REFRACTOMETRIC STUDIES OF COMPLEX SALT FORMATION

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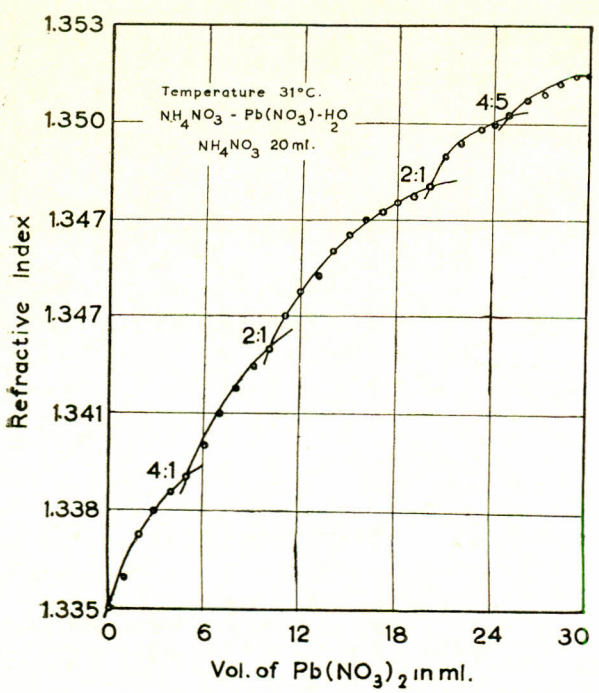
Complex salt formation has been studied by various workers by determination of magnetic susceptibility,[1] which showed an abnormal behaviour in case of formation of complex salts. Other physical properties, like surface tension, viscosity and refractive index, have also been found to give an indication as to the formation of double and complex salts.[2] Since different properties may respond to differant types, therefore we tried to investigate the variation of refractive index for cases in which complex salt formation was noticed by magnetic susceptibility determination. The principle of the refractometric method depends upon the fact that when a certain volume of solution of one substance is added to a definite volume of the solution of another substance at the given temperature, the refractive index goes on increasing or decreasing gradually, but at a certain point the increase or decrease is abnormal. When a graph is plotted between the refractive index and the volume of the solution added, a kink in the curve is noticed at the point where complex salt formation takes place. Several systems were examined by this method, and the present communication deals with the results for:

(1) NH_4NO_3—$Pb(NO_3)_2$-H_2O



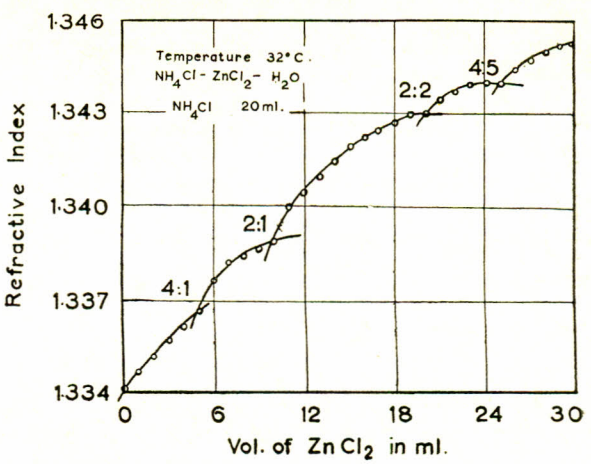
(2) NH_4Cl—$Zn\ Cl_2$-H_2O
(3) NH_4Cl—$Cd\ Cl_2$-H_2O
(4) NH_4OH-$Cu\ SO_4$—$Cu\ (OH)_2.(NH_3)_2$ or $Cu(OH)_2.(NH_3)_4$
(5) $CHCl_3$—$C_2H_5OC_2H_5$ (ether)
(6) $CHCl_3$—$(CH_3)_2.CO$

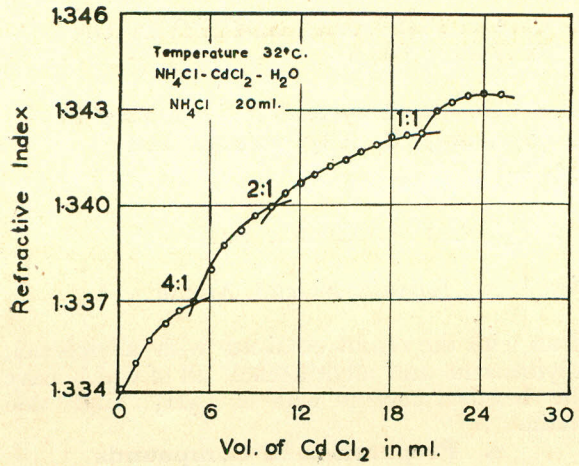
The following systems were also examined, but we failed to get any indication of double salt or complex salt formation due to precipitate formation:

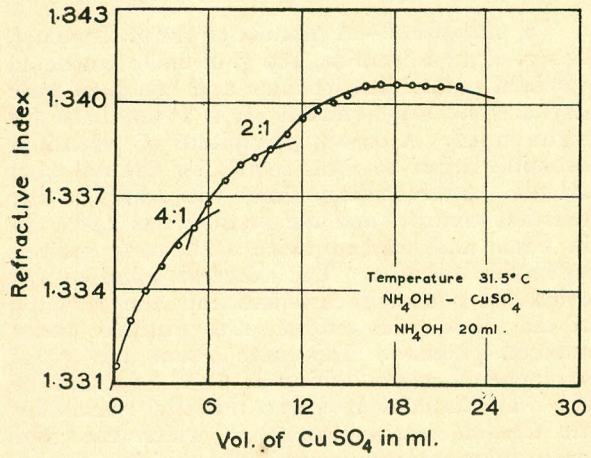
(1) *p*-Toluidine—*p*-chlorophenol
(2) *p*-Toluidine—*o*-chlorophenol
(3) $Ni(SO_4)$—$(NH_4)_2.SO_4$
(4) KCN—$AgNO_3$
(5) $NaOH$—Na_2SO_4
(6) $K_4Fe(CN)_6$—$FeCl_3$

Experimental

Thirty mixtures of each system were made up by adding varying amount (0-30 cc.) of molar solution of one of the components to 20 cc. or 10 cc. of molar solution of another, and the mixture was diluted to 50 cc. in each case. The refractive indices of these mixtures were determined at constant temperature with a critical angle refractometer (Bellingham & Stanley Ltd.) with an accuracy of $\pm$ 0.0002. The temperature of the solution under investigation was controlled within $\pm$ 0.1°. A graph was plotted between the refractive index and the volume of the varying component. Kinks in the curve were obtained at those points where the complex or the double salt formation took place.







From the position of kinks in the curves molar ratios of the components of the double and complex salts were calculated and are detailed below:

(1) NH_4NO_3—$Pb(NO_3)_2$-H_2O 4:1, 2:1, 1:1, 4:5

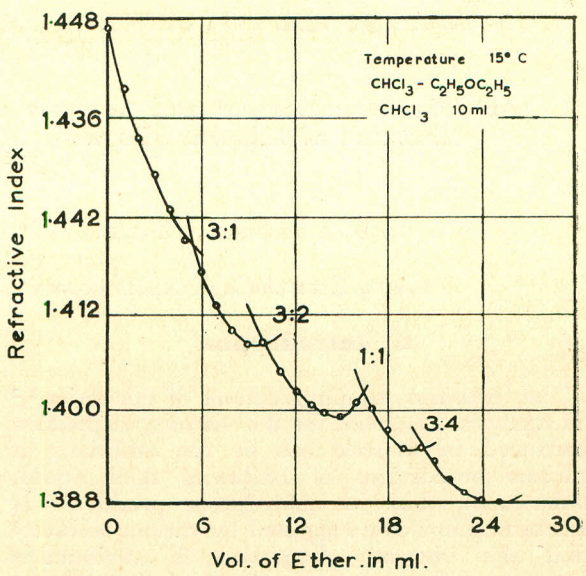
All the first three values, 4:1, 2:1 and 1:1, confirm the results obtained by magnetic susceptibility method but the fourth value, *i.e.*, 4:5, is another ratio found by refractometric method which is probably more sensitive than magnetic method.

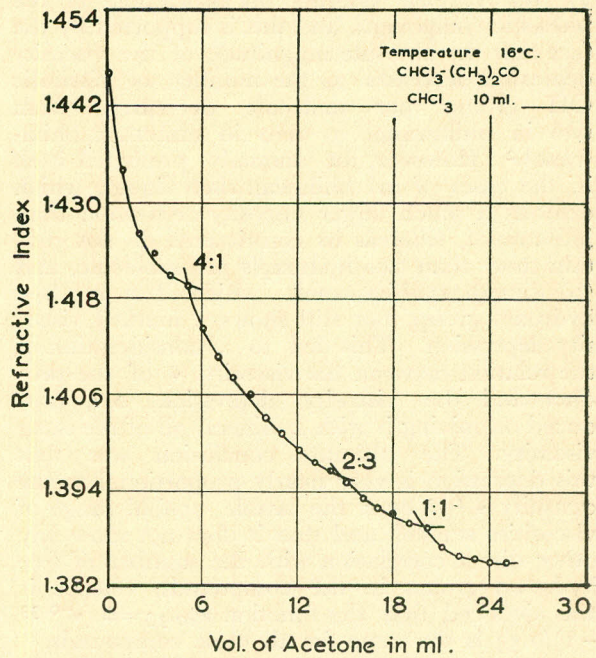
(2) NH_4Cl—$ZnCl_2$-H_2O 4:1, 2:1, 1:1, 4:5

In this case also 4:1, 2:1 and 1:1 values are in agreement with the magnetic susceptibility method but the value 4:5 is another ratio found only by this method.

(3) NH_4Cl—$CdCl_2$-H_2O 4:1, 2:1, 1:1

4:1-1:1 are the values which are obtained by by the magnetic susceptibility method. While 2:1 value obtained by our method is a new value.





(4) NH_4OH-$CuSO_4$—$Cu(OH)_2.(NH_3)$ 4:1, 2:1 or $Cu(OH)_2$-$(NH_3)_4$ Schweitzer's reagent

(5) $CHCl_3$—$C_2H_5OC_2H_5$ 2:1, 1:1, 5:8 and 1:2

(6) $CHCl_3$—$(CH_3)_2CO$ 2:1, 2:3 and 1:2

The values obtained in systems 4 to 6 have not been determined before by any method.

References

1. Prasad and Datar, Proc. Indian Acad. Sci., **36A**, 544 (1952).
2. C.S. Pande and M.P. Bhatnagar, J. Indian Chem. Soc., **31**, 402 (1945).