80. *The Interaction of Metal Chlorides with Organic Chlorides. Part I. Freezing-point Phase Diagrams of Titanium Tetrachloride with Some Alkyl Chlorides.*

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The freezing-point phase diagrams of titanium tetrachloride with each of six alkyl chlorides were determined by using a greaseless high-vacuum system. With methyl chloride, methylene dichloride, and chloroform titanium tetrachloride forms simple eutectic systems. With ethyl chloride, *iso*propyl chloride, and ethylidene dichloride the phase diagrams show discontinuities; these are not due to the formation of complexes in solution. When mixtures of titanium tetrachloride and alkyl chlorides are exposed to direct daylight one product is titanium trichloride.

Investigations on the mechanism of cationic polymerisations indicated the need for information on the interaction of titanium tetrachloride with alkyl chlorides. Only two such studies have been reported. Nasu[1] determined the freezing-point phase diagram for titanium tetrachloride and carbon tetrachloride and found a pure eutectic system. Butta[2] investigated the liquid–vapour equilibrium of mixtures of titanium tetrachloride and *s*-tetrachloroethane, and reported no interaction. We wanted to find out whether titanium tetrachloride reacts with alkyl chlorides, because several alkyl chlorides co-catalyse the polymerisation of olefins by metal halides and the reaction $RCl + MCl_n \longrightarrow R^+MCl_{n+1}^-$, originally suggested by Pepper[3] for the system ethylene dichloride–stannic chloride, has so far not been substantiated directly. We chose to determine the freezing-point phase diagrams of the binary systems, as the technique is

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[1] Nasu, *Bull. Chem. Soc. Japan*, 1933, **8**, 195.

[2] Butta, *Chem. Listy*, 1956, **50**, 1646.

[3] Pepper, *Trans. Faraday Soc.*, 1949, **45**, 397.

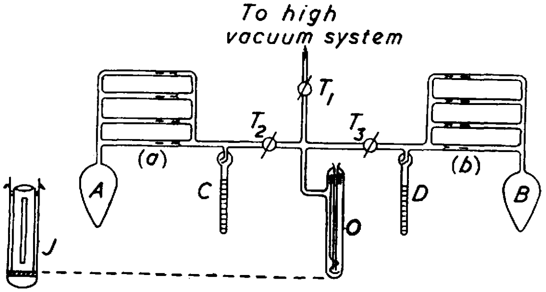
relatively simple, the results fundamentally unambiguous, and the information obtained related to the temperature range of most interest for cationic polymerisations.

EXPERIMENTAL

Materials.—Titanium tetrachloride (British Titan Products Ltd.) was filtered, twice fractionated, and sealed into phials; b. p. 134°/735 mm. Immediately before use the material was thrice fractionated *in vacuo*; triple point −23·9° (lit. −24·2°).

Methylene dichloride, ethylidene dichloride, *iso*propyl chloride, and chloroform were purified as recommended by Weissberger.[4] Immediately before use they were refluxed over calcium hydride and fractionated through a 60 cm. column packed with nickel-gauze rings, and then twice fractionated *in vacuo* from calcium hydride, generous head and tail fractions being rejected. Methylene dichloride, b. p. 40·0° (lit. 39·95°), n_D^{25} 1·4200 (lit. 1·4201), triple point −95·0° (lit. f. p. −96·7°). Ethylidene dichloride, b. p. 57·10° (lit. 57·31°), n_D^{25} 1·4146 (lit. 1·4145), triple point −96·0° (lit. f. p. −96·6°). *iso*Propyl chloride, b. p. 34·94° (lit. 34·80°), n_D^{25} 1·3753 (lit. 1·3755), triple point −117·0° (lit. f. p. −117·0°). Chloroform, b. p. 61·00° (lit. 61·00°), n_D^{25} 1·4431 (lit. 1·4427), triple point −62·5° (lit. f. p. −63·55°). All b. p.s are corrected. All literature values are those quoted by Weissberger.[4]

FIG. 1.



Ethyl chloride gas (I.C.I.) was passed through towers containing soda-lime, calcium chloride, and phosphoric oxide and condensed into a flask containing calcium hydride and twice fractionated *in vacuo*, generous head and tail fractions being rejected; triple point −133·4° (lit. f. p. −136·4°).

Methyl chloride gas (I.C.I.) was passed through towers containing aluminium chloride, soda-lime, and phosphoric oxide, thrice fractionated *in vacuo*, generous head and tail fractions being rejected at each stage, and stored as a gas; triple point −95·1° (lit. f. p. −97·72°).

Thermal Analysis.—*Apparatus.* The apparatus for the thermal analysis had to satisfy stringent conditions: (*a*) Freedom from adventitious moisture. (*b*) Complete absence of organic materials such as tap grease and of mercury, as these are attacked by titanium tetrachloride.

The apparatus is shown in Fig. 1. An observation vessel, *O*, contained a central thermocouple pocket and a reciprocating stirrer, operated by a solenoid (not shown). To obtain slow and uniform cooling, two concentric tubular jackets *J* of copper (inner) and Pyrex glass (outer) were fitted round the observation vessel during the determination of the cooling curves. The pure components were stored in the reservoirs *A* and *B* from which the burettes *C* and *D* could be filled *via* the magnetic " breakseals " (*a*) and (*b*). The all-metal valves T_1, T_2, and T_3 have been described.[5] The 5-point copper–constantan thermocouple, with the constant-temperature junctions in melting ice, was calibrated by the freezing points of carefully purified carbon tetrachloride, mercury, chloroform, and toluene.

In the earlier experiments the E.M.F. of the thermocouple was measured at half-minute intervals on a " Doran Mini " potentiometer. For later experiments a recording potentiometer

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[4] Weissberger, " Techniques of Organic Chemistry, Vol. VII—Organic Solvents," Interscience, London, 1955.

[5] Biddulph and Plesch, *Chem. and Ind.*, 1956, 569.

was constructed to record the E.M.F. continuously on a moving chart, *i.e.*, it drew the cooling curves automatically.

Operation.—The two components were distilled into the observation vessel from the burettes, which were kept in a thermostat of melting ice, by cooling it in liquid air. Before determining the cooling curves of the mixtures, those of the pure materials were always determined. When the required mixture had been made up in the observation vessel, it was allowed to melt, the stirrer was started, the cooling jackets placed in position, and the whole assembly then immersed in liquid air; the level of this was so adjusted that a cooling rate of 7—10° per min. was obtained. The recording of the E.M.F. of the thermocouple was started simultaneously and continued down to or below the eutectic temperature of the mixture. Many cooling curves were repeated two or more times and, in the later experiments particularly, warming curves were also obtained. After a satisfactory cooling curve had been obtained, a small portion of one component was distilled into the observation vessel. The cooling curve was then obtained as before. The procedure was repeated until the observation vessel became too full for satisfactory agitation (approx. 10 ml.). The contents were then either pumped off or distilled into special phials for further observation. The whole procedure was repeated, starting from the opposite end of the composition range. Finally, a third and sometimes a fourth series of measurements was undertaken.

Errors.—*Temperature of inflection.* The E.M.F. of the thermocouple could be read to an accuracy of 0·02 mv, which corresponds to 0·12°. The inflection points on the cooling curves could be located with an accuracy of ±0·5° in the most difficult cases.

Composition. The error in the composition is essentially determined by the precision with which the volumes can be measured and is greatest at the ends of the composition range. To measure this error, four samples of 0·2 ml. of methylene dichloride were distilled into weighed phials by a procedure identical with that used in the runs. From the results we calculated that the uncertainty in composition varies from 8% of the proportion of the scarcer component at the ends, to 0·3% at the centre of the composition range.

Vapour-pressure measurements. The vapour-pressure measurements were not intended to be very accurate, being rather to obtain the general shapes of the vapour pressure–temperature curves for mixtures of methylene dichloride and titanium tetrachloride in order to see whether they showed any inflections. Accordingly, an ordinary mercury manometer was connected to the observation vessel through an all-metal tap. The vapour-pressure measurements were made during the recording of the cooling curves by the automatic recorder, and the time of reading marked on the chart electrically. Thus, the pressure readings could be correlated with the appropriate temperatures. The vapour-pressure curve of pure methylene dichloride so obtained agreed satisfactorily with that in the literature. No interference by mercury vapour was observed: possibly it amalgamated with the metal tap.

Results

Thermal Analysis.—The interpretation of many of the cooling curves, mainly those of the type *A* in Fig. 2, was unambiguous. For many other curves it was less clear, as their shapes differed from the " ideal " shapes; typical examples are curves *B*, *C*, *D*, and *E* (Fig. 2). For curves of these types, the points marked (*a*) were chosen as giving a better indication of the first inflection than those marked (*b*), although expert opinion on this is not unanimous. The eutectic arrests were usually of the type shown at (*t*) in curves *A*, *B*, *D*, and *E* (Fig. 2). In certain cases, usually at the end of the phase diagram distant from the eutectic composition, they were of the type shown at (*d*) in curve *C* (Fig. 2), with a straight sloping branch in place of the true flat. The eutectic temperature was reasonably constant near the eutectic composition but tended to drift as the composition moved away from this.

With methylene dichloride, ethyl chloride, methyl chloride, and *iso*propyl chloride, a hump, shown at (*f*) in curve *B* (Fig. 2), was found after the first inflection point, which was normal, and before the eutectic, which was also quite normal. This phenomenon appeared only in the region of the phase diagram below the steeply falling portion of the liquidus curve. In this region very little solid is deposited for a given fall in temperature, so it is notoriously difficult to obtain accurate liquidus points by total thermal analysis. The inflection (*a*) is the true liquidus point and the hump (*f*), due to delayed precipitation, can be ignored.[6]

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[6] Axon (Metallurgy Dept., The University, Manchester), personal communication.

In several curves additional inflection points occurred such as those shown at α and β on curve *E* (Fig. 2). The change in slope was always small and, in view of the well-defined first inflection point (*a*), the equally well-defined eutectic (*t*), and the fact that these points did not occur in the warming curves, they were regarded as spurious.

FIG. 2.

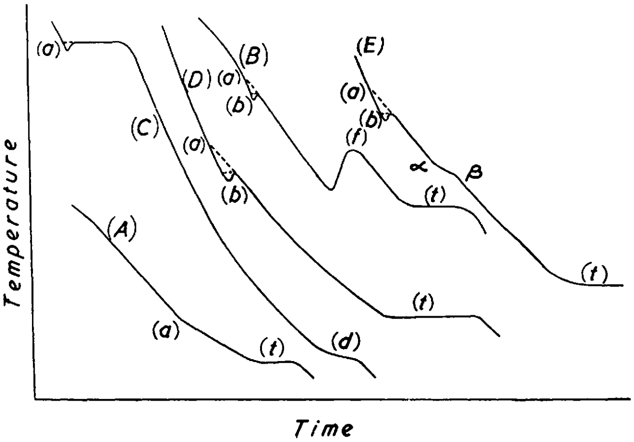
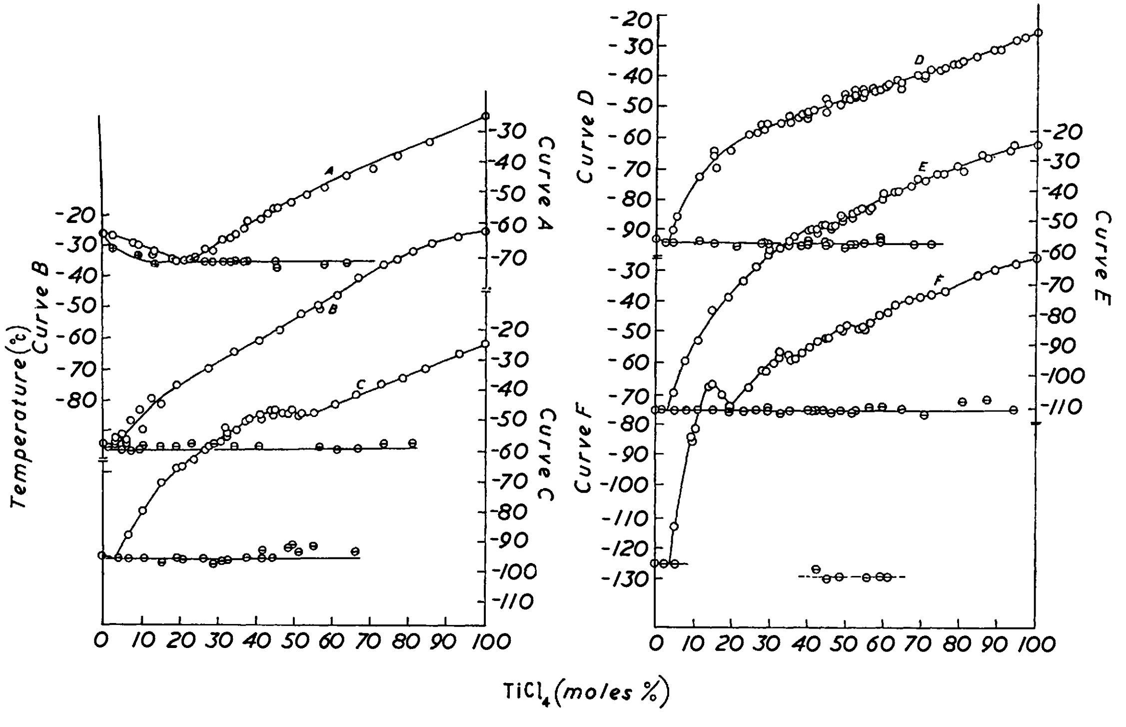


FIG. 3. *Phase diagrams of systems of* $TiCl_4$ *with A,* $CHCl_3$; *B,* MeCl; *C,* $Me{\cdot}CHCl_2$; *D,* CH_2Cl_2; *E,* Me_2CHCl; *F,* EtCl.



The presence of a liquidus point and a eutectic point in all the phase diagrams, with the exception of the left-hand branch of the chloroform–titanium tetrachloride diagram, rules out the possibility of solid solutions over a wide range of the phase diagrams; but near the extremities, solid solutions might have escaped detection.

Qualitative Observations.—The colour and appearance of the material were noted at the end of each cooling curve, and in some cases the cooling curve was interrupted to observe the solid formed at the first transition point. This always consisted of colourless plate-like crystals. In four of the six systems, yellow colorations were observed at the lower temperatures. This colour, when formed, was discharged on warming, and reappeared on cooling. The liquid phase was always colourless. With methylene dichloride, a thin yellow layer appeared at the top of an otherwise colourless solid mass at the eutectic temperature (−96·1°) in mixtures containing 5·43, 28·35, 52·10, 55·50, and 76·80 moles % of methylene dichloride severally. All other mixtures were colourless even below the eutectic temperature.

With ethyl chloride, a yellow colour appeared at approximately −105°, *i.e.*, above the eutectic temperature. This also disappeared as the temperature was raised and was found in mixtures containing 11·45, 33·99, 39·29, 41·58, 43·70, and 57·59 moles % of ethyl chloride. The mixture containing 72·00 moles % of ethyl chloride had a yellow layer on top of the solid mass at the eutectic temperature (−138·00°), and the mixture containing 34·88 moles % of ethyl chloride was yellow throughout at this temperature.

FIG. 4.

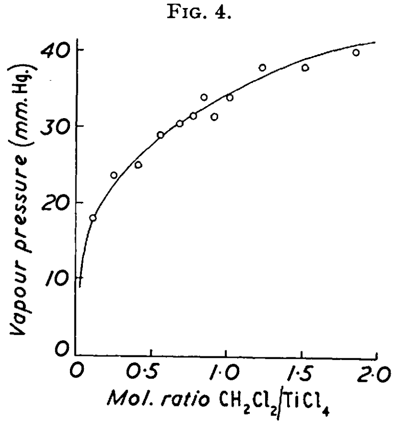
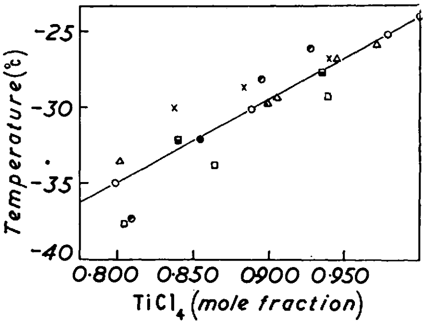


FIG. 5. *Solubilities.*



○ Ideal solubility of $TiCl_4$.

Solubility of $TiCl_4$, taken from the phase diagrams, in ● $CHCl_3$, ◓ MeCl, ⬓ $Me{\cdot}CHCl_2$, △ CH_2Cl_2, □ Me_2CHCl, × EtCl.

In the *iso*propyl chloride system, the yellow colour appeared at approximately −85° to −92° and was discharged on further cooling, the mixture being colourless at the eutectic temperature; the colour reappeared on warming to approximately −90°. This colour was noted in 26 runs, the composition varying from 6·20 to 97·80 moles % of *iso*propyl chloride.

With methyl chloride, the solid at the eutectic temperature was coloured throughout with mixtures containing more than 33·35 moles % of methyl chloride. Below this concentration, no colour was observed.

No colour changes were observed in the systems chloroform– and ethylidene dichloride–titanium tetrachloride.

Effect of Light.—When mixtures of titanium tetrachloride and various alkyl chlorides, sealed *in vacuo* into phials, were exposed to direct daylight a deposit was formed whose colour varied from bright purple to brown; this was due to lower chlorides of titanium, probably mostly the trichloride. We therefore kept all the pure components and the mixtures used for the thermal analyses in subdued light. The photochemical reaction is being investigated. Puxeddu[7] found that mixtures of various metal chlorides, including titanium tetrachloride, with diethyl ether yielded lower chlorides in sunlight.

Phase Diagrams.—The results obtained by thermal analysis of titanium tetrachloride–methylene dichloride, –chloroform, –ethylidene dichloride, –*iso*propyl chloride, and –methyl chloride are represented in the phase diagrams (Fig. 3) which show the following features (all records of moles % relate to the organic chloride).

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[7] Puxeddu, *Gazzetta*, 1929, **59**, 160.

(a) *Chloroform.* A simple eutectic system with solid solution formation on the chloroform-rich side of the eutectic composition. Eutectic temperature −71·4° and eutectic composition approximately 81·0 moles %.

(b) *Methyl chloride.* A simple eutectic system with eutectic temperature −97·0° and eutectic composition between 98·0 and 100 moles %.

(c) *Ethylidene dichloride.* In this diagram there is a flat hump with a peak near −45·7° and composition 55·0 moles %. There is a single eutectic at −97·25° and 96·0 moles %.

(d) *Methylene dichloride.* A simple eutectic system with the eutectic temperature −96·1° and the eutectic composition approx. 97·6 moles %.

(e) iso*Propyl chloride.* There is a flat hump with a peak near −64·5° and composition 44·0 moles %. The temperature of the single eutectic is −117·0° and the composition 98 moles %.

(f) *Ethyl chloride.* This diagram shows one pronounced peak and three smaller ones; the peak temperatures are −66·0°, −56·3°, −46·5°, and −36·3°, respectively, and the corresponding compositions 85·0, 65·6, 50·0, and 29·0 moles %.

Vapour-pressure Measurements on the System Titanium Tetrachloride–Methylene Dichloride.— The pressure–temperature curves had two inflection points, corresponding to the deposition of a solid phase and of the eutectic solid. In most cases the points of inflection were easily seen but in some, especially at the methylene dichloride-rich end of the phase diagram, they were very obscure. The liquidus curve and the eutectic line defined by these inflection points were identical with those of Fig. 3(*D*). An isotherm at −29·0° (Fig. 4) was constructed from the *P–T* curves covering the range 0—2 molar ratio $[CH_2Cl_2]/[TiCl_4]$; beyond this the points were too scattered to be significant. Fig. 4 shows that in this system there is no compound formation and thus supports the conclusions from the thermal analysis.

DISCUSSION

These phase diagrams are condensed phase diagrams as the effect of changing pressure has been ignored. Their interpretation is complicated by the fact that the presence of a hump or peak in a melting-point phase diagram does not necessarily indicate the existence of a compound in solution; such discontinuities may arise from the formation of superlattices.

The phase diagrams for titanium tetrachloride–methylene dichloride, –chloroform, and –methyl chloride are those of simple eutectic systems and show no evidence of interaction.

The systems titanium tetrachloride–ethylidene dichloride and –*iso*propyl chloride show a discontinuity in the liquidus curve. However, the occurrence in each diagram of a single eutectic covering the greater part of the concentration range, and the absence, in both systems, of a second eutectic at the temperature of the discontinuity, make it extremely unlikely that the discontinuities are due to compound formation in solution.

The phase diagram of the system titanium tetrachloride–ethyl chloride is completely different. In spite of its peculiar character, we present it with some confidence because it agrees very closely with earlier unpublished results obtained here by a similar but more primitive technique.[8] Although the peaks correspond closely to $[C_2H_5Cl]/[TiCl_4]$ ratios of 6 : 1, 2 : 1, 1 : 1, and 1 : 3, we do not consider that they can be attributed to the existence of compounds in solution because a very careful search failed to reveal any trace of the corresponding eutectics. Moreover, the eutectic in the vicinity of −133° occurs also in the central region of the phase diagram.

The ideal solubility of titanium tetrachloride can be calculated from the formula:

$$\log X_A = (-L_f/2{\cdot}303\boldsymbol{R})(1/T_0 - 1/T)$$

where X_A is the mole-fraction of titanium tetrachloride, by using $T_0 = 249{\cdot}1°\text{K}$ and $L_f = 2371{\cdot}6$ cal./mole.[9] This is shown in Fig. 5, together with the actual solubilities of titanium tetrachloride in the various alkyl chlorides taken from the phase diagrams.

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[8] Plesch and Rigbi, unpublished results.

[9] Clabaugh, Leslie, and Gilchrist, *J. Res. Nat. Bur. Stand.*, 1955, **55**, No. 5.

These points all lie very close to the ideal solubility curve, and this apparently nearly ideal behaviour over a considerable concentration range also suggests that there is no strong interaction in solution between titanium tetrachloride and these alkyl chlorides.

It thus appears that the ionogenic reaction suggested by Pepper [3] occurs either not at all or only so very slightly that its detection may require more subtle methods. Even without detailed analysis,[10] it is evident that the energetics of the ionisation are governed by the heterolytic bond-dissociation energy (θ) of the organic chloride.[11] The fact that the ionisation is not readily detectable in the systems investigated here, but is quite easily demonstrable in systems involving triarylmethyl halides,[12,13] is undoubtedly primarily due to the fact that for triphenylmethyl chloride θ is of the order of 125 kcal./mole, whereas for our chlorides it ranges from 165 kcal./mole for *iso*propyl chloride to 230 kcal./mole for methyl chloride. A preliminary investigation of the system titanium tetrachloride–*tert.*-butyl chloride ($\theta = 147$ kcal./mole) revealed a complex behaviour which may indicate ionisation. This work is continuing.

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[10] Plesch, *Z. Elektrochem.*, 1956, **60**, 325.
[11] *Idem*, " Simposio Internazionale di Chimica Macromoleculare," *Ricerca sci.*, 1955, 140.
[12] Fairbrother and Wright, *J.*, 1949, 1058.
[13] A. G. Evans *et al.*, *Research*, 1952, **5**, 535; *J.*, 1955, 206; 1955, 3104; 1957, 1020.