Absorption Spectra of Molecular Compounds of Diethyl Ether with Several Metallic Chlorides

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Some metallic chlorides such as aluminum chloride or stannic tetrachloride produce stable molecular compounds with diethyl ether. Dipole moments of some of them were measured in non-polar solvents by several investigators[1]; however, no spectroscopic data are obtainable at all. The author measured the absorption spectra of the molecular compounds in solutions of ether and *n*-heptane.

Apparatus.—Shimadzu Photoelectric Spectrophotometer Type QB-50 (the measured range of wave number, 45,000-17,000 kayser[2]; quartz cell length, 1.00 cm.; temperature, 10-15°C).

Materials.—Anhydrous aluminum chloride, of commercial highest class, was sublimed in a current of dry nitrogen gas, and the product was resublimed directly into sample tubes. Anhydrous ferric chloride was purified similarly in an atmosphere of chlorine instead of nitrogen. Anhydrous zinc chloride, of highest purity, was heated in dry air and dehydrated by phosphoric pentoxide. Anhydrous stannic and titanium tetrachlorides were fractionally distilled twice. Diethyl ether of the commercial product was distilled fractionally several times in an atmosphere of dry air by a Wydmer's distillator. Heptane was purified by the Potts' method[3].

Results and Discussion

Absorption spectra of the solutions of aluminum chloride, zinc chloride and titanium

tetrachloride in diethyl ether are shown in Fig. 1. Absorption spectra of the solutions of aluminum chloride-ether, stannic chloride-

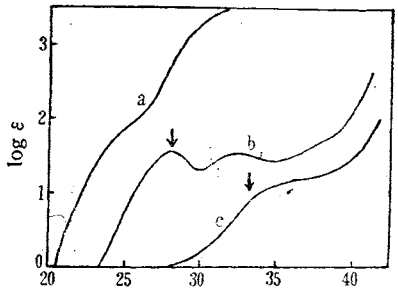

Fig. 1. Absorption curves of solutions of $TiCl_4$ (curve a), $AlCl_3$ (curve b) and $ZnCl_2$ (curve c) in diethyl ethep expressed in extinction coefficient. (ε's are expressed as values per mole of chlorides)

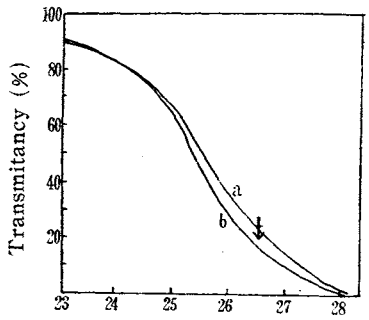

Fig. 2. Absorption curves of solutions in heptane, which is saturated by $AlCl_3$, of 0.02M ether (curve a) and of 0.2M ether (curve b).

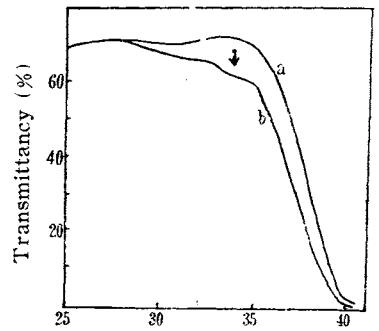

Fig. 3. Absorption curves of solutions in heptane of 0.01 M $SnCl_4$ and 0.01 M ether (curve a) and of 0.01 M $SnCl_4$ and 0.1 M ether (curve b).

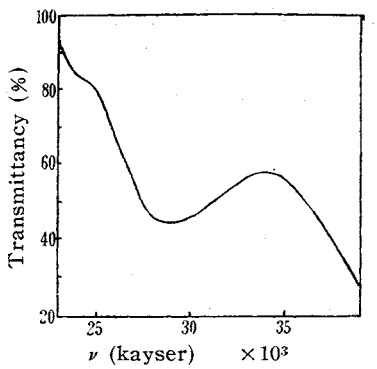

Fig. 4. Absorption curve of saturated soluton of $FeCl_3$ in heptane containing 0.1 M ether.

ether and ferric chloride-ether in heptane are shown in Fig. 2, 3 and 4 respectively. The extinction coefficient could not be determined from the spectra of solutions in heptane because of slight solubilities of the chlorides in heptane.

The author regards the absorption bands marked by arrows in the figures as the characteristic absorption of the molecular compounds. However, for the solutions of titanium tetrachloride and ferric chloride, none could be concluded for lack of exact informations about the spectra of titanium and ferric chlorides themselves, although their solutions showed remarkable absorptions. The ultra-violet absorptions obtained for the molecular compounds of aluminum, stannic and zinc chlorides are considered to correspond to the intermolecular charge transfer spectra defined by R.S. Mulliken[4].

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2) Kayser (formerly cm^{-1}). See Transactions of the Joint Commission for Spectroscopy, *J. Opt. Soc. Am.*, **43**, 410 (1953).

3) W. J. Potts, *J. Chem. Phys.*, **20**, 809 (1952).

4) R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952), **76**, 386 (1954); *J. Phys. Chem.*, **56**, 801 (1952).

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