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The Composition and Stability of the Germanium Phenylfluoronate Complex

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Germanium phenylfluoronate is formed in solution as an orange coloured complex at pH 2.5–3.4. Its composition has been studied by continuous variation, slope ratio and molar ratio methods. The results indicate that the complex formed is of 1:2 type, and its stability constant is 6.80×10^2. The solid complex was prepared and examined by various methods including chemical analysis, infrared spectroscopy and differential thermal analysis. It conforms to the formula: $(C_{19}H_{11}O_5)_2Ge.4H_2O$, and the bonding to the metal was found to be at $>C=O$ and –OH groups.

Phenylfluorone (2:3:7-trihydroxy-9-phenyl-6-fluorone) was first introduced and tested as an analytical reagent by Gillis *et al.* (1947). It has been used as an acid-base indicator (Sastri 1956) for the titration of strong acids and bases at the concentration range (0.1–1N). It is also used in the detection and the determination of germanium (Gillis *et al.* 1947), zirconium (Nazarenko *et al.* 1962), titanium (Damodaren 1957), and tantalum (Luke 1959).

The reaction between germanium and phenylfluorone has been previously studied (Tobia *et al.*) in order to find the optimum conditions under which a stable coloured complex is formed and applied for spectrophotometric determination of germanium. The present work is concerned with the determination of the composition of the complex, and its stability constant.

Experimental

Reagent & apparatus

Phenylfluorone, and germanium solutions were prepared as previously described (Tobia *et al.* 1978).

The pH was measured by a pH-meter type PROLABO, TS4N.

A Perkin-Elmer 4000 A and SPEKTRO MOM 204 Spectrophotometer has been used for the spectral studies.

Preparation of the solid complex

Transfer 25 ml of 0.1 M germanic acid into 250 ml beaker at room temperature, add 50 ml of 0.1 M phenylfluorone solution in hydrochloric acid (0.1 M) dropwise with constant stirring. After a few minutes, the orange solid complex begins to precipitate. It is left overnight for complete precipitation. Filter by using a sintered glass crucible porosity G-4 and wash several times with ethyl alcohol, dry in air till constant weight. Heat portion of the solid complex at 110°C for 3 hours to determine water of hydration.

The air-dry sample was investigated by the following technique to elucidate the structure of the complex.

Chemical Analysis

Carbon, and hydrogen have been determined by standard microchemical methods. Germanium has been determined by heating the solid complex at 1000°C for 3 hours to constant weight for conversion into GeO_2.

Results and Discussion

Composition of the complex

The composition of the complex has been determined by the continuous variation method by using a series of solutions in which the ratio of germanium to phenylfluorone ranges between 0.1–0.9 at constant molarity. Absorbance was measured at 525 nm against a blank solution containing all reagents except germanium.

The results show that at a mole fraction of 0.66, a maximum is obtained, indicating that the complex formed is of the 1:2 type.

In the slope Ratio Method, two series of solutions were prepared, in the first, the concentration of germanium was kept constant at 1 mM while that of Ph.Fl. was varied in the range 0.9–3.8 mM. In the other series, the concentration of Ph.Fl. was kept constant (1.8 mM) and that of germanium varied between 0.5–2 mM. The pH of each was adjusted at 2.4 and absorbance was measured at 525 nm.

Two straight lines were obtained (Fig. 1), the slope ratio (the ratio of the slopes curve a/

curve b) was found to be 0.5, which is in agreement with the results obtained by the continuous variation method.

Figures 2a & 2b represent the graphical representation of the molar ratio method, indicating again a 1:2 ratio.

A potentiometric titrations of phenylfluorone in absence and in presence of germanium have been carried out, and the results obtained clarify that the additional amount of alkali (0.005 m. mole) consumed in the presence of 0.0025 m. mole of metal ion are equivalent to the hydrogen ions liberated by complexation. This indicates that the complex is 1:2 type and germanium ion is bonded with phenylfluorone through one phenolic group.

Determination of stability constant

The stability of germanium phenylfluoronate was calculated according to Molar ratio method and using the following equation:

$$A = A_m - \frac{1}{k}\frac{A}{(H_3L)}n$$

where A is the absorbance, A_m is the limiting absorbance and k is the stability constant. The slope of the line in Fig. 3 is a measure of k and is equal to 6.80×10^2.

The results in Table 1 agree with the formula $(C_{19}H_{11}O_5)_2Ge.4H_2O$, *i.e.*, it contains four water molecules, either found in the primary sphere (co-ordinated) or in the secondary sphere.

Table 1

Element	Obs. %	Calc.% $(C_{19}H_{11}O_5)_2Ge.4H_2O$
C	57.6	57.96
H	4.70	3.90
Ge	9.8	9.24

The i.r. spectra of the free ligand and that of the complex are obtained and the assignment of bands is given in Table 2.

Phenylfluorone exhibits a sharp band at 3440 cm^{-1} due to the aromatic OH group with single hydrogen bridge. In case of the complex, a broad band in the range 3500–3300cm^{-1} was observed. This could be attributed to OH stretching frequency of water molecules associated with complex formation. The strong band at 1460 is assigned to carbonyl group and is weakened by resonance between (C-O-M) and (C-O...M) (Le Comte 1950, Daval *et al.* 1952).

Table 2. Comparison between observed vibrational frequency for free ligand and complex studies

Compound		Assignment
Ligand	1307 cm^{-1}	ether linkage
	1380 – 1400 cm^{-1}	deformation of C–O
	1500, 1540, 1570 cm^{-1}	frequency of CH in conjugated aromatic ring
	1620 cm^{-1}	C = O -hydroxy, and unsaturated ketone
	1705 – 1730 cm^{-1}	C = O of -diketone
	3440 cm^{-1}	phenolic OH group
Complex	1340 – 1390 cm^{-1}	ether linkage and C – O deformation
	1560 cm^{-1}	conjugated benzene ring
	1490 cm^{-1}	C – O – M
	2870 or 2490 cm^{-1}	– CH – of cyclic alkane
	3500 – 3300 cm^{-1}	water molecules associated with complex

Differential Thermal Analysis

The DTA curve obtained when the complex is heated uniformly is shown in Fig. 4. It was noticed that an endothermic peak was observed at 110°C; this peak is due to the loss of lattice water. Decomposition of the solid complex when heated in air is indicated by two exothermic peaks at 435 and 535°C.

Conclusion

Germanium and phenylfluorone form a complex compound in solution with the composition 1:2, and its stability constant is equal to 6.80×10^2. The solid complex has the formula $(C_{19}H_{11}O_5)_2Ge.4H_2O$. Each ligand is bonded to germanium by bonds from the 2 oxyen atoms belonging to a C = O and OH groups.

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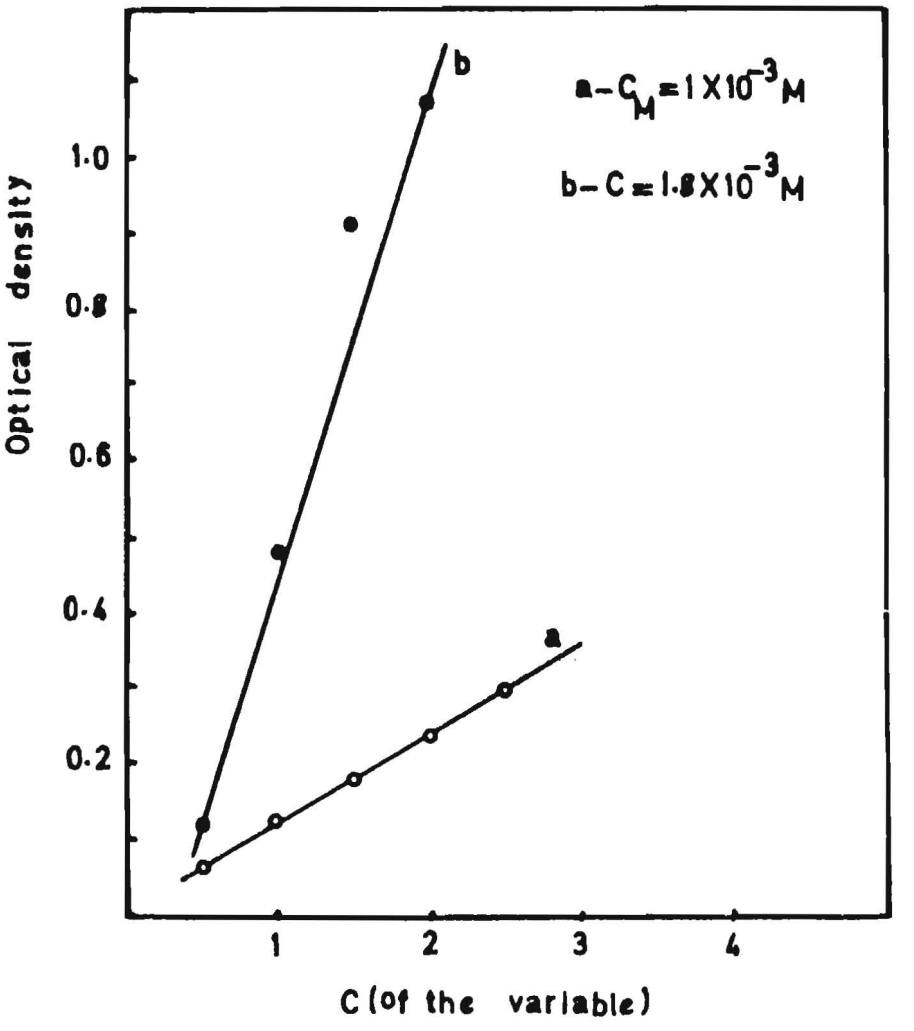

Fig. 1. Slope ratio method of Ge (IV) – Ph.Fl. complex

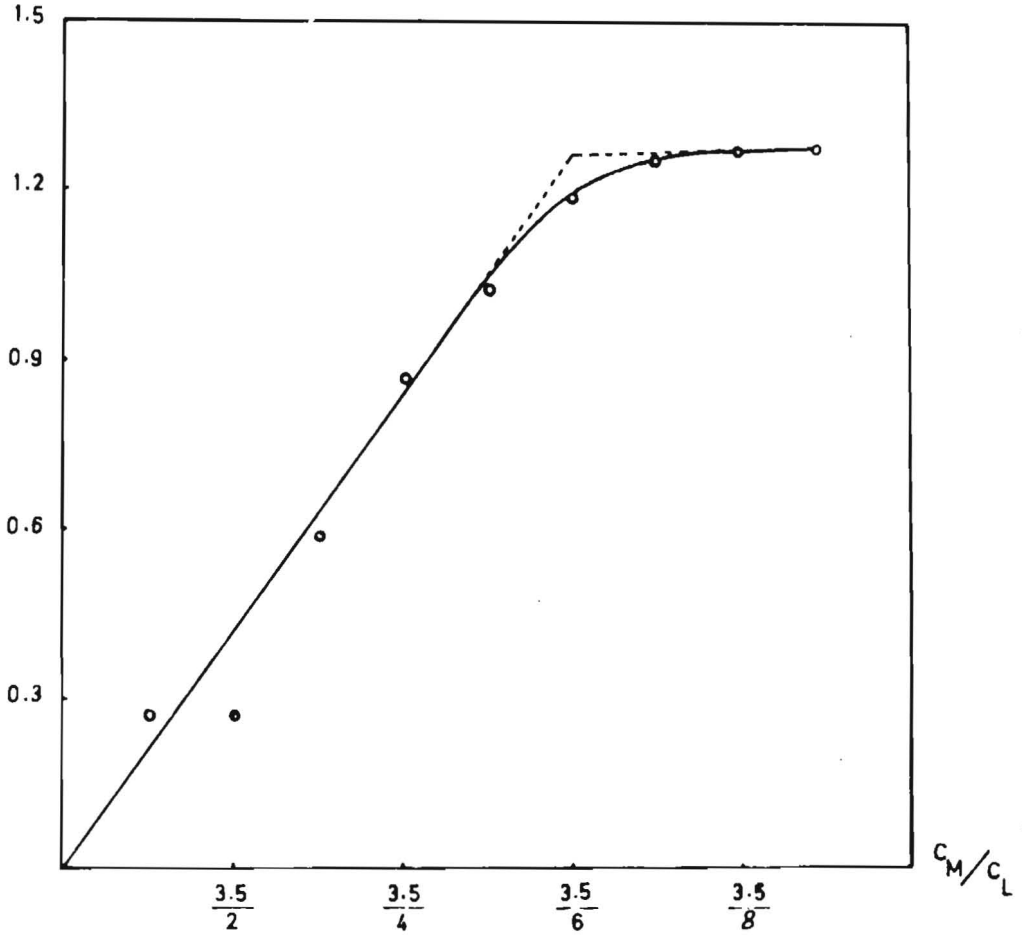

Fig. 2a. Molar ratio method for Ge (IV) – Ph.Fl. complex [Ge (IV)] = 8.75×10^{-4} M

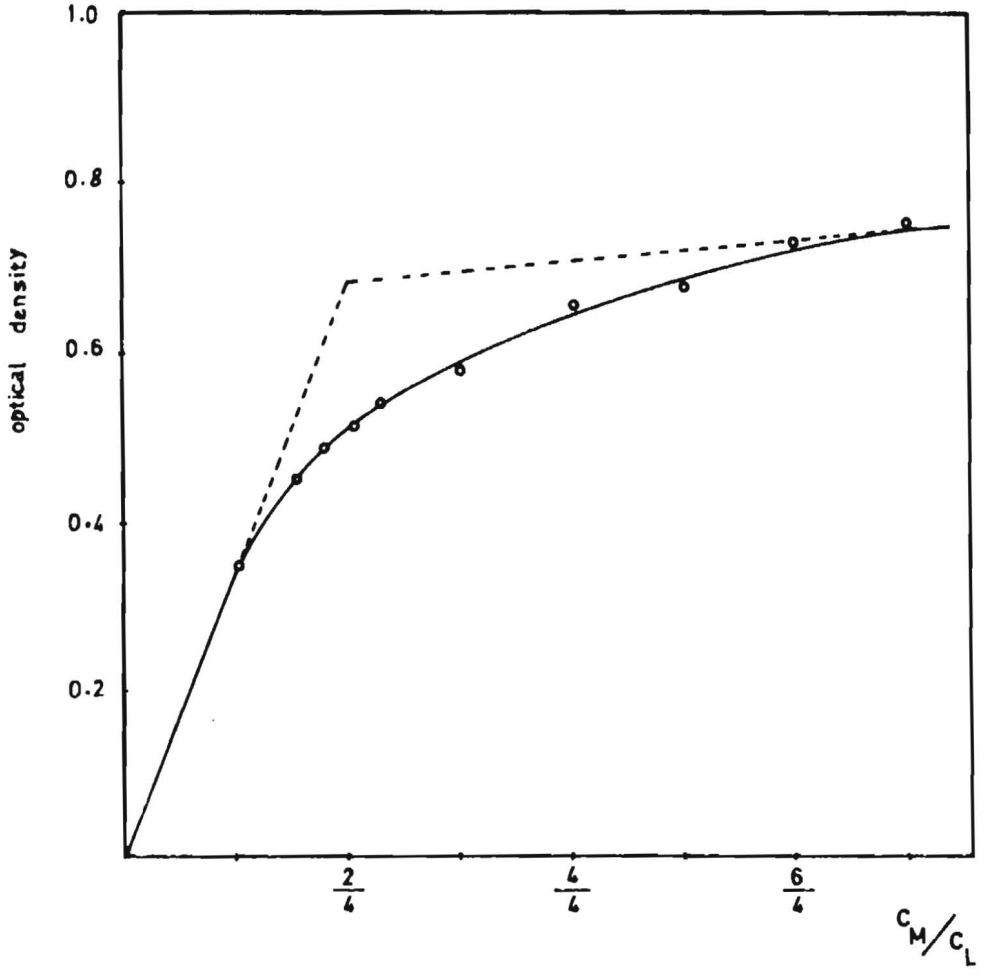

Fig. 2b. Molar ratio method for Ge (IV) – Ph.F1. complex [Ph.Fl.] = 10^{-3}

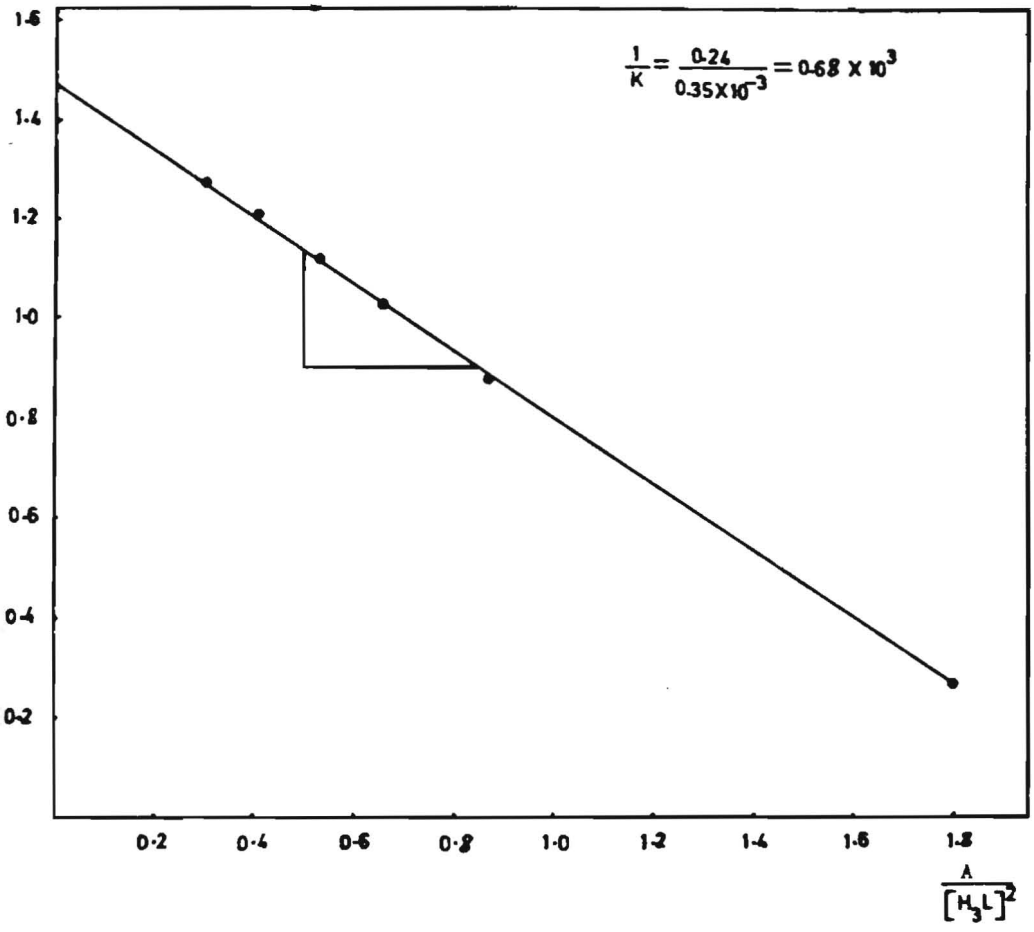

Fig. 3. Relation between optical density and concentration of Ph.Fl. solution

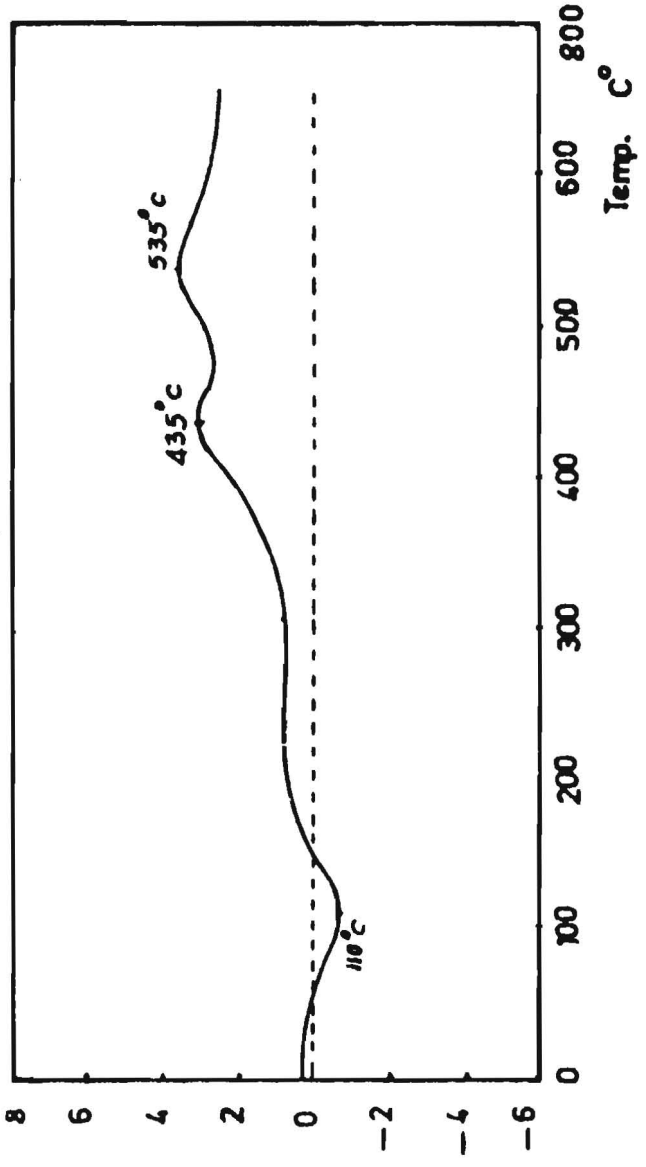

Fig. 4. Differential thermal analysis of Ge – complex

دراسة تركيب استقرار متراكب الجرمانيوم فنيل الفلورون

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يتكون متراكب الجرمانيوم فنيل الفلورون في المحلول عند أس هيدروجين ٢,٥ - ٣,٤ بلون برتقالي . وقد درس التفاعل باستخدام طرق التغيير المستمر والميل النسبي والنسب الجزئية . دلت النتائج على أن المتراكب يحتوي على الجرمانيوم والفنيل فلورون بنسبة ١:٢ وأن ثابت الاستقرار له يساوي $٦,٨ \times ١٠^{٢}$.

أمكن تحضير المتراكب في الحالة الجامدة ودرس بطرق مختلفة منها التحليل الكيميائي والتحليل الحراري التفاضلي وطيف الأشعة تحت الحمراء . واستنتج الصيغة الجزيئية كالآتي :

$(C_{19}H_{11}O_5)_2Ge.4H_2O$ وأن الجرمانيوم يترابط مع الفنيل فلورون عن طريق مجموعتي $-OH$, $\geq C = O$.