

diagrams. Thanks are also due to Dr. H. DERFLER for discussions and Miss C. WALLNER for typing the manuscript.

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Infrared Spectroscopy and Hydrogen Bonding: Complexing of γ -Butyrolactone with o-Cresol

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Investigations to study the effect of different solvents on the frequency, intensity, and band width of the carbonyl band of γ -butyrolactone were carried out on the basis of the mixed solvent techniques with carbon tetrachloride, being the inert solvent. The solvent used for such investigations is o-cresol. The results establish the existence of the 1 : 1 and 1 : 2 complexes at fairly low concentrations for the γ -butyrolactone-o-cresol system. The formation constants for these complexes were determined and used to resolve the observed carbonyl bands into the spectra of individual complexes. The observed large frequency shift for the 1 : 2 complex favours a structure in which two molecules of o-cresol are directly bonded to the carbonyl group. The free energies of formation at 25 °C by using these formation constants show that the strength of the interaction increases in going from the 1 : 1 complex to the 1 : 2 complex of the same γ -butyrolactone-o-cresol system. These results have been discussed in relation to the frequency shift, intensity changes, and half width changes.

Introduction

Experimental and theoretical investigations of solvent shifts for the various characteristic infrared absorption bands have been extensively carried out by many investigators but with results of conflicting nature on the solvent induced frequency shift as well as the variation in intensity and band width. A few investigators¹⁻⁴ interpreted the frequency shifts on the basis of the bulk dielectric properties of the solvents, while BELLAMY and WILLIAMS⁵ did so on the basis of the specific (localized) solvent-solute interactions. Interpretations of the solvent induced frequency shifts were later given by CALDOW and THOMPSON⁶ by taking into account both these bulk dielectric effects and specific interaction effects.

A comprehensive review of the current theories of solvent shifts and their experimental verifications has recently been published by WILLIAMS⁷. HORÁK and his associates^{8,9} explained the conditions for the applicability of various theories of solvent shifts of characteristic bands based on the reaction field model, proposed a new process known as the collision complexes, and provided evidence for the existence of weak complexes of phenol with nonpolar solvents. On the basis of the mixed solvent techniques initiated by BELLAMY and HALLAM¹⁰, WHETSEL and KAGARISE^{11,12} calculated the individual spectra of 1:1 and 1:2 complexes by studying the different types of solute-solvent (weak as well as strong) interactions and concluded that the non-dipolar interactions such as the dispersion for-



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ces are also, in addition to the bulk dielectric effects and specific interaction effects, responsible for the solvent induced frequency shifts.

Strong or specific interactions result in the formation of more or less stable complexes of polar solutes with polar liquids. This kind of interaction is usually of the donor-acceptor type and has been the subject of numerous investigations¹³. Complexes of this type may possess a more or less well-defined geometry and the stoichiometric ratio of solvent to solute molecules in the complex is 1:1. A rather large interaction energy, more or less equivalent to the energy of donor-acceptor bond will be involved in the formation of such complexes. The width of the characteristic band in the spectrum of the complex is very broad and there will be a considerable low frequency shift from the value of the free group. Weak or nonspecific interactions between polar solutes and nonpolar or weakly polar liquids studied particularly by BELLAMY and WILLIAMS¹⁴ result in the formation of weak complexes of polar solutes with even solvents which are considered to be quite nonpolar. It is, on the basis of the mixed solvent techniques, aimed here to study the effects of *o*-cresol (a strong proton-donor) on the carbonyl band of γ -butyrolactone, to determine the formation constants, and to calculate the spectra of the individual complexes. From such data, it should be possible to accurately predict the position and nature of the spectra of different species present in the γ -butyrolactone-*o*-cresol system, and also to get a better idea about the most important qualitative characteristics of the bond formation, i. e., the energy change that is involved in the reaction.

Experimental Section

The measurements of the spectra were made in the carbonyl region of γ -butyrolactone and in the hydroxyl region of *o*-cresol with a Perkin-Elmer Model 521 Spectrophotometer. The atmospheric water vapour was removed from the spectrophotometer housing by flushing with dry nitrogen. In the high frequency region, the instrument was calibrated in the usual manner¹⁵. The frequencies reported here are expected to be accurate to better than 2 cm^{-1} for sharp bands, but the relative frequency shifts should be considerably better.

The sample of γ -butyrolactone was obtained from General Aniline and Film Corporation, New York and distilled under reduced pressure. Pure sample of *o*-cresol distilled under reduced pressure and at constant boiling point was used. Spectroquality carbon tetra-

chloride from Matheson Company, Inc., East Rutherford, New Jersey was directly used without purification. The mixed solvent technique was used with carbon tetrachloride, being the inert solvent, and careful consideration was given to intensity effects as well as the frequency shifts. The gain, slit program, attenuator, scanning time, suppression, and scale expansion were kept constant at 3.0, 10, 11, 0.16, 0, and IX, respectively, in recording the spectra. All the measurements were made on approximately 0.04 M solutions of γ -butyrolactone in a 0.2 mm path length cell equipped with NaCl windows.

Results and Discussion

In order to determine the formation constants, the methods developed by BROWN and KUBOTA¹⁶, and WHETSEL and KAGARISE¹¹ have been followed. Accordingly, for the γ -butyrolactone-*o*-cresol system in which the following equilibria



exist, the formation constants are given as

$K_{11} = [AB]/[A][B]$ and $K_{12} = [AB_2]/[AB][B]$, where A represents γ -butyrolactone and B represents *o*-cresol in the monomeric form. Here, the values of $[AB]$ and $[AB_2]$ are, in terms of concentrations and formation constant, expressed in the form $[AB] = p/(1 + 2K_{12}b)$ and $[AB_2] = (p - [AB])/2$, where p is the total concentration of *o*-cresol participating in the complex formation and b is the equilibrium concentration of *o*-cresol in the monomeric form.

Measurements in the hydroxyl region were made to determine the p and b values by the method of WIDOM, PHILIPPE, and HOBBS¹⁷. A calibration curve (Fig. 1) for the free O-H band near 3600

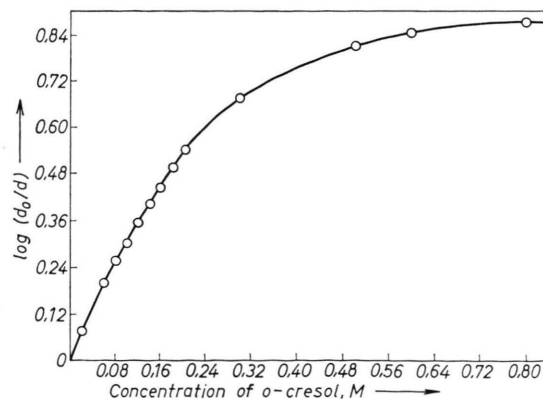


Fig. 1. Absorbance versus total concentration for the free O-H band of *o*-cresol in carbon tetrachloride.

cm^{-1} was prepared by plotting absorbance versus total concentration of *o*-cresol in carbon tetrachloride. Another curve (Fig. 2) was also prepared by plotting absorptivity versus concentration, from which the absorptivity of the free O—H band was determined by extrapolating the line to the zero concentration. The corresponding value (ϵ_m^0) was found to be $3.75/l$, where l is the thickness of the cell used (Fig. 2). Then, the values of b were de-

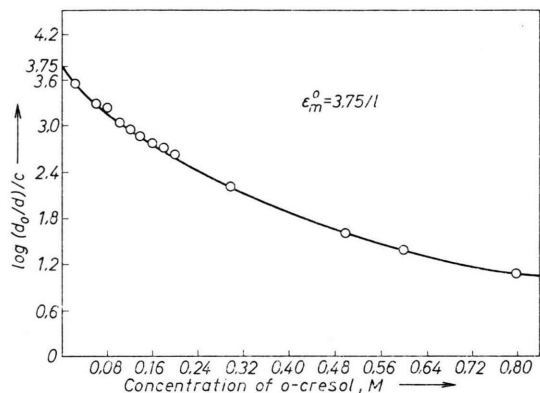


Fig. 2. Absorptivity versus total concentration for the free O—H band of *o*-cresol in carbon tetrachloride.

termined from the relation $b = \text{absorbance}/\epsilon_m^0$, where absorbance is of the O—H band (*o*-cresol monomer) of various concentrations in the γ -butyrolactone-*o*-cresol system in carbon tetrachloride. The concentrations corresponding to the absorbances of O—H band of *o*-cresol of different concentrations in the system were found from the absorbance-concentration calibration curve (Fig. 1). The total concentration of the free and self associated *o*-cresol at equilibrium was easily determined from the absorbance of the free O—H band and the calibration curve (Fig. 1). The difference between the value obtained and the total amount of *o*-cresol added was equal to p , the total amount of *o*-cresol complexed with γ -butyrolactone.

Different values of p and b were determined for a series of solutions in which the concentration (0.04 M) of γ -butyrolactone was constant and that of *o*-cresol varied up to 1.8 M. Using these values of p and b , and the assumed values of K_{12} , the values of $[AB]$ and $[AB_2]$ were determined from the equations given above. From the values of $[AB]$, and $[AB_2]$, and K_{12} , the values of $[B]$ were then easily calculated. The values of $[A]$ were then obtained by subtracting the sums of $[AB]$ and $[AB_2]$

from the initial concentration (0.04 M) of γ -butyrolactone. From the values of $[A]$, $[B]$, and $[AB]$, the values of K_{11} were easily obtained, and they were then plotted against the concentration of *o*-cresol added to the samples. This procedure was repeated with different assumed values of K_{12} to yield a series of lines with different slopes and intercepts. The slopes and intercepts of these lines were then plotted against the assumed values of K_{12} (Fig. 3). The value of K_{12} which gave a line of zero slope was chosen as the best value for this constant ($K_{12} = 50$ l/mole) and the intercept of this line must be the formation constant for the 1:1 complex ($K_{11} = 8$ l/mole) of the γ -butyrolactone-*o*-cresol system. This is the most reliable method of getting the formation constants.

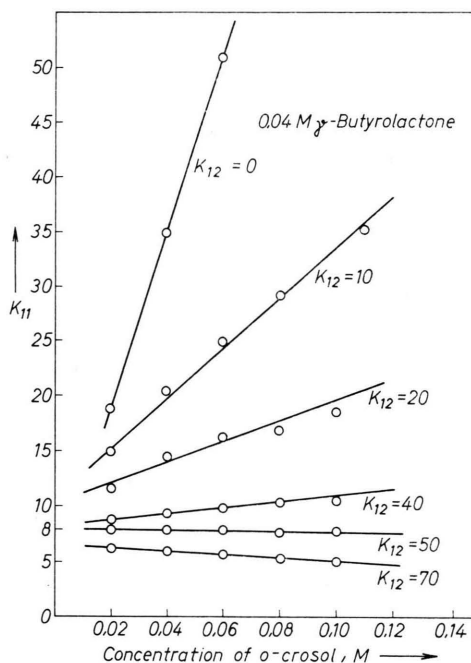


Fig. 3. Formation constants for the 1:1 and 1:2 complexes of γ -butyrolactone and *o*-cresol in carbon tetrachloride.

It is also possible to determine the formation constant for the 1:1 complex by the NASH method¹⁸. Accordingly, a curve Y against X was plotted (Fig. 4), where Y is equal to $1/b$, the reciprocal of the concentration of *o*-cresol monomer at equilibrium; and $X = 1/[1 - (A/A_0)]$, where A_0 and A are the absorbances of γ -butyrolactone at a given frequency in the absence and in the presence of *o*-cresol, respectively. The intercept of the plot of Y against X is the negative value of the formation constant for

the 1:1 complex. This value ($K_{11}=9$ l/mole) obtained here (Fig. 4) is in good agreement with the value ($K_{11}=8$ l/mole) obtained from the previous method (Fig. 3).

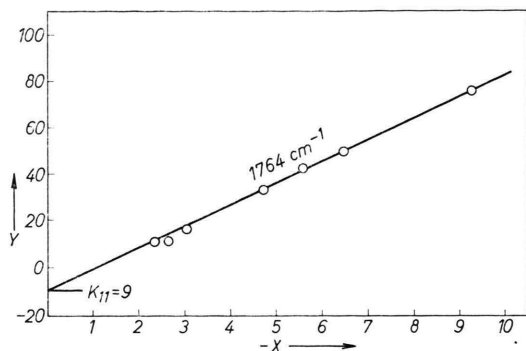


Fig. 4. Formation constant for the 1:1 complex of γ -butyrolactone and *o*-cresol in carbon tetrachloride.

Figure 5 shows the carbonyl absorption of 0.04 M solutions of γ -butyrolactone in carbon tetrachloride containing various amounts of *o*-cresol. In the pure solvent a single band is found at 1772 cm^{-1} . The value of this band in the vapour phase¹⁹ has been found at 1816 cm^{-1} . When the concentration of *o*-cresol increases, the intensity of the original band

decreases and the half width increases. The intensity was calculated in the usual manner from the relation of molecular extinction coefficient

$$E_{\max} = (1/cl) \log_{10}(d_0/d)_{\nu_{\max}},$$

where c is the concentration of the solute in gram moles per liter, l is the path length in cm, and d_0 and d are the apparent intensities of the incident and transmitted radiation when the spectrophotometer is set at frequency ν . The frequency shift, intensity, and half width of the carbonyl band of γ -butyrolactone with varying concentration of *o*-cresol in carbon tetrachloride are given in Table 1. A new band appears at 1764 cm^{-1} at a concentration of about 0.14 M of *o*-cresol. The half width of the original band is 32 cm^{-1} and that of the new one is 48 cm^{-1} . Thus, the half width is increased by 16 cm^{-1} . The intensity of the new band increases as the *o*-cresol concentration is increased up to 0.5 M. The original band shows a gradual decrease in intensity with an isosbestic point near 1770 cm^{-1} . This shows the existence of an equilibrium system involving two species, probably free γ -butyrolactone and a hydrogen-bonded complex of γ -butyrolactone and *o*-cresol. However, the curves in Fig. 5 are

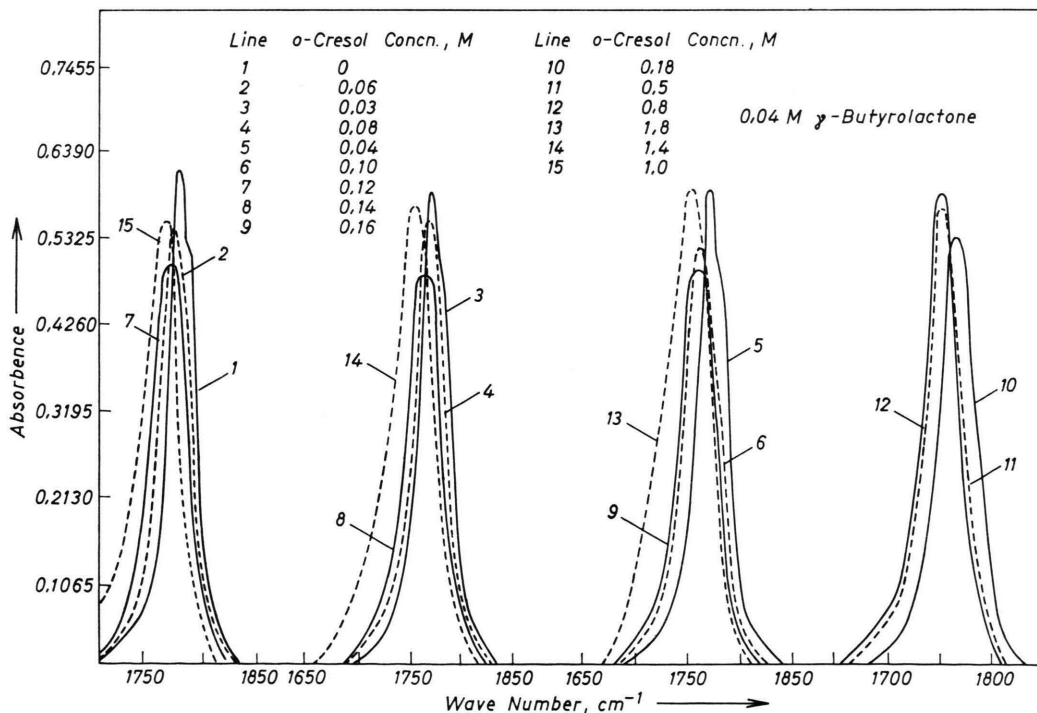


Fig. 5. Spectra of γ -butyrolactone in mixtures of *o*-cresol and carbon tetrachloride.

Environment	Carbonyl frequency in cm^{-1}	$\Delta\nu$ ν 10^3	Intensity in 10^3 $l \text{ mole}^{-1} \text{ cm}^{-1}$	Half width in cm^{-1}
Vapour	1816	—	—	—
In carbon tetrachloride	1772	24.23	1.187	32
In o-cresol at 0.08 M	1770	25.33	0.514	44
In o-cresol at 0.14 M	1764	28.63	0.475	48
In o-cresol at 0.2 M	1758	31.94	0.509	44
In o-cresol at 0.5 M	1754	34.14	0.534	40
In o-cresol at 1.4 M	1751	35.79	0.556	44
In o-cresol at 1.8 M	1751	35.79	0.556	44

Table 1. Frequency shift, intensity, and half width of the carbonyl band of γ -butyrolactone with varying concentrations of o-cresol in carbon tetrachloride.

shown far apart and not consecutively with the increase in concentration in order to demonstrate the differences in intensity and half width of the bands with varying concentrations.

The high frequency band continues to decrease in intensity as the concentration of o-cresol is increased beyond 0.14 M and only a shoulder appears in the spectrum of the solution containing 0.5 M o-cresol (curve 11 in Fig. 5). The low frequency band becomes more and more intense as the concentration of o-cresol increases and shifts to a lower frequency. At a concentration of 0.14 M o-cresol, the half width of the band is 48 cm^{-1} and this is distinctly greater than it is either at lower or higher concentrations of o-cresol. It is shown in Fig. 5 that an initial asymmetry on the low frequency side is replaced by asymmetry on the high frequency side with increased concentration of o-cresol. The half width gradually decreases as the concentration of o-cresol increases up to 1.0 M. Then, the half width suddenly increases at 1.4 M o-cresol. Increasing the concentration of o-cresol from 0.5 M to 1.4 M has little additional effect on the intensity of the band. The band at 1764 cm^{-1} now diminishes in intensity and only one band at 1751 cm^{-1} appears for 1.4 M o-cresol. This clearly indicates the existence of two or more complexes of o-cresol with γ -butyrolactone at o-cresol concentrations greater than 1.4 M.

The amount of different species present in the system of γ -butyrolactone-o-cresol could also be calculated. A graph between the total concentration of o-cresol and the relative concentration of the three γ -butyrolactone species was plotted (Fig. 6). With

a total γ -butyrolactone concentration of 0.04 M, the fraction present as the 1:1 complex appears to reach a maximum of about 63% as the o-cresol concentration approaches 0.15 M. The relative concentration of 1:2 complex at this point is about 58% and still increasing. The curve 11 of Fig. 5 shows that there is very little free carbonyl absorption at 0.5 M o-cresol and the spectrum indicates that a high fraction of the complexed γ -butyrolactone is present as the 1:2 species. When the concentration of o-cresol is further increased to 0.8 M and above, the 1:2 species is predominant but the conversion of the 1:1 species to the 1:2 complex is not rapid. On the basis of the nature of the curves in Fig. 6, it is seen that the spectrum of the 1:1 complex cannot be experimentally obtained because of the interfering absorption of the free γ -butyrolactone and the 1:2 complex. It is also seen from the nature of the curves in Fig. 5 that the interferences from higher complexes or from the bulk dielectric effects thus be-

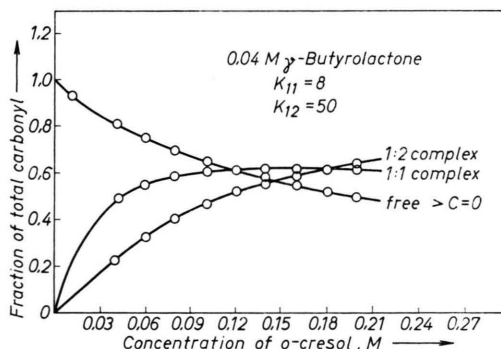


Fig. 6. Relative abundance of free and complexed γ -butyrolactone in mixtures of o-cresol and carbon tetrachloride.

came important before the 1:1 complex is completely converted into the 1:2 complex.

Though the spectrum of the 1:1 complex cannot experimentally be obtained because of the interfering absorption of γ -butyrolactone and the 1:2 complex, the spectra of the individual species could, however, be calculated¹¹ by using the formation constants of the complexes as well as the spectra of γ -butyrolactone (solute) in pure carbon tetrachloride, and in carbon tetrachloride containing two different concentrations of o-cresol. The relative concentrations of free (solute) γ -butyrolactone and the 1:1 and the 1:2 complexes in the two solutions containing o-cresol were obtained from the curves in Figure 6. The values of the relative concentrations of γ -butyrolactone and the 1:1 and 1:2 complexes in the two solutions containing 0.08 M o-cresol are 0.71, 0.58, and 0.44, respectively; and similarly they are 0.52, 0.66, and 0.62, respectively, for the solution containing 0.18 M o-cresol. Then, the absorption of free γ -butyrolactone in each solution was thus calculated and subtracted from the measured spectrum of the solution. The remaining spectra represent the total absorption of the two complexes in the solutions. The spectra were then resolved into those for the individual complexes by simultaneous solution of the following equations:

$$A_{0.08} = 0.58 A_1 + 0.44 A_2$$

and

$$A_{0.18} = 0.66 A_1 + 0.62 A_2$$

where $A_{0.08}$ and $A_{0.18}$ are the absorbances for the remaining spectra at a given frequency, and A_1 and A_2 are the absorbances of 0.04 M solutions of the 1:1 and 1:2 species, respectively, at the same frequency. Solution of the above equations yields to the following A_1 and A_2 values:

$$A_1 = 8.9595 A_{0.08} - 6.3584 A_{0.18}$$

$$\text{and } A_2 = 8.3815 A_{0.18} - 9.5376 A_{0.08}.$$

As an example, the numerical calculations of A_1 and A_2 at 1732 cm^{-1} are given below: The experimental values of the absorbances at this frequency for the solutions containing 0 M, 0.08 M, and 0.18 M o-cresol are approximately 0.05324, 0.0901, and 0.1065, respectively (Fig. 5). From these values and those of the relative concentrations of free γ -butyrolactone, one may obtain the following:

$$A_{0.08} = 0.0901 - 0.71(0.05324) = 0.0523,$$

$$A_{0.18} = 0.1065 - 0.52(0.05324) = 0.0788,$$

$$A_1 = 8.9595(0.0523) - 6.3584(0.0788) = 0.0324,$$

and

$$A_2 = 8.3815(0.0788) - 9.5376(0.0523) = 0.1617.$$

The values of A_1 and A_2 were determined at different frequencies and plotted to give the spectra as shown in Figure 7. The calculated spectra of the 1:1 and 1:2 complexes of γ -butyrolactone exhibit ma-

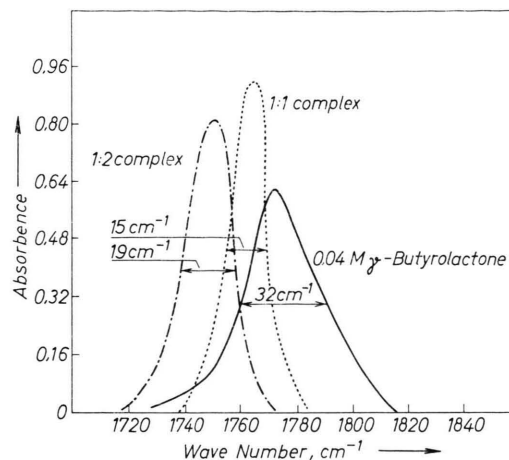


Fig. 7. Calculated spectra of γ -butyrolactone-o-cresol complexes (0.04 M in carbon tetrachloride).

xima at 1764 cm^{-1} and 1750 cm^{-1} . Experimentally, the observed frequencies for these complexes are 1764 cm^{-1} , and 1751 cm^{-1} , respectively. The observed values of the half widths for the free γ -butyrolactone, 1:1 complex and 1:2 complex are 32 cm^{-1} , 48 cm^{-1} , and 44 cm^{-1} , respectively, whereas the calculated ones are 32 cm^{-1} , 15 cm^{-1} , and 19 cm^{-1} , respectively. The low frequency band is weaker and broader than the high frequency one, and the reason may be due to the fact that the low frequency band is always a composite of two or more overlapping bands. The calculated value of the half width for the free γ -butyrolactone is greater than the calculated values of the half widths for the 1:1 and 1:2 complexes, and this situation is exactly reversed for the corresponding observed values. The calculated peak absorptivities of the complexes are almost 50% greater than that of the free γ -butyrolactone.

The formation of the complexes can generally be explained in the following manner: The oxygen atom of the carbonyl group in γ -butyrolactone has two lone pairs of electrons in hybrid orbitals which are oriented at 120° to each other. When the concentration of the donor (o-cresol) is increased, a

complex begins to form. During the complex formation, the donor hydrogen aligns itself with one of the lone pairs to form a bond $O-H \cdots O=C$. Thus, initially the 1:1 complex is formed. When the concentration of the donor (o-cresol) is further increased, molecules of the donor tend to combine with the second lone pairs to form the 1:2 complex. Because of the decrease in bond length, the carbonyl frequency shifts to the low frequency side. The intensity of the 1:2 complex reaches a constant value after a particular concentration of the donor, and thereby establishes the fact that all the lone pairs of the carbonyl groups of γ -butyrolactone have been completely shared in the hydrogen bonding.

On the basis of the confirmation of the complexes of the solute (γ -butyrolactone) with the donor (o-cresol), two possible structures (Fig. 8) have been,

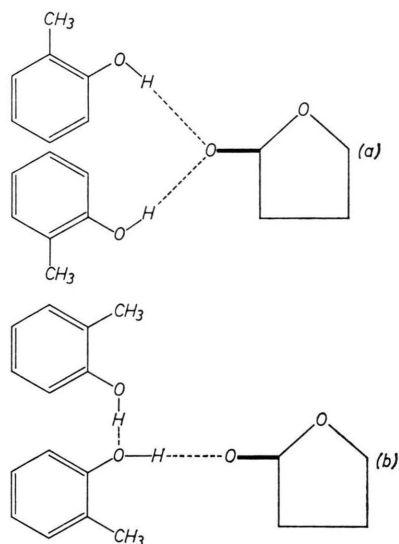


Fig. 8. Structures for the 1:2 complex of the γ -butyrolactone-o-cresol system.

in line with the earlier investigations¹¹, considered here for the 1:2 species. In the first structure (Fig. 8 a), two molecules of o-cresol are directly bonded to the carbonyl group of γ -butyrolactone and the frequency shift can be expected to be quite large. In the second structure (Fig. 8 b), the second molecule of o-cresol is not directly bonded to the oxygen atom of γ -butyrolactone but is directly bonded to the oxygen atom of o-cresol; and thus, the bonding

of the second o-cresol molecule does not directly influence the bonding of the carbonyl group, so the extent of frequency shift is expected to be small. The frequency shift observed for the 1:1 complex in the γ -butyrolactone-o-cresol system is 8 cm^{-1} , whereas the frequency shift for the 1:2 complex is 13 cm^{-1} from the 1:1 complex. Thus, these results are in favour of the first structure (Fig. 8 a) in which two molecules of o-cresol are directly bonded to the carbonyl group of γ -butyrolactone in comparison to the other systems studied. The 1:1 and 1:2 complexes are formed at fairly low concentrations. In addition to the change in the bulk dielectric properties of o-cresol, two or more specific interactions between γ -butyrolactone and o-cresol may contribute to the over-all frequency shift.

The free energies of formation for the 1:1 and 1:2 complexes of the γ -butyrolactone-o-cresol system were calculated by using the formation constants from the relation $\Delta G = -RT \ln K$. The calculated values of the 1:1 and 1:2 complexes at 25°C are $-1.24\text{ Kcal}\cdot\text{deg}^{-1}\cdot\text{mole}^{-1}$, and $-2.32\text{ Kcal}\cdot\text{deg}^{-1}\cdot\text{mole}^{-1}$, respectively. Thus, the free energy of formation for the 1:2 complex is nearly twice the value for the 1:1 complex at the same temperature. The higher value of the free energy of formation with negative sign for the 1:2 complex of the γ -butyrolactone-o-cresol system shows that the degree of interaction increases in going from the 1:1 complex to the 1:2 complex. Thus, these values clearly establish the relative strength of the 1:1 and 1:2 complexes of the same system. For every change in the concentration of the solvent, there are corresponding changes in the intensity, frequency, and half width of the band. The observed large frequency shift may be due to both the bulk dielectric and specific interactions. It is also clear from these that γ -butyrolactone makes complexes only with monomer o-cresol molecules but not with dimers or higher associated species.

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Thermoluminescence of ZnS

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A number of zinc sulphide phosphors containing cobalt was prepared with various concentrations of additional impurities. Co^{2+} -ions in both copper and silver activated phosphors produce a characteristic glowcurve, showing three distinct peaks above liquid nitrogen temperature. It was established that the first and probably the second glowpeak is connected with distinct traps, while the third peak is caused by a continuous distribution of traps. Measurements of thermoluminescence spectra as well as investigations of energy storage capacity and temperature dependence of electron capture in traps pointed to a local association of traps and luminescence centres in the case of the first two glowpeaks, whereas electron transfer via the conduction band from traps to separated luminescence centers was assumed for the third peak. An already existing model was used for discussing the experimental results obtained.

1. Introduction

Regardless of the many various publications in this field so far, it is rather unclear what physical processes actually take place in the luminescence of zinc sulphide phosphors. A series of different models was proposed which in most cases could only partially be fulfilled by the various experiments ¹⁻⁴. Even the uniform luminescence model for zinc sulphide phosphors suggested in 1966 ⁵, which makes a particularly easy understanding cannot be considered final.

The aim here was to acquire some more knowledge of the various luminescence centres and mechanisms in ZnS. It was of special interest whether an explanation for the thermoluminescence could be found within the framework of existing models.

2. Experimental

For the thermoluminescence measurements an apparatus developed by ROTHERMEL ⁶ was used with slight modifications. The arrangement allowed a simultaneous recording of the total luminescence and the thermoluminescence spectra. Glowcurves could also

be registered in place of the spectra at various wavelengths. All the measurements were taken at the same photomultiplier voltage, so that given intensities (photocurrents) of the spectrally undistributed (EMI 6256 S) as well as those of the spectrally distributed glowcurves (EMI 9558 QB, S 20 cathode) are approximately comparable. The phosphors were excited with the UV-part of the spectrum of a high pressure mercury lamp (Schott-filter UG 11) usually to saturation. Fluorescence spectra at different temperatures could also be measured after some simple alterations to the device. For measurements of the electron paramagnetic resonance (EPR) an AEG 20-X-spectrometer was used.

Pure ZnS was used in preparing the various phosphors. These were accordingly doped with nitrates and chlorides, which were added in the form of highly diluted solutions. In addition 2 mole percent NaCl were added in the same way ⁷.

After drying at 120 °C the substance was fired at 1000 °C for an hour in a nitrogen atmosphere. As shown later by ESR measurements (Mn^{2+} -signals), the result was an almost pure cubic structure ⁸. All doping concentrations are given in mole per mole ZnS.

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