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Phenol as a Non-aqueous Solvent

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Organic tertiary bases form 1:1 and 1:2 adducts with phenol. Tetrachlorides of tin and titanium form $\text{SnCl}_4(\text{OC}_6\text{H}_5)_2 \cdot \text{C}_6\text{H}_5\text{OH}$ and $\text{TiCl}_4(\text{OC}_6\text{H}_5)_2 \cdot \text{C}_6\text{H}_5\text{OH}$ when dissolved in phenol. Acid-base titrations of tetraphenoxides of tin and titanium against pyridine and sodium phenoxide have been carried out to establish the autoionization of phenol as $2\text{C}_6\text{H}_5\text{OH} \rightleftharpoons \text{C}_6\text{H}_5\text{OH}_2^+ + \text{C}_6\text{H}_5\text{O}^-$.

ORGANIC polar solvents have been extensively investigated as non-aqueous solvents. However, no such studies with phenol are available in literature though some phenoxides of the metals have been prepared by the solvolysis of metal chlorides in phenol¹⁻³.

Phenol is slightly acidic in nature ($pK_a = 1.0 \times 10^{-10}$). Its physical properties like dielectric constant (9.78 at 45°), dipole moment (1.76 D) and specific conductance ($1.8 \times 10^{-10} \text{ ohm}^{-1} \text{ cm}^{-1}$) are comparable to those of acetic acid (dielectric constant, 6.0; dipole moment, 1.76 D). It has been shown⁴⁻⁶ that, in fluorosulphuric acid, phenol is protonated at the ring rather than at the oxygen while in disulphuric acid, it gets sulphonated⁷. It is amphoteric in nature. It is, therefore, of interest to investigate its solution chemistry and explore the possibility of isolation of its adducts with Lewis acids and bases and characterize them.

TABLE 1 — SPECIFIC CONDUCTANCES OF SOME SOLUTES IN PHENOL AT 50°

Compound	Conc. (mole/litre)	Sp. conductance $\times 10^6$ ($\text{ohm}^{-1} \text{ cm}^{-1}$)
Sodium phenoxide	0.012	7.67
α -Picoline	0.020	1.96
Pyridine	0.039	1.47
Tin(IV) chloride	0.034	2.52
Antimony(V) chloride	0.031	2.38
Titanium(IV) phenoxide	0.021	2.81
Tin(IV) phenoxide	0.038	3.09

Phenol was purified by distilling it twice and collecting the fraction boiling at 179°. It was crystallized twice by cooling in ice-water. Any traces of moisture were removed by keeping it *in vacuo* over P_2O_5 for 48 hr. Samples of phenol having m.p. 43° and specific conductance $1.8 \times 10^{-8} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 50° were used in this investigation. The conductance measurements were carried out using a Toshniwal conductivity bridge Sr No. 447. All the solutions were prepared in moisture-free atmosphere. IR spectra were recorded in nujol on a Perkin-Elmer spectrophotometer No. 337.

Dilute solutions of organic tertiary bases and alkali metal phenoxides in phenol are far more conducting than either of the components. Though the specific conductance values of these solutions are not very high (Table 1), yet these are quite significant in view of the low conductances of the components and the low dielectric constant of the medium. This suggests that bases form complexes with phenol, and at lower concentrations these are ionized. No solid compound of these bases with phenol could be isolated under the present experimental conditions suggesting weak interaction between the two components. Nevertheless, conductometric studies on the mixture of the two components show breaks in the conductance-composition curves at the molar ratio (base: phenol) of 1:1 and 2:1.

IR spectral studies of the 1:1 liquid compound show that the spectral bands of the pure components undergo similar changes as are observed in the case of pyridinium chloride⁸ complexes of tertiary bases with tellurium tetrachloride⁹, acetyl chloride¹⁰ and selenium tetrachloride¹¹. The bands at 1622, 1608, 1503, 1480, 1385 and 1322 cm^{-1} are due to pyridinium ion. A new band observed at 1432 cm^{-1} , not present in the pure components, may be assigned to $\nu\text{-N-H}$. The bands at 1250, 1204, 1165, 1080, 993, 890, 750 and 680 cm^{-1} also support the formation of pyridinium ion. The broad band present at 3360 cm^{-1} in phenol, assigned to hydrogen-bonded OH group, shifts to 3160 cm^{-1} in these compounds. The O-C stretching mode present at 1350 cm^{-1} in the phenol shifts to 1400 cm^{-1} . These observations suggest that OH group in phenol is retained and is hydrogen-bonded to the nitrogen atom of the tertiary base¹². The spectral changes in the compounds of

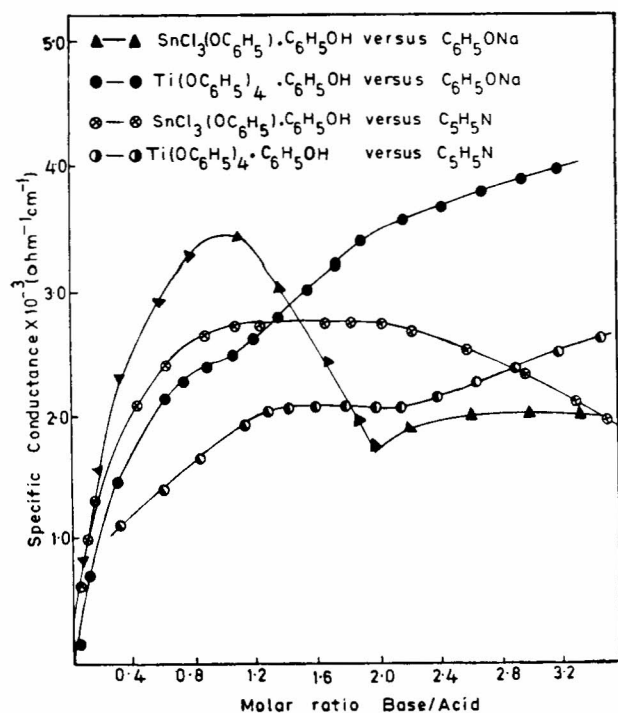
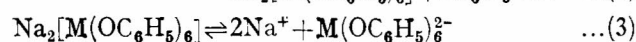
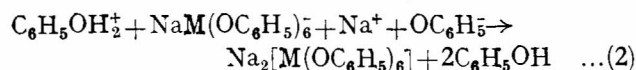
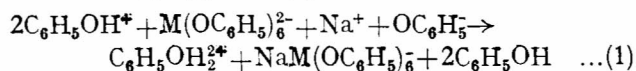


Fig. 1 — Conductometric titrations between acids and bases in phenol at 50°

other tertiary bases with phenol follow a similar pattern (unpublished data).

Strong acceptor molecules such as antimony pentachloride, boron trichloride, aluminium trichloride, etc., readily get solvolyzed in fused phenol at 45°. In the case of tetrachlorides of tin and titanium, partially solvolyzed products of composition $\text{SnCl}_3(\text{OC}_6\text{H}_5)_3 \cdot \text{C}_6\text{H}_5\text{OH}$ and $\text{TiCl}_3(\text{OC}_6\text{H}_5)_3 \cdot \text{C}_6\text{H}_5\text{OH}$ are obtained. Complete solvolysis of these compounds has been carried out to get $\text{Sn}(\text{OC}_6\text{H}_5)_4$ and $\text{Ti}(\text{OC}_6\text{H}_5)_4 \cdot \text{C}_6\text{H}_5\text{OH}$ respectively (unpublished data). Acid-base titrations of $\text{SnCl}_3(\text{OC}_6\text{H}_5)_3 \cdot \text{C}_6\text{H}_5\text{OH}$ against $\text{C}_6\text{H}_5\text{ONa}$ or $\text{C}_5\text{H}_5\text{N}$ have been carried out. These titrations have been followed both conductometrically and with the help of visual indicators such as malachite green and crystal violet (Fig. 1). There are two breaks in the conductance-composition curves (Fig. 1) suggesting the dibasic character of the acid. Similarly titrations of $\text{Ti}(\text{OC}_6\text{H}_5)_4 \cdot \text{C}_6\text{H}_5\text{OH}$ against pyridine or sodium phenoxide have also been carried out. Compounds of composition $\text{Na}_2\text{Ti}(\text{OC}_6\text{H}_5)_6$ and $\text{Ti}(\text{OC}_6\text{H}_5)_4 \cdot 2\text{C}_5\text{H}_5\text{N}$ have been isolated from the solutions. Compounds of similar nature have already been reported in the case of alkoxydes^{13,14}. The titrations apparently follow reactions (1), (2) and (3).



By analogy with the behaviour of methyl alcohol¹⁵ and acetic acid¹⁶⁻¹⁸ and in the light of above observa-

tions, the possible mode of ionization of phenol may be postulated as



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Co(II) Complexes of Pyridine-2-aldoxime & 6-Methylpyridine-2-aldoxime

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The reaction in acetone of $\text{CoCl}_2 \cdot \text{H}_2\text{O}$ with pyridine-2-aldoxime (HPOX) and 6-methylpyridine-2-aldoxime (HMePOX) in different stoichiometric ratios (1:2 and 1:3) in the absence and presence of hydrogen peroxide has yielded different Co(II) complexes. One of these, viz. $\text{Co}(\text{HPOX})_2\text{Cl}_2$ is identical with that reported earlier in literature [*Aust. J. Chem.*, **27** (1974), 2475]. The IR studies on these complexes indicate that in some cases, one ligand is ionized and the other unionized whereas in some cases both the ligands in the complexes are unionized. All the complexes are cationic. The measured high magnetic moments rule out +3 oxidation state of the metal ion in any of these complexes.

THE ligands pyridine-2-aldoxime (HPOX) and its 6-methyl derivative (HMePOX) are useful analytical reagents¹⁻⁵. Stability constants of their complexes with trivalent lanthanon ions have been reported⁶ and complexes of HPOX with Ni(II), Pt(II), Pd(II)^{7,9} and Cu(II)^{10,11} have also been