknesses (1.02 , 0.25 and 0.03 mm) were checked by an interference technique [3].

The solvents used were carbon tetrachloride, hexane and dioxane. The region of valence vibrations of the hydroxyl group was measured in solutions of concentrations of 2 , 1 , 0.5 , 0.2 , 0.1 and 0.05 mol/liter . The substances used in this work were carefully purified, and the purity grade was established by recording the infrared absorption spectra of these substances in the range from 400 cm^{-1} to 4000 cm^{-1} . The densities of the solutions deter-

* Address: Instytut Fizyki, Uniwersytet Śląski, Katowice, Bankowa 12, Poland.

mined with a pycnometer enabled us to recalculate the concentration c (in mol/liter) into molar fractions $f = \frac{n_2}{n_1 + n_2}$, where n_1 and n_2 are the numbers of molecules of the solvent and alcohol in the solution.

Determined in this work are the frequencies of the absorption bands ν_0 of the alcohol hydroxyl group, the maximum extinction coefficients at ν_0 , where

$$\epsilon_{\max} = \frac{1}{cl} \ln \left(\frac{I_0}{I} \right)_{\nu_0}$$

TABLE I

Primary butyl alcohol

Solvent	c mol liter	f	polymer band			monomer band			
			ν_0 cm ⁻¹	$\Delta\nu_{1/2}$ cm ⁻¹	ϵ_{\max} liter mol · mm	ν_0 cm ⁻¹	$\Delta\nu_{1/2}$ cm ⁻¹	ϵ_{\max} liter mol · mm	$\frac{A'}{cl} \cdot 10^4$
									liter mol · cm ²
carbon tetrachloride	2.0	0.191	3344	230	16.97	3636	25	0.95	—
	1.0	0.097	3346	223	14.36	3638	28	1.51	—
	0.5	0.046	3352	260	11.27	3638	29	4.97	1.60
	0.2	0.019	3356	—	4.88	3638	29	7.14	2.37
	0.1	0.009	3380	—	—	3639	28	10.13	2.45
	0.05	0.005	—	—	—	3639	26	10.42	3.02
hexane	2.0	0.244	3343	224	20.38	3642	—	—	—
	1.0	0.127	3348	204	18.38	3642	—	—	—
	0.5	0.065	3350	208	17.99	3646	31	2.12	0.74
	0.2	0.026	3350	197	11.75	3648	22	3.12	1.24
	0.1	0.013	3359	203	5.88	3648	25	5.22	1.78
	0.05	0.007	—	—	—	3650	25	6.36	2.35
dioxane	2.0	0.173	3500	127	22.74				
	1.0	0.086	3500	100	25.01				
	0.5	0.043	3505	100	25.98				
	0.2	0.017	3507	88	31.10				
	0.1	0.009	3519	102	23.73				

c is the concentration of the solution in mol/liter, l is the tray thickness, and I_0 and I are the respective intensities of the incident radiation and after the beam as passed through the examined sample. Moreover, the half-widths of the bands $\Delta\nu_{1/2}$ and the integrated absorption intensities defined as

$$A = \frac{1}{cl} \int \ln \left(\frac{I_0}{I} \right)_{\nu} d\nu$$

were determined. For determining the latter use was made, in accordance with the 3rd method of Ramsey [4], of the areas under the absorption A' curve found directly from the recorded spectra. The values of the areas divided by the product of solution concentration and tray thickness are given in the last column of Tables I to VI.

TABLE II

Secondary butyl alcohol

Solvent	c mol liter	f	polymer band			monomer band			
			ν_0	$\Delta\nu_{\frac{1}{2}}$	ϵ_{\max}	ν_0	$\Delta\nu_{\frac{1}{2}}$	ϵ_{\max}	$\frac{A'}{cl} \cdot 10^4$
			cm ⁻¹	cm ⁻¹	liter mol · mm	cm ⁻¹	cm ⁻¹	liter mol · mm	liter mol · cm ²
carbon tetrachloride	2.0	0.193	3364	197	17.23	3629	—	1.96	—
	1.0	0.097	3364	196	13.55	3628	—	3.41	—
	0.5	0.048	3365	—	9.78	3628	32	5.55	1.96
	0.2	0.019	3380	—	4.19	3630	30	7.12	2.59
	0.1	0.009	—	—	—	3628	26	9.26	2.86
	0.05	0.005	—	—	—	3630	27	9.32	3.05
hexane	2.0	0.244	3357	179	20.07	3635	—	—	—
	1.0	0.127	3361	168	17.34	3635	—	—	—
	0.5	0.069	3360	199	15.79	3638	29	2.73	0.97
	0.2	0.026	3368	—	7.61	3638	28	4.18	1.16
	0.1	0.013	3380	—	2.89	3640	28	5.38	1.86
	0.05	0.006	—	—	—	3640	28	6.38	2.16
dioxane	2.0	0.173	3495	115	21.68				
	1.0	0.086	3500	97	23.85				
	0.5	0.043	3503	90	24.91				
	0.2	0.017	3506	88	27.28				
	0.1	0.009	3520	97	22.04				

2. Results

All determined values are gathered in the Tables I to VI.

Spectra. Pure alcohols exhibit a broad band in the vicinity of 3350 cm⁻¹ ascribed to polymers. Many things affect the extreme breadth of the polymer band, but the decisive factor is the appearance of various mers in the system. With dilution of the alcohols with inactive solvents, the 3350 cm⁻¹ band gradually diminishes to the advantage of the narrow band near 3620 cm⁻¹, ascribed to monomers, and an emerging broader band at about 3510 cm⁻¹, ascribed to dimers [2, 10]. In the described measurements a hump on the slope of the diffuse polymer band at about 3580 cm⁻¹ was also observed. The invariance of this band's frequency with changing concentration and solvent would suggest an assignment of this band to the cyclic structure. The shapes of the bands observed in the spectra of the

TABLE III

Tertiary butyl alcohol

Solvent	c $\frac{\text{mol}}{\text{liter}}$	f	polymer band			monomer band			
			ν_0	$\Delta\nu_{1/2}$	ϵ_{max}	ν_0	$\Delta\nu_{1/2}$	ϵ_{max}	$\frac{A'}{cl} \cdot 10^4$
			cm^{-1}	cm^{-1}	$\frac{\text{liter}}{\text{mol} \cdot \text{mm}}$	cm^{-1}	cm^{-1}	$\frac{\text{liter}}{\text{mol} \cdot \text{mm}}$	$\frac{\text{liter}}{\text{mol} \cdot \text{cm}^2}$
carbon tetrachloride	2.0	0.194	3380	210	15.98	3620	—	—	—
	1.0	0.096	3384	218	12.62	3621	—	3.08	—
	0.5	0.046	3384	241	8.92	3623	31	6.89	1.69
	0.2	0.019	3400	—	4.19	3623	30	9.12	2.02
	0.1	0.010	—	—	—	3622	27	11.09	2.06
	0.05	0.005	—	—	—	3625	27	11.91	2.60
hexane	2.0	0.246	3365	197	20.13	3625	—	—	—
	1.0	0.128	3368	188	18.88	3626	—	—	—
	0.5	0.065	3367	191	15.65	3625	21	3.42	0.85
	0.2	0.026	3367	189	9.57	3625	21	5.18	1.66
	0.1	0.013	3377	—	5.76	3627	20	5.76	1.34
	0.05	0.006	—	—	—	3628	20	6.23	1.70
dioxane	2.0	0.173	3491	107	23.10				
	1.0	0.086	3497	90	25.01				
	0.5	0.043	3498	85	25.98				
	0.2	0.017	3507	90	35.83				
	0.1	0.008	3512	95	22.04				

TABLE IV

Primary amyl alcohol

Solvent	c $\frac{\text{mol}}{\text{liter}}$	f	polymer band			monomer band			
			ν_0	$\Delta\nu_{1/2}$	ϵ_{max}	ν_0	$\Delta\nu_{1/2}$	ϵ_{max}	$\frac{A'}{cl} \cdot 10^4$
			cm^{-1}	cm^{-1}	$\frac{\text{liter}}{\text{mol} \cdot \text{mm}}$	cm^{-1}	cm^{-1}	$\frac{\text{liter}}{\text{mol} \cdot \text{mm}}$	$\frac{\text{liter}}{\text{mol} \cdot \text{cm}^2}$
carbon tetrachloride	2.0	0.198	3340	232	18.32	3635	36	1.55	—
	1.0	0.099	3345	214	15.81	3636	30	2.63	—
	0.5	0.048	3352	257	12.58	3637	33	5.34	2.25
	0.2	0.019	3360	—	5.90	3637	30	8.41	3.09
	0.1	0.010	—	—	—	3639	29	10.73	3.39
	0.05	0.005	—	—	—	3640	28	11.89	3.79
hexane	2.0	0.251	3341	232	20.01	3647	—	0.71	—
	1.0	0.129	3348	214	18.64	3650	—	0.92	—
	0.5	0.065	3351	215	17.22	3650	34	2.12	0.91
	0.2	0.026	3350	202	12.21	3649	24	3.93	1.36
	0.1	0.013	3357	217	6.40	3648	28	5.95	2.06
	0.05	0.006	—	—	—	3650	27	6.47	2.31

TABLE V

Primary hexyl alcohol

Solvent	c $\frac{\text{mol}}{\text{liter}}$	f	polymer band			monomer band			
			ν_0	$\Delta\nu_{1/2}$	ϵ_{max}	ν_0	$\Delta\nu_{1/2}$	ϵ_{max}	$\frac{A'}{cl} \cdot 10^4$
			cm^{-1}	cm^{-1}	$\frac{\text{liter}}{\text{mol} \cdot \text{mm}}$	cm^{-1}	cm^{-1}	$\frac{\text{liter}}{\text{mol} \cdot \text{mm}}$	$\frac{\text{liter}}{\text{mol} \cdot \text{cm}^2}$
carbon tetrachloride	2.0	0.205	3339	230	18.82	3634	41	1.71	—
	1.0	0.100	3341	234	15.81	3635	33	2.62	—
	0.5	0.049	3348	240	13.09	3635	30	5.81	2.00
	0.2	0.020	3350	—	5.61	3637	30	8.45	2.74
	0.1	0.010	—	—	—	3638	26	10.75	3.16
	0.05	0.005	—	—	—	3637	28	11.88	3.40
hexane	2.0	0.259	3341	222	20.11	3642	—	0.59	—
	1.0	0.131	3345	206	19.58	3644	—	0.55	—
	0.5	0.065	3347	209	17.87	3647	30	2.32	0.89
	0.2	0.026	3349	196	13.02	3648	22	3.81	1.40
	0.1	0.013	3356	214	6.20	3649	23	5.82	1.94
	0.05	0.007	—	—	—	3650	26	6.99	2.48

TABLE VI

Primary heptyl alcohol

Solvent	c $\frac{\text{mol}}{\text{liter}}$	f	polymer band			monomer band			
			ν_0	$\Delta\nu_{1/2}$	ϵ_{max}	ν_0	$\Delta\nu_{1/2}$	ϵ_{max}	$\frac{A'}{cl} \cdot 10^4$
			cm^{-1}	cm^{-1}	$\frac{\text{liter}}{\text{mol} \cdot \text{mm}}$	cm^{-1}	cm^{-1}	$\frac{\text{liter}}{\text{mol} \cdot \text{mm}}$	$\frac{\text{liter}}{\text{mol} \cdot \text{cm}^2}$
carbon tetrachloride	2.0	0.213	3340	246	18.82	3638	41	1.40	—
	1.0	0.102	3345	254	15.51	3637	40	2.53	—
	0.5	0.050	3350	265	17.05	3638	38	5.44	2.16
	0.2	0.019	3354	—	6.53	3636	34	8.81	3.18
	0.1	0.010	—	—	—	3638	31	10.70	3.12
	0.05	0.005	—	—	—	3639	27	11.81	3.71
hexane	2.0	0.266	3340	220	20.71	3642	—	—	—
	1.0	0.133	3342	208	19.30	3645	—	—	—
	0.5	0.066	3344	207	19.42	3647	36	2.42	1.12
	0.2	0.026	3348	206	11.74	3648	25	4.23	1.25
	0.1	0.013	3355	204	7.25	3648	28	6.11	2.23
	0.05	0.006	—	—	—	3649	25	6.99	2.24

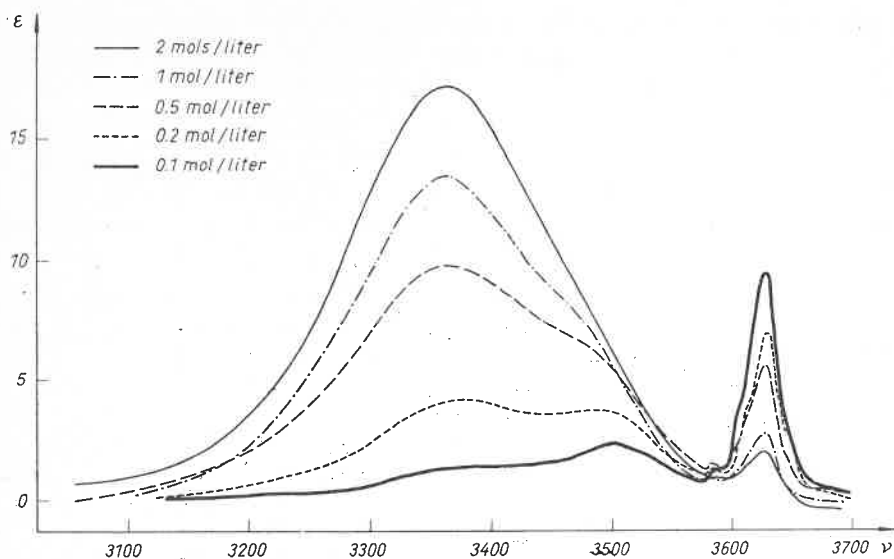


Fig. 1. Infrared absorption spectrum of secondary butyl alcohol *versus* concentration in CCl_4

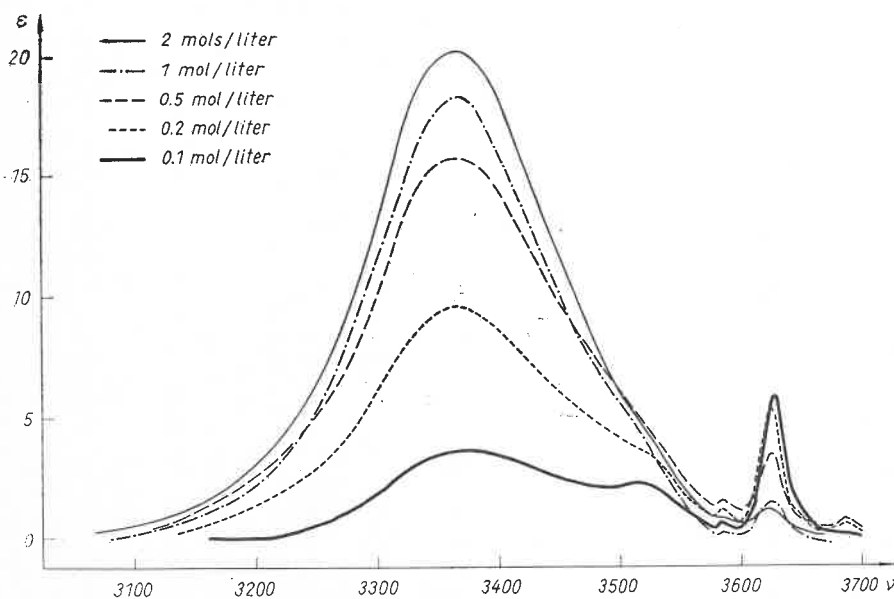


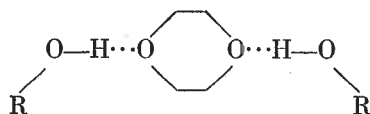
Fig. 2. Infrared absorption spectrum of secondary butyl alcohol *versus* concentration in C_6H_{14}

examined solutions are various. A simple symmetric contour is inherent only of the polymer band at high concentrations. On the other hand, the monomer band displays no symmetry. The deformations of this band may appear because of the existence of rotational isomers in the solution [11].

Such changes in the shapes of the bands and their frequencies with a change of con-

centration in inactive solvents are characteristic of all examined alcohols, what is given by way of illustration by the spectra of secondary butyl alcohol solutions in CCl_4 and C_6H_{14} , shown in Figs 1 and 2.

There is only one band at about 3500 cm^{-1} in the spectrum of butyl alcohol solutions in dioxane, and it is considerably different than the band for solutions in inactive solvents. Dioxane, being an active solvent, interacts with the alcohol molecules through the oxygen atom, forming complexes with them. The spectra imply that the acceptor properties of the dioxane oxygen are comparable with those of the oxygen atom of an alcohol molecule. At the highest examined concentration there are only traces of self-association which show up as a spread of the band towards the lower frequencies to the region (about 3300 cm^{-1}) where the polymer band should be appearing. The observed 3500 cm^{-1} band has been assigned to the alcohol-dioxane complexes of the type 2:1



what is compatible with the results of other investigations [5]. At the same time, at the lowest examined concentrations there is observed a hump on the band of the complexes on the high-frequency side. This hump may be ascribed to complexes of the 1:1 type,

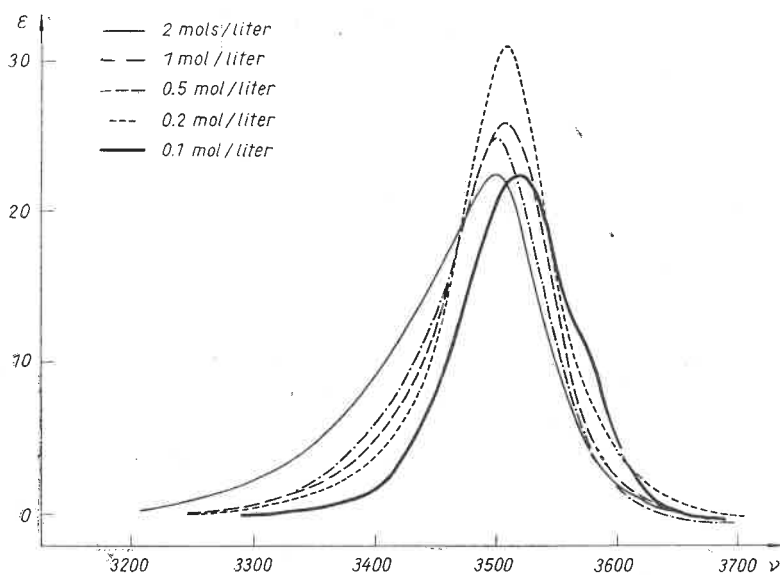


Fig. 3. Infrared absorption spectrum of secondary butyl alcohol versus concentration in $\text{C}_4\text{H}_8\text{O}_2$

whose emergence should be expected owing to the disintegration of 2:1 complexes at high dilution. The higher frequency of vibration of the hydroxyl group for these complexes is the result of a decreased reduced mass. The supposed competitive formation of 2:1 and 1:1 type complexes at low concentrations also stems from dielectric research [5]. In order

to illustrate the described changes, we present the spectra of secondary butyl alcohol in dioxane solution (Fig. 3).

Frequencies. The curves in Figs 4 and 5 illustrate the dependence of the frequency ν_0 of the bands of polymers and monomers upon concentration. As is seen from these curves, the frequency ν_0 of the polymer band shifts toward the monomer frequency when dilution is enhanced. This is in accordance with expectations, for the role the used inactive solvents is to disrupt larger aggregates into smaller ones; hence, increased solvent content shifts the equilibrium toward the lower mers, which feature higher frequencies of OH group valence vibrations.

The band of the monomer does not exhibit such large changes in frequency when the solution concentration is altered. The obtained linear dependence of small slope may be explained by the dielectric influence of the solvent. The rise in frequency with decrease

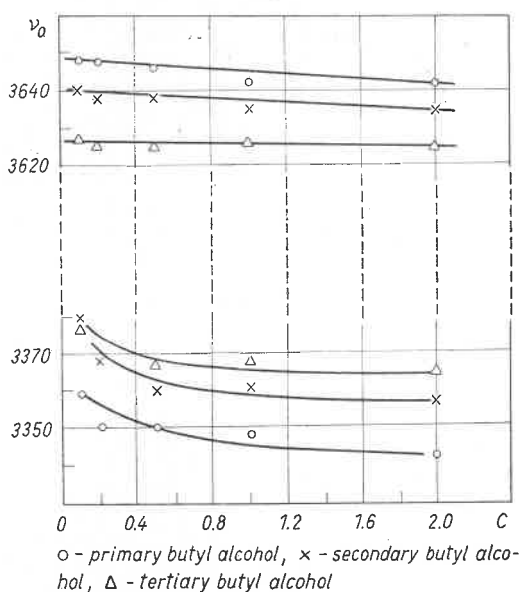


Fig. 4. Dependence of frequency ν_0 of polymer band (3350 cm^{-1} region) and monomer band (3600 cm^{-1} region) upon alcohol concentration in C_6H_{14}

in concentration is in accord with the theory of the dielectric effect [6]. Also in conformity with this theory, the frequency of the monomer in C_6H_{14} is higher than in CCl_4 $\left(\frac{\epsilon-1}{2\epsilon+1}\right)$ is 0.3024 and 0.2232 for C_6H_{14} and CCl_4 , respectively). In the carbon tetrachloride and hexane alike the monomer frequency decreases in the primary, secondary and tertiary butyl alcohol series. This is a result of the change of the environment of the hydroxyl group of the $\text{C}_4\text{H}_9\text{OH}$ molecule. The gradual building over of the OH group brings about an increase in its interaction with methyl groups and thereby an increase in reduced mass. Another consequence of this cause is the observed rise in frequency of the polymer with increasing order of the

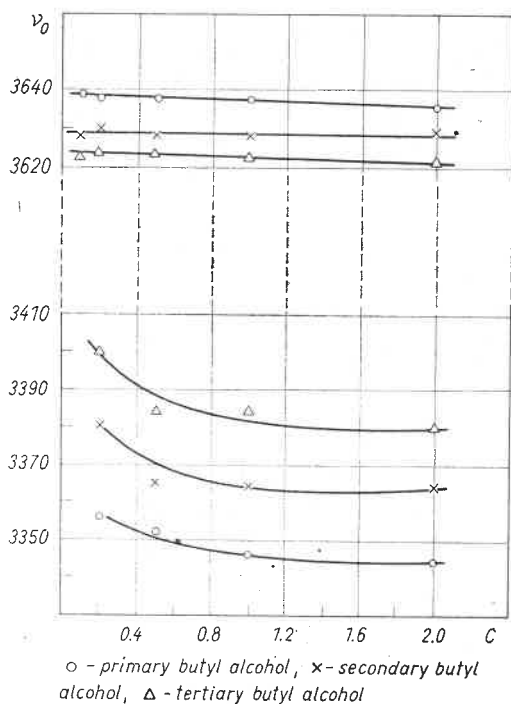


Fig. 5. Dependence of frequency ν_0 of polymer band (3350 cm^{-1} region) and monomer band (3600 cm^{-1} region) upon alcohol concentration in CCl_4

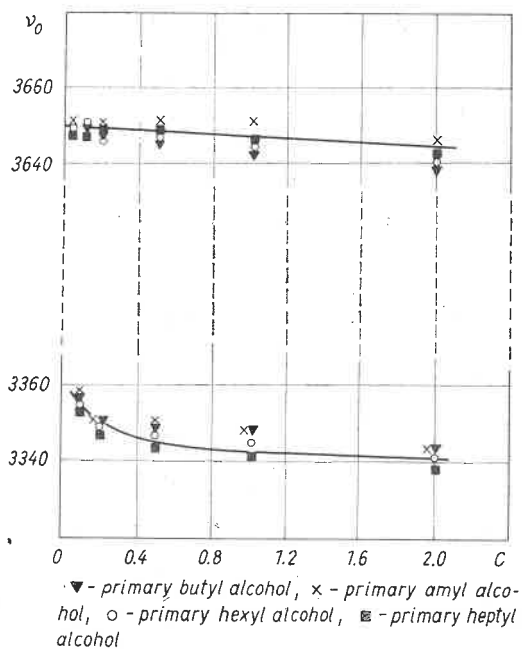


Fig. 6. Dependence of frequency ν_0 of polymer band (3350 cm^{-1} region) and monomer band (3600 cm^{-1} region) upon alcohol concentration in C_6H_{14}

alcohol. The difference between the frequency ν_0 of the monomer and polymer is, among other things, a measure of the binding energy of the hydrogen, and on this basis it is possible to state that the hydrogen bond in tertiary butyl alcohol is weaker than in the secondary and primary alcohols. This dependence of hydrogen bond energy upon order of the alcohol is justified, for because of the molecule geometry the proton of the OH group of the primary alcohol is exposed the most and thereby has the highest chance of forming a hydrogen bond. This conclusion is confirmed by dielectric investigations of butyl alcohols [7].

Figure 6 shows the dependence of the frequency of the polymer and monomer bands upon concentration as a function of length of alcohol molecule chain. It is seen that contrary to the order of the alcohol the chain length does not affect, within error limits, the change of the vibrational frequency of the alcohol's hydroxyl group.

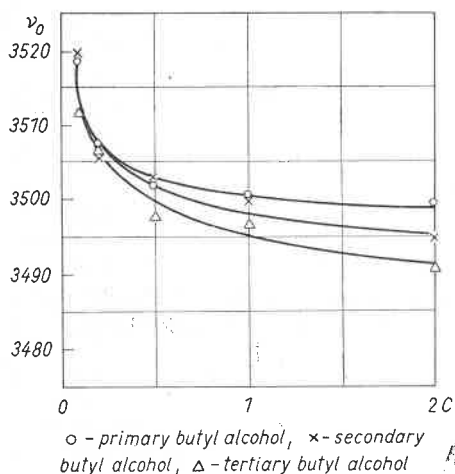


Fig. 7. Dependence of frequency ν_0 of band of complexes upon alcohol concentration in $C_4H_8O_2$

When an active solvent (dioxane) is used, the dependence of frequency ν_0 upon alcohol concentration in the dioxane is like that of the band of the alcohol polymer in inactive solvents (Fig. 7).

Maximum extinction coefficients. More information on the solutions is provided by the investigated dependences of the maximum extinction coefficients upon concentration. The changes of ϵ_{\max} of the bands of polymers in inactive solvents for different alcohols, gathered in Tables I to VI, are hard to interpret because of the fact that the range within which these changes take place (about 20 per cent of the value of ϵ) is comparable with the range of error made when determining the maximum extinction coefficients of polymer bands (about 15 per cent). The dependence of ϵ_{\max} of the polymer band upon concentration of alcohol in inactive solvent changes in a way that is expected, namely, increased dilution causes a drop in the maximum extinction coefficient, what is due to a decrease in the number of polymers in the solution.

The $\epsilon_{\max}(c)$ dependence for the monomer band is also as expected. A drop in concentration goes together with an increase in the number of monomers and an increase of the maximum

extinction coefficient. The increase in ϵ_{\max} with rising order of the alcohols is associated with the decreasing energy of the hydrogen bond in the same succession; this is why the number of monomers in tertiary butyl alcohol is greater than in primary and secondary alcohols at the same concentration.

Within error limits, the value of the maximum extinction coefficient is independent of the length of the alcohol molecule chain (see Tables I and VI).

Butyl alcohols in dioxane exhibit a characteristic shape of maximum extinction coefficient as a function of concentration (Fig. 8). Initially the maximum extinction coefficient grows with decreasing concentration. At the same time, the band becomes narrowed on the low-frequency side. Whence the conclusion may be arrived at that dilution to a certain concentration goes together with the formation of more and more 2:1 type complexes because the

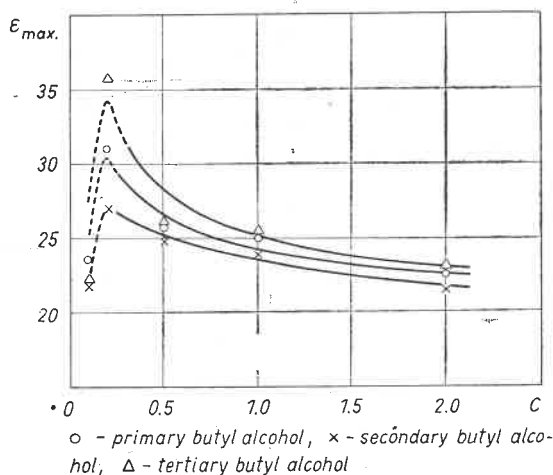


Fig. 8. Dependence of maximum extinction coefficient of band of complexes upon alcohol concentration in $C_4H_8O_2$

dioxane binds alcohol molecules participating previously in the self-association. Beginning with a definite concentration (0.2 mol/liter), ϵ_{\max} drops quite strongly for alcohol of all orders. This drop occurs together with the appearance of the hump on the high-frequency side, hence, it may be explained by the appearance of the new band. This also speaks for the appearance of 1:1 type complexes arising from the disintegration of 2:1 complexes. The changes in the run of the maximum extinction coefficient with alcohol order do not exhibit any regularities and lie within the limits of error of ϵ_{\max} determinations.

Integrated absorption intensities. Integrated absorption intensities were determined for the bands of monomers in inactive solvents. The obtained A -values (gathered in Table VII) constitute the characteristic of the monomer bands in CCl_4 and C_6H_{14} , for these are values extrapolated to zero alcohol concentration. Changes in integrated absorption intensity with the order and molecule chain length of the alcohol cannot be discussed, in principle, because they occur within the error range, although larger changes in carbon tetrachloride rather than in hexane would be justifiable. Interpretation of the $\epsilon_{\max}(c)$ depend-

TABLE VII

Values of integrated absorption intensities A of examined alcohols determined by Ramsey's 3rd method
(data for monomer band)

Alcohol	$A \times 10^4$ (liter \times mol $^{-1} \times$ cm $^{-2}$) solvent	
	CCl $_4$	C $_6$ H $_{14}$
primary butyl	3.4	2.3
secondary butyl	3.2	2.2
tertiary butyl	2.6	2.1
primary amyl	4.1	3.1
primary hexyl	3.8	2.9
primary heptyl	3.9	2.7

ence and results of other research [8] imply that a specific interaction occurs in CCl $_4$ solutions, whereas C $_6$ H $_{14}$ is a more neutral solvent. In such case a change in molecule geometry has a more pronounced mark on the properties of the solutions in carbon tetrachloride than in hexane. The stronger specific interactions may also be responsible for the larger integrated

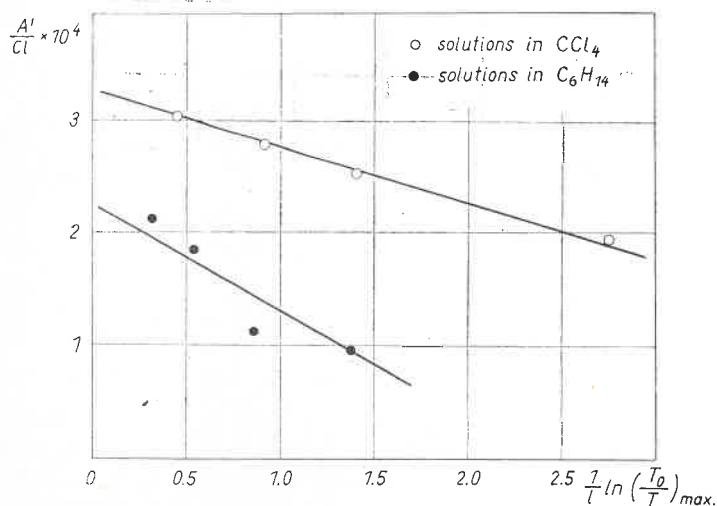


Fig. 9. Illustration of the application of Ramsey's 3rd method for determining integrated absorption intensities A of tertiary butyl alcohol solutions

absorption intensities for solutions in CCl $_4$, for an increase in the participation of specific interactions leads to an increase in the A -values [9].

Half-widths. Analysis of the dependences associated with the changes in the half-widths of the monomer bands did not lead to any results, what is caused by, among other things the considerable error made when determining $\Delta\nu_{1/2}$. The half-widths of the polymer bands were not measured. In the examined range of concentrations this band is "broken up"

for almost all solutions. Hence, it is impossible to determine $\Delta\nu_{1/2}$ without performing separation.

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REFERENCES

- [1] G. C. Pimentel, A. L. McClellan, *The Hydrogen Bond*, San Francisco, London 1960.
- [2] L. J. Bellamy, *Advances in Infrared Group Frequencies*, Methuen 1968.
- [3] W. Brugel, *Einführung in die Ultrarotspektroskopie*, Steinkopff, Darmstadt 1962.
- [4] D. A. Ramsey, *J. Amer. Chem. Soc.*, **74**, 72 (1952).
- [5] J. Hurwic, W. Waclawek, *Z. Phys. Chem.*, **235**, 3, 4 240 (1967).
- [6] E. Bauer, M. Magat, *J. Phys. Radium*, **9**, 319 (1938).
- [7] I. Danielewicz-Ferchmin, *Bull. Acad. Polon. Sci. Ser. Sci. Math. Astron. Phys.*, **XIV**, 1 (1966).
- [8] A. V. Stuart, *J. Chem. Phys.*, **21**, 1115 (1953).
- [9] G. M. Barrow, *J. Phys. Chem.*, **59**, 1129 (1955).
- [10] C. R. Hammaker, *J. Phys. Chem.*, **72**, 1837 (1968).
- [11] F. Dalton, G. D. Meakins, J. H. Robinson, W. Zaharia, *J. Chem. Soc.*, **5**, 1566 (1962).