On the Structures of p-tert-Butyl Phenol Resin and α-Naphthol Resin. II. Infrared Absorption Spectra of p-tert-Butyl Phenol and α-Naphthol

By Reisuke SODA

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It was previously reported[1] that a polymer, synthesized from *p-tert*-butyl phenol and formaldehyde, was a suitable material for coating the fiber of a dust respirator to obtain a high efficiency of filtration. This polymer showed anomalous phenomena in its benzene solution.

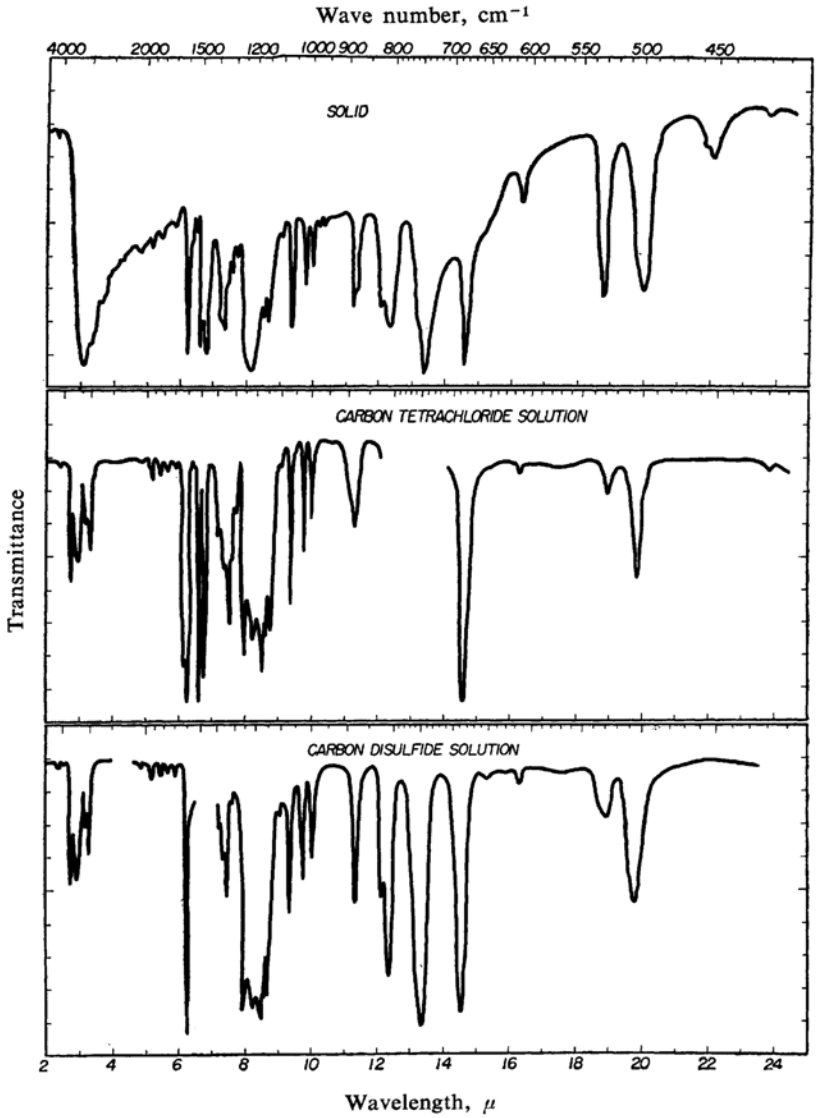

Fig. 1. Spectra of phenol in solid and solutions. Spectrum is cut off in the region of interference due to solvents. Concentration of solution is about 0.1 M in carbon tetrachloride and 0.5 M in carbon disulfide.

1) R. Soda, *Bull. Natl. Inst. Ind. Health*, No. 3, 40 (1960).

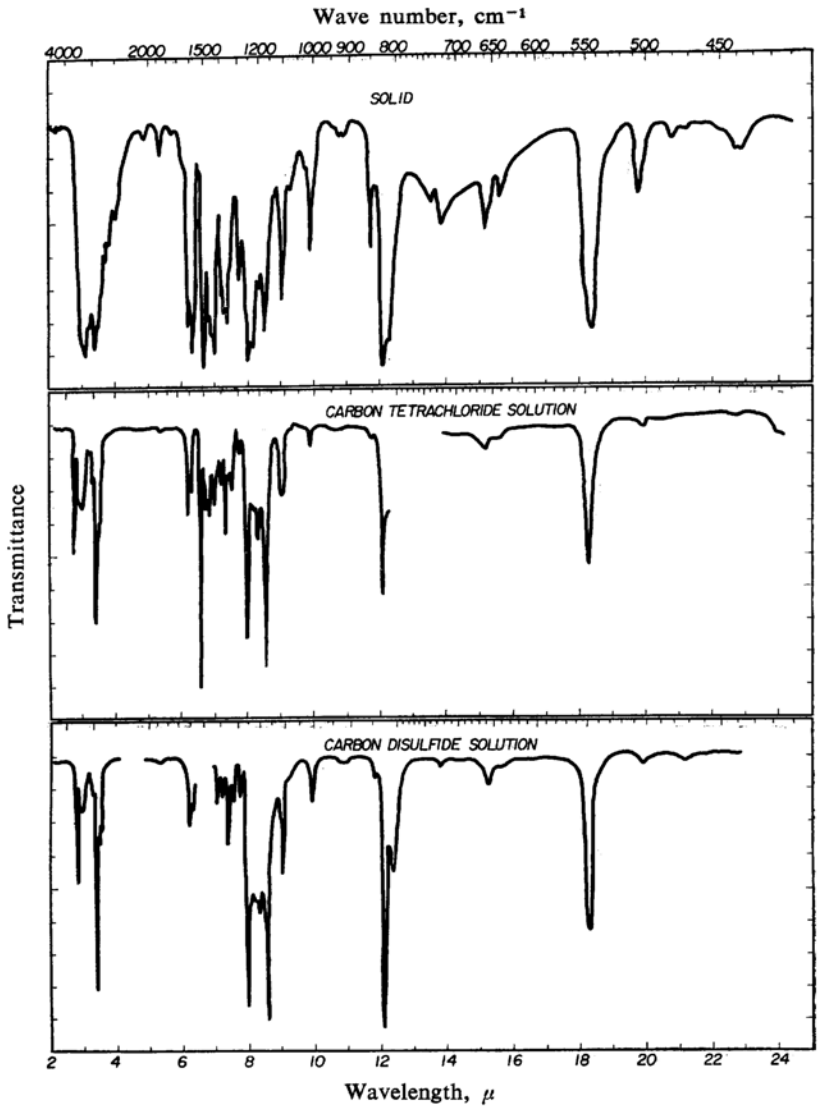

Fig. 2. Spectra of *p-tert*-butyl phenol in solid and solutions. Spectrum is cut off in the region of interference due to solvents. Concentration of solution is about 0.3 M in carbon tetrachloride and 0.4 M in carbon disulfide.

The polymer had a relatively small molecular weight and both sides of the polymer chain were *p-tert*-butyl phenol. Also the OH bonds of the polymer were bound by a very strong intramolecular hydrogen bonding and this intramolecular hydrogen bonding was made partly loose only when the polymer was dissolved in benzene. Bands of the spectrum obtained in the region of sodium chloride prism were assigned, but some ambiguity remained in these assignments.

In the present work, to eliminate the above stated doubtfulness of the assignment, the infrared absorption spectra of *p-tert*-butylphenol and the other O–H compounds were precisely measured and the observed region was extended to about 33 μ in the region of cesium bromide optics, particularly the in-plane and the out-of-plane O–H deformation vibration were investigated in more detail.

Experimental

p-tert-Butyl phenol was purified by recrystallizing it from its saturated benzene solution and by vacuum distillation. α-Naphthol was recrystallized from ethyl alcohol. Phenol was purified by distillation. The solvents used were carbon tetrachloride and carbon disulfide, each being distilled once. The potassium bromide powder used for the measurement of the solid spectrum, was heated, ground to particle size of 200 to 300 mesh and dried by heating at 200°C. For the measurement of the spectrum of a solid some samples were resolidified

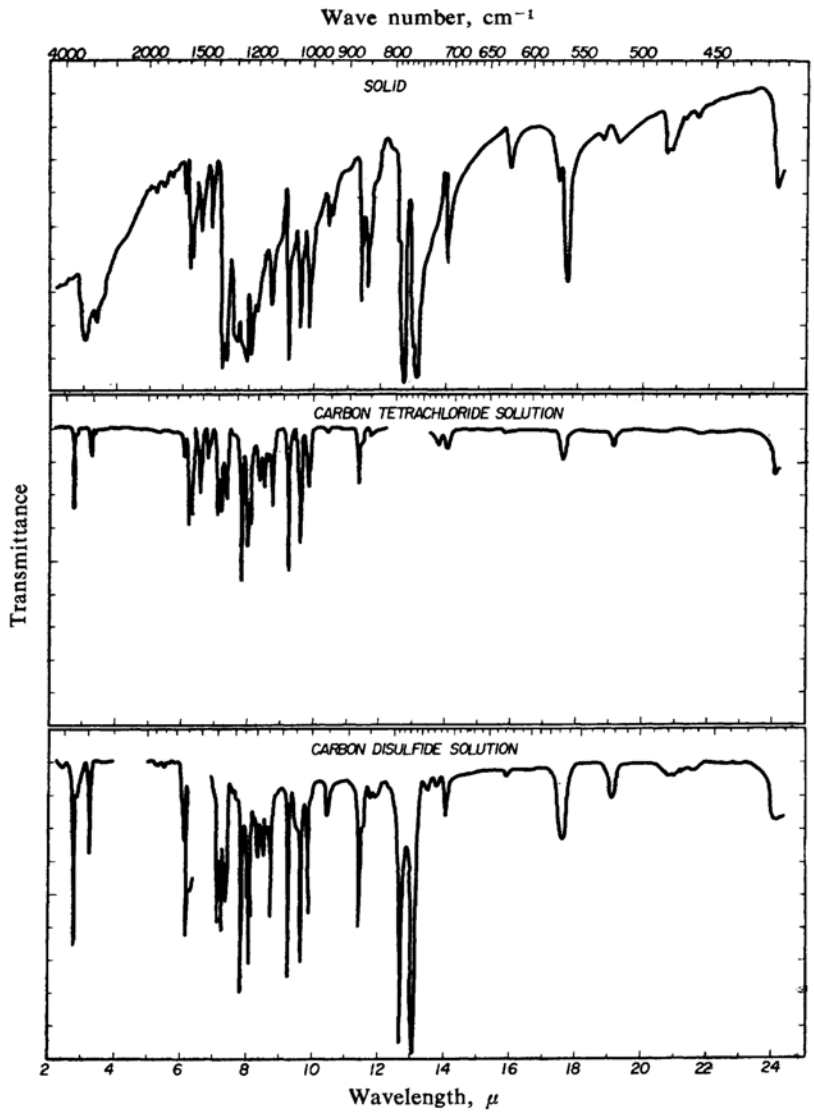

Fig. 3. Spectra of α-naphthol in solid and solutions. Spectrum is cut off in the region of interference due to solvents. Concentration of solution is about 0.05 M in carbon tetrachloride and 0.1 M in carbon disulfide.

between two rock salt plates or potassium bromide plates which were polished at both surfaces to make flat. The sample powder was sandwiched between two heated window plates and cooled moderately to make a solid film. The other spectra were obtained with potassium bromide disks.

The cell used for the solution had the thickness of 1 mm. and its window was of potassium bromide or rock salt. The infrared spectrum was observed by a Perkin-Elmer Model 137 Infracord spectrophotometer, Perkin-Elmer Model 21 spectrophotometer and Perkin-Elmer Model 221 spectrophotometer.

Results and Discussion

The spectrum of solid of fused film between window plates was approximately the same as that of a potassium bromide pellet. It may be considered that the orientation effect does not exist in this case. Therefore the spectrum of solid obtained could be analyzed without caution of experimental condition. The spectra of phenol in the solid state, in solutions of carbon tetrachloride and of carbon disulfide are shown in Fig. 1. Those of *p-tert*-butyl phenol and of α-naphthol are illustrated in Figs. 2 and 3, respectively. The spectra of solids of these three compounds differ from those of solutions in several regions. The spectra of these compounds in solution change their features with the concentration of solution in some regions. Those changes of spectra are illustrated in Figs. 5 to 16. The spectra

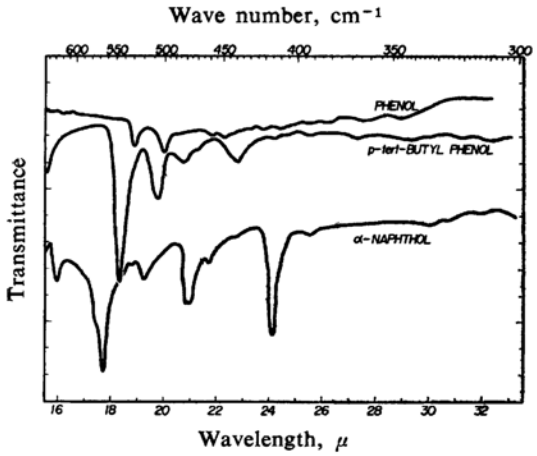

Fig. 4. Spectra of *p-tert*-butyl phenol and α-naphthol in CsBr region (KBr disk).

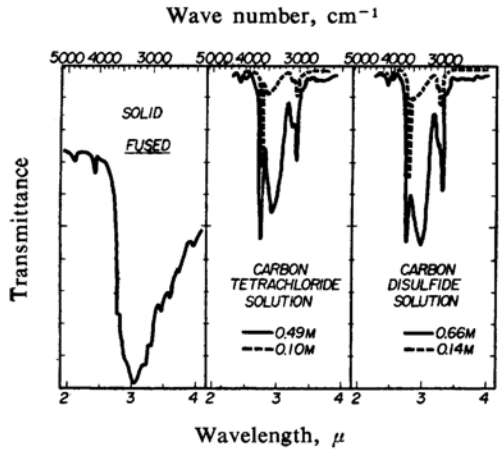

Fig. 5. Spectra of phenol in 3 μ region.

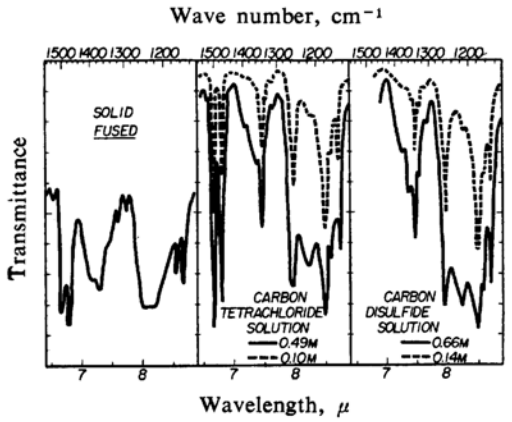

Fig. 6. Spectra of phenol in the region of 1500~1150 cm^{-1}. Spectrum is cut off in the region of interference due to solvents.

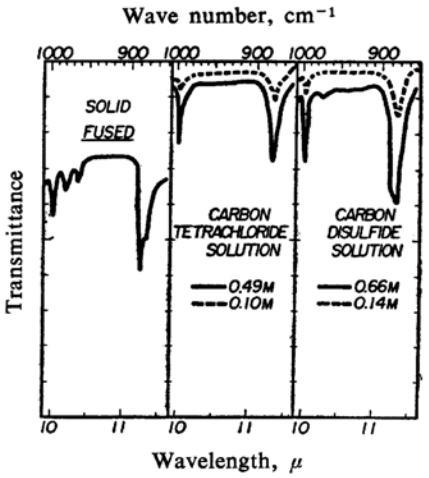

Fig. 7. Spectra of phenol in the region near 1000 cm^{-1}.

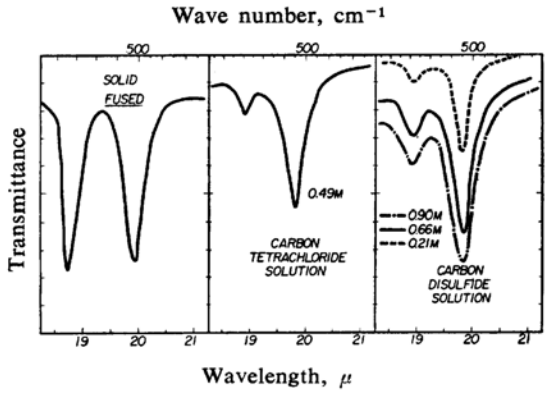

Fig. 8. Spectra of phenol in the region close to 500 cm^{-1}.

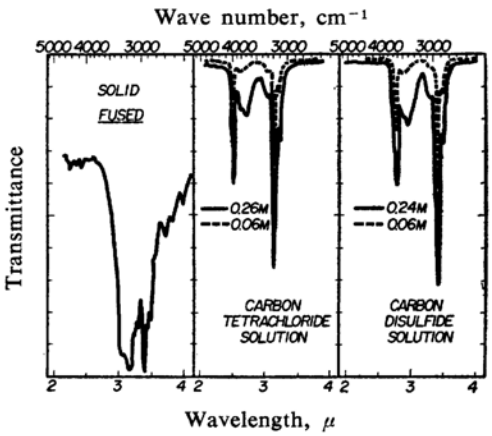

Fig. 9. Spectra of *p-tert*-butyl phenol in 3 μ region.

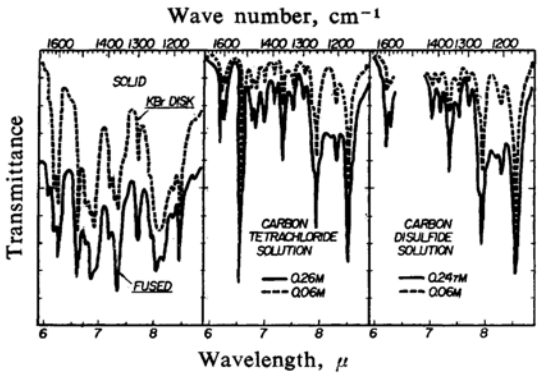

Fig. 10. Spectra of *p-tert*-butyl phenol in the region of 1600~1150 cm^{-1}. Spectrum is cut off in the region of interference due to solvents.

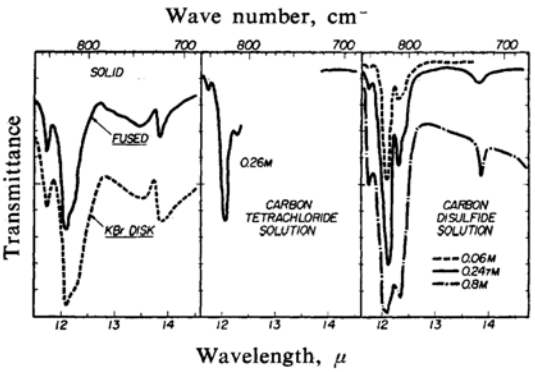

Fig. 11. Spectra of *p-tert*-butyl phenol in the region near 800 cm^{-1}. Spectrum is cut off in the region of interference due to solvents.

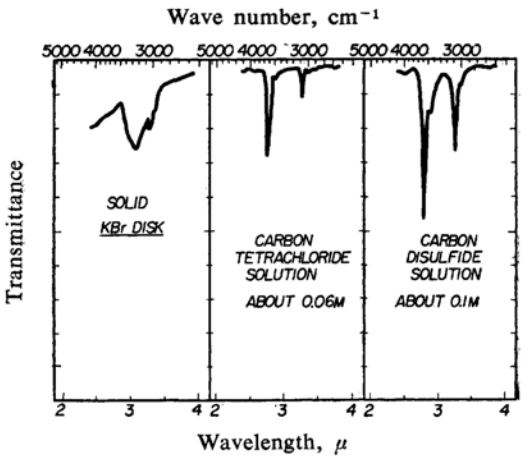

Fig. 13. Spectra of α-naphthol in 3 μ region.

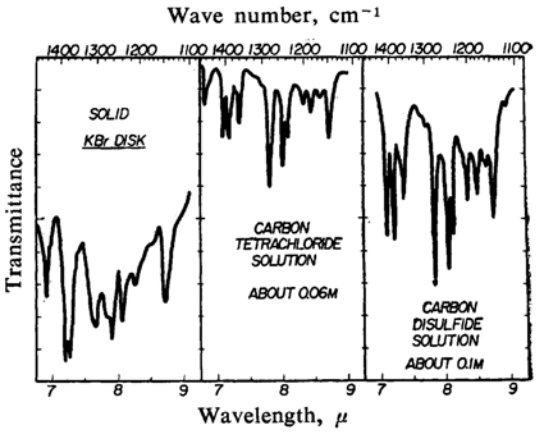

Fig. 14. Spectra of α-naphthol in 8 μ region. Spectrum is cut off in the region of interference due to solvents.

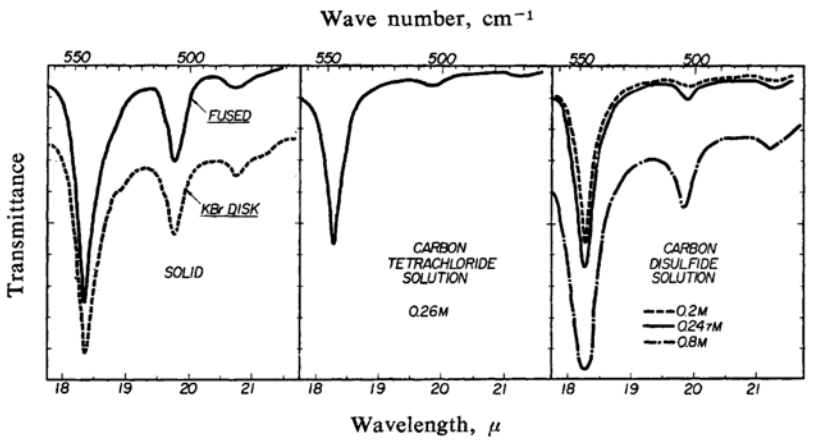

Fig. 12. Spectra of *p-tert*-butyl phenol in the region of 550~460 cm^{-1}.

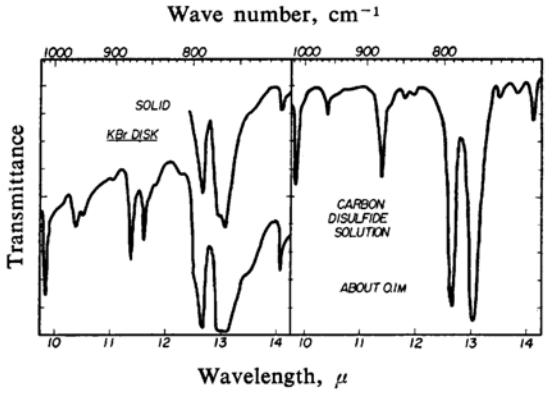

Fig. 15. Spectra of α-naphthol in the region of 1000~700 cm^{-1}.

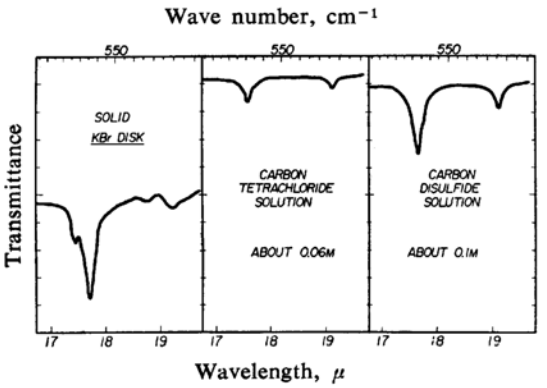

Fig. 16. Spectra of α-naphthol in the region near 550 cm^{-1}.

of these compounds in the region of cesium bromide optics are shown in Fig. 4. No strong band which is observable at ordinary concentration is found in the region of 25 to 34 μ. Considerable changes of spectra of these compounds are observed in three regions at 3, 7 to 8 and near 18 μ when the phase and the concentration alter. The other remarkable changes are found in the regions of 6, 11 and 14 μ, but these changes are much less than those in the former regions. The changes in the regions at 6, 11 and 14 μ are observed when the solids are brought into solution but are not observed when the concentrations of solutions alter. Changes of spectral region at 18 μ of *p-tert*-butyl phenol and α-naphthol are not clear compared with that of phenol.

Phenol. — The spectrum of phenol has been investigated by several authors. Kuratani[2] assigned OH deformation vibrations to it and concluded that this vibration coupled with C–O stretching vibration. He reported that these vibrations gave rise to the bands at 1280 and 1195 cm^{-1} respectively. Mecke and Rossmy[3] reported that these bands which occurred at 1339 and 1174 cm^{-1} shifted by complete deuteration to 1294 and 915 cm^{-1}, respectively, and that the band at 1174 cm^{-1} had a larger part of O–H deformation vibration character than the band at 1339 cm^{-1}.

In the present experiment, as shown in Figs. 1 and 6, the appreciable change is found in region at 1200 cm^{-1} with the change of phase and concentration of solution. The change at 1300 cm^{-1} region is so complex that it is not easy to make a unique assignment. The band at 1220 cm^{-1} of solid spectrum shifts to 1210 cm^{-1} in solution spectrum and the intensity of this band decreases when the concentration of solution is lower. In the solution, a new band appears near 1180 cm^{-1} and its relative intensity to that of 1210 cm^{-1} band increases at the lower concentration. The 1390 cm^{-1} band of solid decreases its intensity and a strong band appears near 1340 cm^{-1} in the solution. The relative intensity of the latter band to the former increases in a lower concentration of solution. Then it may be concluded that the bands 1390 and 1220 cm^{-1} in solid state and the bands 1380 and 1210 cm^{-1} in solution are assigned to coupled modes of C–O stretching vibration and hydrogen-bonded O–H deformation vibration. The bands at 1340 and 1180 cm^{-1} may be assigned to the coupled modes of C–O stretching vibration and free O–H deformation vibration. These conclusions do not contradict the results of other papers[2-5]. These conclusions agree with what is observed in 3 μ region. In this region the stretching vibration of the O–H bond gives rise to a broad at its center at 3300 cm^{-1} in solid but in solution sharp band at 3600 to 3620 cm^{-1} and broad band at 3370 cm^{-1} or higher. The phenol molecule will associate to a large aggregate through the hydrogen bonding in the solid state. In the solution these molecules are dispersed into monomer with free O–H bond and partly associate to build up a small polymer through O–H···O linkage. Therefore the O–H vibration of solid shows the strong hydrogen bonding character due to a larger associated molecule and that of solution shows the characters of free hydroxyl bond and partly of the weakly hydrogen-bonded bond. Other changes are observed

2) K. Kuratani, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **73**, 758 (1952).

3) R. Mecke, and C. Rossmy, *Z. Elektrochem.*, **59**, 866 (1955).

4) L. J. Bellamy, "The Infrared Spectra of Complex Molecules", Metheu & Co., Ltd., London, J. Wiley & Sons Inc., New York (1954), pp. 64~69 and 96.

5) "Chemical Application of Spectrocopy", Ed. by W. West, Interscience Pub., Ltd., London (1956), pp. 388~434,

TABLE I. BAND POSITIONS AND ASSIGNMENT OF SPECTRUM OF PHENOL

Band, cm^{-1}		Assignment
Solid	Solution	
	3610	ν(O-H), free
	3480	ν(O-H), bonded
3360	3380	ν(O-H), bonded
3090	3070	ν(C-H), aromatic
3010	3030	ν(C-H), aromatic
1605	1605	Ring vibration
1597	1597	Ring vibration
1502	1501	Ring vibration
1473	1470	Ring vibration
1389	1387 to 1380	δ(O-H), bonded and ν(C-O)?
1370	1355	δ(O-H), bonded and ν(C-O)?
	1341	δ(O-H), free and ν(C-O)
1337	1330	Skeletal vibration
1318	1310	Skeletal vibration
1245	1256	Skeletal vibration
1222	1211	δ(O-H), bonded and ν(C-O)
	1177	δ(O-H), free and ν(C-O)
1168	1166	δ(C-H) or skeletal vibration
1153	1150	δ(C-H) or skeletal vibration
1071	1067	δ(C-H) or skeletal vibration
1024	1023	δ(C-H) or skeletal vibration
998	998	Skeletal vibration
883	882	Skeletal vibration
822	824	
810	809	
752	750	δ(C-H), out-of-plane
689	687	δ(C-H), out-of-plane
663	656	
615	616	Skeletal vibration
533	527	δ(O-H), out-of-plane?
503	505	δ(O-H), out-of-plane?

near 890 and 980 cm^{-1}. But these changes do not clearly show its origin and are smaller than those in the above-mentioned regions. Furthermore the changes in this region are not observed with variation of concentration of solution. These changes may be explained as influence of crystal field[6]. Each band is tentatively assigned as shown in Table I. Out-of-plane O-H deformation vibration is considered to give rise to the band in lower frequency region. As shown in Fig. 4, the main intense bands arise at 530 and 500 cm^{-1}. These bands change their relative intensities when this substance is dissolved from a solid. The frequency shifts are slight as shown in Fig. 8. In carbon disulfide solution and in a solid form this relative absorbance ratio (E_{530}/E_{500}) varies as follows:

State	Relative intensity Ratio
Solid	1.10
CS_2 soln.	
0.9 M	0.22
0.66 M	0.21
0.21 M	0.19
CCl_4 soln.	
0.49 M	0.19

Then the band at 530 cm^{-1} is tentatively assigned to OH out-of-plane deformation vibration of a solid and the 500 cm^{-1} band to that of free O-H bond and some other vibrations. No benzene gives rise to absorption bands in these regions but with toluene a weak band arises at 521 cm^{-1}. Chlorobenzene, bromobenzene and iodobenzene give rise to a strong band near 450 to 460 cm^{-1} and ethylbenzene at 486 cm^{-1}. Therefore the bands at 530 and 500 cm^{-1} may be connected with the O-H out-of-plane deformation vibration and the other skeletal vibration[5].

***p-tert*-Butyl Phenol.** — The spectra of this compound as illustrated in Figs. 2, 4, 9, 10, 11 and 12, are similar to those of phenol, particulary the bands which concern the O-H vibrations. Phenol is a monosubstituted benzene derivative and *p-tert*-butyl phenol is a 1,4 disubstituted derivative. These spectra differ from each other at the bands due to some benzene ring vibrations and ring C-H vibrations. As the latter substance has further a tertiary butyl group, there appear also the bands due to the methyl group and the C·$(CH_3)_3$ group vibrations.

The change of phase and concentration causes changes of its association degree and state of molecule. This resembles that of phenol and hence O-H stretching vibration and O-H in-plane deformation vibration change their frequencies and intensities. These facts are illustrated in Figs. 9, 10 and 12. In Fig. 11, the bands at 820 and 760 cm^{-1} change slightly their features with phase. The reason is still unexplained exactly but may be attributed to the crystal field effect[6]. The assignments of bands are summarized in Table II.

The spectrum of phenol in the region at 18 to 22 μ is different from that of *p-tert*-butyl phenol. It is generally accepted that in this region the band is highly sensitive to the substituent[5]. 1, 4-Dimethyl benzene gives rise to a weak band at 645 cm^{-1} and a very strong band at 480 cm^{-1}. This strong band shifts to 432 cm^{-1} in 1, 3-dimethyl benzene and to 436 cm^{-1} in 1, 2-dimethyl benzene. Therefore it may be reasonable to conclude[5] that disubstituted

6) R. J. Grisemthwaite, and R. F. Hunter, *J. Appl. Chem.*, 6, 324 (1956).

TABLE II. BAND POSITIONS AND ASSIGNMENT OF SPECTRUM OF *p-tert*-BUTYL PHENOL

Band, cm^{-1}		Assignment
Solid	Solution	
	3610	ν(O-H), free
	3480	ν(O-H), bonded
3230	3380	ν(O-H), bonded
3060		ν(C-H), aromatic
3020	3030	ν(C-H), aromatic
2950	2960	ν(C-H), $-CH_3$
2900	2910	ν(C-H), $-CH_3$
2860	2880	ν(C-H), $-CH_3$
1613	1612	Ring vibration
1597	1595	Ring vibration
1520	1521	Ring vibration
1477	1477	δ(C-H), $-CH_3$
1460	1463	δ(C-H), $-CH_3$
1442	1425	δ(O-H), bonded and ν(C-O)
1391	1391	δ(C-H), $-CH_3$
1361	1363	δ(C-H), $-CH_3$
	1328	δ(O-H), free and ν(C-O)
1298	1294	Skeletal vibration
1263	1256	C-CH_3 rocking
1230	1217	δ(O-H), bonded and ν(C-O)
1200	1203	δ(C-H), aromatic and C-CH_3 rocking
	1173	δ(O-H), free and ν(C-O)
1112	1110	δ(C-H), aromatic
1084	1083	δ(C-H), aromatic
931	931	ν(C-C), C-CH_3
851	849	ν(C-C), C-CH_3
827	828	δ(C-H), out-of-plane
818	812	δ(C-H), aromatic or ν(C-C), C-CH_3
723	724	
660	659	Skeletal vibration or substituent characteristic
641	641	Substituent characteristic or skeletal vibration
545	546	δ(O-H), out-of-plane ?
507	503	δ(O-H), out-of-plane and others
472	473	
	469	δ(O-H), out-of-plane : free O-H
442	442	
416		C-C bending, C-CH_3

benzene gives rise to the band at 500 to 400 cm^{-1}. Solid of *p-tert*-butyl phenol absorbs at 545 cm^{-1} (strong), 506 cm^{-1} (medium), 482 cm^{-1} (weak) and 472 cm^{-1} (very weak). The band at 545 cm^{-1} remains unchanged when the compound is dissolved. The band at 482 cm^{-1} disappears and a new band appears at 470 cm^{-1}. No regularity is found among the relative intensities of bands at 545, 506, 482 and 470 cm^{-1}. The effect of the condition of measurement on these values is so remarkable that a quantitative argument has little meaning. Qualitatively, the bands at 506 and 480 cm^{-1} of solid and those at 503 and 472 cm^{-1} of solution are perhaps concerned with O-H out-of-plane deformation vibration, considering that of phenol. The other vibration may couple with this vibration. Further discussion can not be carried out now.

Other assignments are nearly the same as in the previous report[1] in the region of sodium chloride optics. These assignments are obtained with consideration of those of phenol, 1,4-disubstituted benzene and *tert*-butyl compounds.

α-Naphthol.—α-Naphthol is an aromatic O-H compound which has one group of three adjacent free hydrogen atoms and one group of four adjacent free hydrogen atoms. α-Naphthylamine in solid gives rise to a broad band near 3200 cm^{-1} but in solution gives rise to a sharp band at 3620 cm^{-1} and a weak band at 3500 cm^{-1}. This aspect of OH stretching vibration band is the same as those of phenol and *p-tert*-butyl phenol stated already. Regions 1400 to 1350 cm^{-1}, 1330 to 1250 cm^{-1} and 1210 to 1160 cm^{-1} vary with the change of phase. From those results it may be considered that the band due to OH deformation vibration appears near 1170 and 1330 to 1340 cm^{-1} for free α-naphthol molecule. There is also some possibility of considering the coupling of OH deformation vibration with the other mode of vibration rather than with the C-O stretching vibration. Then the above-mentioned regions which show the different features with the change of phase and concentration of solution, may be concerned with the OH deformation vibration. Tentatively for free α-naphthol, the bands near 1180 and 1359 cm^{-1} are assigned to those vibrations.

Out-of-plane deformation vibration of aromatic C-H bonds may give rise[4,5,7] to the bands at 760 to 740 cm^{-1} and 780 to 760 cm^{-1} (more generally 800 to 760 cm^{-1}) or 770 to 735 cm^{-1} and 810 to 750 cm^{-1} for α-naphthol. The other characteristic bands to the substitution may be considered to appear near 725 to 680 cm^{-1}, or more precisely at 740 to 710 cm^{-1}, (720 to 710 cm^{-1}), 710 to 690 and 650 cm^{-1}. Then the bands at 789 and 765 cm^{-1} may be assigned to that mode of vibration and other characteristic bands may be attributed to those at 730, 710 and 629 cm^{-1}. According to the literature[5,7] the three bands at 730, 710 and 629 cm^{-1} can be assigned to the in-plane deformation vibration of aromatic C-H bond.

The change of spectra in the region below 1000 cm^{-1} with phase change is yet to be explained clearly. The doublet of 959 cm^{-1},

7) H. Luther and H. Gunzler, *Z. Naturforsch* **10b**, 445 (1955).

the band at 867 cm^{-1} and bands at 769 and 765 cm^{-1} in solid are different from these in solution. The doublet bands disappear and the single band appears at 959 and 767 cm^{-1}, and the band 867 cm^{-1} disappears completely when the solid sample is dissolved. It is not suitable to consider that these bands are attributable to the vibration mode concerned with O–H vibration because O–H vibration does not give rise to bands in these regions in general. These changes may be caused from crystal field effect[6].

TABLE III. BAND POSITIONS AND ASSIGNMENT OF SPECTRUM OF α-NAPHTHOL

Band, cm^{-1} Solid	Band, cm^{-1} Solution	Assignment
	3620	ν(O-H), free
	3500	ν(O-H), bonded
3240		ν(O-H), bonded
3110		ν(O-H), bonded
3050	3060	ν(C-H), aromatic
1634	1634	Ring vibration
1600	1600	Ring vibration
1582	1582	Ring vibration
1560	1546	Ring vibration
1515	1517	Ring vibration
1453	1453	Ring vibration
1439	1404	
1387 or 1377	1388	δ(O-H), bonded and ν(C-O)
	1358	δ(O-H), free and ν(C-O)
1315	1312	δ(O-H), bonded and ν(C-O)?
1300	1297	δ(O-H), bonded and ν(C-O)?
1264	1276	Skeletal vibration
1253	1245	Skeletal vibration
1239	1235	Skeletal vibration
	1199	δ(O-H), free and ν(C-O)?
	1181	δ(O-H), free and ν(C-O)?
1172	1175	Skeletal vibration
1148	1145	δ(C-H)
1083	1082	δ(C-H) or skeletal vibration
1044	1040	Skeletal vibration
1015	1015	δ(C-H)
959	958	Skeletal vibration
875	877	Skeletal vibration
856	850	δ(C-H), out-of-plane ?
843	837	δ(C-H), out-of-plane
789	790	δ(C-H), out-of-plane
768	768	δ(C-H), out-of-plane
740	742	Skeletal vibration or δ(C-H), out-of-plane
731	725	δ(C-H), out-of-plane
712	710	δ(C-H), out-of-plane
628	629	Skeletal vibration
573 or 564	568	δ(O-H), out-of-plane ?
521	524	δ(O-H), out-of-plane ?
482	480	Substituent characteristic skeletal vibration
478	476	Substituent characteristic skeletal vibration
461	461	Substituent characteristic skeletal vibration
416	416	Substituent characteristic skeletal vibration

The tentative assignments are summarized in Table III. In the present experiment the concentration of solution is not altered. Therefore the assignment of the band concerned with OH vibration can not be carried out decidedly. Out-of-plane OH deformation vibration is expected to give rise to the bands in the region near 500 cm^{-1} with consideration of these bands of phenol and *p-tert*-butyl phenol: But α-naphthol shows such a complex aspect in this region that a simple assignment can not be carried out at present. Perhaps bands at 530, 520 and 460 cm^{-1} may be concerned with this vibration mode.

It may be accepted as true that the above three compounds give rise to the bands near 3600 cm^{-1} due to OH stretching vibration, those near 1170 cm^{-1} and near 1330 cm^{-1} due to free OH in plane deformation vibration and those near 500 cm^{-1} concerned in OH out-of-plane deformation vibration. These bands are attributed to free OH bond, but in a case of solid state or associated state, the bands at 3300 cm^{-1}, those at 1200 to 1230 cm^{-1} and 1380 to 1430 cm^{-1}, and those near 500 cm^{-1} may be assigned to the above mentioned vibration modes respectively. The bands in the region of 500 cm^{-1} can not be decidedly assigned now but may be determined by deuteration of OH bond, considering the argument given above.

In the next paper the assignment will be made of the absorption bands of *p-tert*-butyl phenol resin and α-naphthol resin according to the result of this work.

Summary

In connection with the work on a resin for dust respirator, the spectra of phenol, *p-tert*-butyl phenol and α-naphthol were observed in solid and in solution. Infrared absorption spectra can be explained by considering that these compounds associate by hydrogen bonding in solid form and that they hold the equilibrium between monomer and associated molecule in solution. Reasonable assignments were made to some of the bands observed. The deformation vibration of O–H (free) and stretching vibration of C–O seem to couple with each other and give rise to bands near 1340 and 1180 cm^{-1} in any of these three compounds. Bands due to the out-of-plane O–H deformation vibration could not be determined but it was found that the bands in the

550～500 cm^{-1} region were concerned with this vibrational mode.

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National Institute of Industrial Health
Kawasaki-shi, Kanagawa-ken