

color. Heating crystals of the type here considered necessarily leads to irregularity in the interatomic distances at any one instant. The unusually long distances cause light absorption farther in the red and therefore increasing color. This is observed very definitely in all cases. In the liquids the state is similar but even further developed. On vaporization, however, these relatively long bond distances become enormously less probable, because the molecules are closely bound internally and are usually very far apart. The intense absorption at long wave lengths should then disappear on vaporization. We have observed exactly this result for mercuric iodide.

While many of the arguments presented above lack rigor and the experimental data are incomplete, nevertheless, we believe that there is ample reason to regard this picture as substantially correct. Since these ideas are based upon such simple and direct observations, there seems little excuse for neglecting them in further work on these

substances. On the other hand, the question as to the extent of quantitative development remains entirely open for future consideration.

Summary

An idea mentioned by Bichowsky in 1918 is extended into the following postulate. When the color of a compound deviates from that of its constituent ions, then this may be taken as an index of the deviation from pure ionic bond character.

The properties of the iodides of some heavy metals are discussed from this point of view. Vapors, polar and non-polar solutions, complex ions, solids, and molten salts are considered. Deductions from this principle are found to be in agreement with other criteria.

It is also shown that these ideas have reasonable interpretation in terms of the excited electronic state responsible for light absorption, and in terms of the Franck-Condon principle.

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Maximum Boiling Mixtures of Chloroparaaffins with Donor Liquids

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This paper is concerned with azeotropic binary mixtures exhibiting maximum boiling points, each mixture consisting of a donor liquid and a liquid containing active hydrogen. The azeotropic behavior can be attributed to the formation of hydrogen bonds between the oxygen of the donor liquid, for example acetone, and the active hydrogen of the second liquid, for instance chloroform. The negative deviation from Raoult's law arises in such cases because neither chloroform nor acetone have any hydrogen bonds in the pure liquids, but hydrogen bonds are formed between the unlike molecules on mixing.

There are many pieces of evidence that some sort of bond is formed between chloroform and acetone, although there is no reason to expect hydrogen bonds in either of the pure liquids. There is a large evolution of heat and a decrease in volume on mixing, and there are minima in the fluidity-composition and vapor pressure-composition curves.^{1,2} Many other mixtures of this gen-

eral type, *i. e.*, a haloform as one component and a donor liquid, such as an ester, ketone, etc., as the other component, show similar pronounced negative deviations from the ideal solution laws.^{1,2} Gaseous haloforms, such as dichlorofluoromethane have abnormally high solubilities in donor liquids.³ The C-H absorption band in the spectra of chloroform and bromoform is shifted when these liquids are mixed with donor liquids.^{4,5} Thus it seems that not only hydrogen atoms attached to nitrogen, oxygen or fluorine are capable of forming hydrogen bonds, as in ammonia, water, hydrogen fluoride and many related compounds, but also hydrogen atoms attached to carbon if there are some electronegative atoms or groups attached to the carbon.

Lecat⁶ lists about forty maximum boiling azeo-

(3) Zellhoefer, Copley and Marvel, *THIS JOURNAL*, **60**, 1337 (1938).

(4) Gordy, *J. Chem. Phys.*, **7**, 163 (1939).

(5) Buswell, Rodebush and Roy, *THIS JOURNAL*, **60**, 2528 (1938).

(6) Lécat, "L'Azeotropisme," M. Lamartin, Brussels, 1918. This work was followed by a series of 25 supplementary lists of azeotropes published in various journals, 1926-1929. Most of the azeotropes in all of Lécat's publications are also listed in Timmermans, "Les Solutions Concentrées" (ref. 1), which is more widely available than Lécat's book.

(1) Timmermans, "Les Solutions Concentrées," Masson et Cie., Paris, 1936.

(2) Hildebrand, "Solubility," A. C. S. Monograph 17, 2nd ed., Reinhold Publishing Corp., New York, N. Y., 1936.

trope of the type under consideration, in which the donor liquids are esters, ketones or aldehydes. The present work shows that ethers and tertiary amines function as donor liquids as well as ketones, aldehydes and esters, and greatly extends the number and types of chloroparaffins which contain active hydrogens.

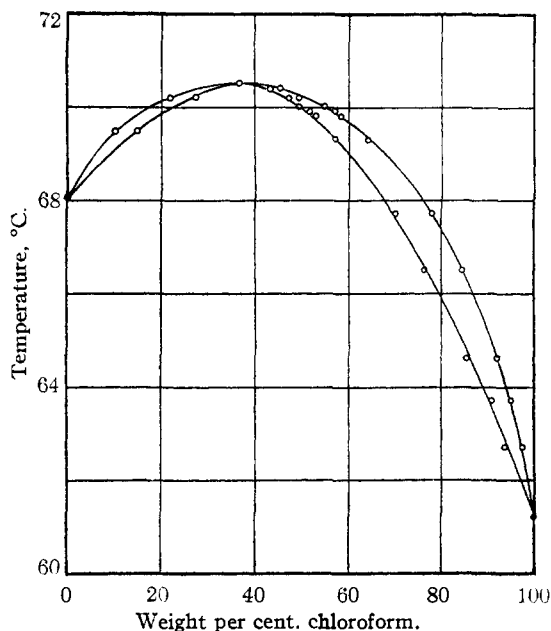


Fig. 1.—Boiling point *vs.* composition for chloroform-isopropyl ether mixtures.

Experimental

The experimental arrangement consisted of a 50-ml. flask with an extra wide, water-jacketed side arm tube (1 cm. i.d.) placed perpendicular to the neck of the flask. The flask was provided with a thermometer through a cork. Various compositions of the mixture being studied were placed in the flask and boiled gently with the water-jacketed side arm turned up at a 45° angle acting as a condenser. The flask was placed over a hole in an asbestos sheet, and the flame was adjusted so that there was no overheating. The temperature was noted when it became constant, and then the side arm was turned down and 4 or 5 drops of distillate taken off. The index of refraction of the liquid and distillate were measured on an Abbe refractometer. The compositions were then read off a curve previously prepared for each system. These data sufficed to draw the complete temperature-composition phase diagram (boiling point diagram). Many of the maxima were very flat, but the maximum point could be narrowed down very closely by observing the compositions between which the relative magnitudes of the indices of refraction of liquid and distillate were interchanged. Short range thermometers calibrated at the National Bureau of Standards were used, and stem corrections were applied. The liquids used were purified by rectification in a column of 20-25 theoretical plates.

Figures 1 and 2 give two complete liquid-vapor phase diagrams, as examples. However, the principal point of interest in each mixture was the qualitative fact of whether or not it formed a maximum boiling mixture, so that the complete phase diagram and the exact temperature and composition of the maximum point were not determined in most cases. When both liquids had nearly the same boiling point, particular care was taken to make determinations near both ends of the composition range. Most of the mixtures had boiling point rises of one to four degrees above the higher boiling component, but frequently the rise was only a few tenths of a degree, and sometimes only one tenth of a degree, in which case particular care was necessary in observing the temperatures. In the two examples shown in Figs. 1 and 2 the rises are 2.5 and 1.3°, respectively. The largest rise recorded in maximum azeotropes of this type is 7.45°, shown by the system dichlorobromomethane-ethyl propionate.⁵

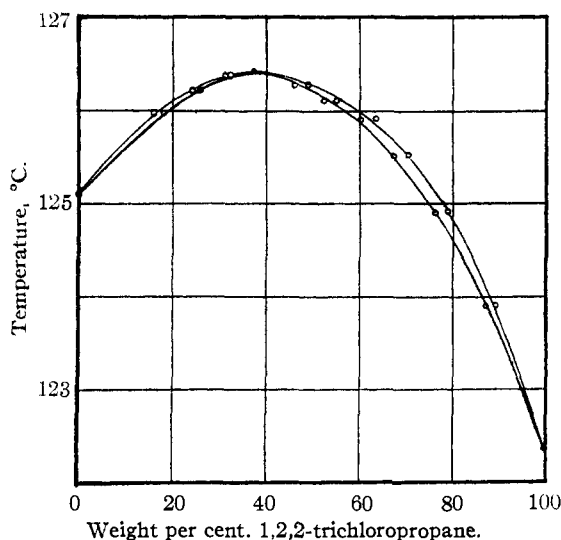


Fig. 2.—Boiling point *vs.* composition for 1,2,2-trichloropropane-*n*-butyl acetate mixtures.

Results

Thirty-five new maximum boiling mixtures between chloro-paraffins and donor liquids were found. These are combined with twenty-one such mixtures given by Lécát (indicated by superscript L) in the following complete list. After each chloroparaffin the donor liquids are listed in increasing order of boiling points of the pure components (given in parentheses).

Methylene chloride (40°) with ethyl ether (35°), propylene oxide (35°), methylal (42°), propionaldehyde (50°), isobutylene oxide (50°).

Chloroform (61°) with methylal (42°), propionaldehyde (50°), isobutylene oxide (50°), ethyl formate^L (54°), acetone^L (56°), methyl acetate^L (59°), isobutyraldehyde (63°), isopropyl ether (68°), *n*-butyraldehyde (76°), methyl ethyl ketone^L (80°).

1,1-Dichloroethane (57°) with isobutylene oxide (50°), acetone^L (56°), methyl acetate (59°).

1,2-Dichloroethane (84°) with methyl ethyl ketone (80°), propyl formate^L (81°).

1,2,2-Trichloroethane (114°) with dioxane (101°), pyridine (115°), ethyl butyrate (121°).

1,1,2,2-Tetrachloroethane (146°) with mesityl oxide^L (130°), ethyl valerate^L (135°), isobutyl propionate^L (137°), isoamyl acetate^L (142°), *n*-propyl *n*-butyrate^L (143°), ethyl chloroacetate^L (144°), isobutyl isobutyrate^L (147°), methyl *n*-caproate^L (150°), *n*-heptaldehyde (155°), cyclohexanone^L (156°), isobutyl *n*-butyrate^L (156°), furfural^L (161°).

Pentachloroethane (162°) with *n*-heptaldehyde (155°), cyclohexanone^L (156°), methylheptanone^L (173°).

1,1-Dichloropropane (90°) with triethylamine (89°), isopropyl acetate (90°).

1,2-Dichloropropane (97°) with ethyl propionate (99°), dioxane (101°), methyl *n*-propyl ketone (102°).

1,1,3-Trichloropropane (148°) with *n*-amyl acetate (148°), methyl *n*-amyl ketone (150°).

1,2,2-Trichloropropane (122°) with di-isopropyl ketone (124°), *n*-butyl acetate (125°), ethyl carbonate (126°).

1,2,3-Trichloropropane (156°) with methyl phenyl ether (155°), *n*-heptaldehyde (155°), cyclohexanone^L (156°).

1,1,2,2-Tetrachloropropane (153°) with methyl *n*-amyl ketone (150°), methyl phenyl ether (155°), *n*-heptaldehyde (155°), cyclohexanone (156°).

1,1,2,3-Tetrachloropropane (180°) with benzaldehyde (179°).

1,2,2,3-Tetrachloropropane (164°) with di-isobutyl ketone (165°).

A great many mixtures, which might possibly have given maximum azeotropes, were tried and found to give normal boiling point curves, *i. e.*, no azeotropes. In almost all these cases the boiling point differences between the components were greater than those that did give azeotropes, for example:

Methylene chloride (40°) with methyl formate (32°), ethyl formate (54°), acetone (56°).

Chloroform (61°) with ethyl ether (35°), propylene oxide (35°), triethylamine (89°), dioxane (101°).

1,1-Dichloroethane (57°) with propionaldehyde (50°), isobutyraldehyde (63°), di-isopropyl ether (68°).

1,2,2-Trichloropropane (122°) with pyridine (115°), isopropyl *n*-butyrate (128°), cyclopentanone (129°).

Discussion

For the formation of a maximum boiling mixture it is necessary that there be a minimum in the vapor pressure-composition curve. The occurrence of such minima is determined by (1) the magnitude of the deviation from Raoult's law, which in these cases is presumably due to the number and strength of the intermolecular hydrogen bonds formed, (2) the difference between the boiling points of the components, (3) the temperature range concerned. Obviously a much smaller deviation from Raoult's law is required to cause a minimum in the vapor pressure curve if the boiling points of the components are close together. For instance, chloroform (61°) will reach down to methylal (42°) and up to methyl ethyl

ketone (80°) to form maximum boiling mixtures, but ethyl ether (35°) and dioxane (101°) are too far away, even though there are large negative deviations from Raoult's law in these latter cases. Thus, the donor liquids that will give maximum boiling mixtures with a given chloroparaffin are centered about the boiling point of the chloroparaffin. These cover a range of 38° in the case of chloroform, but only 15° in the case of methylene chloride, leading to the conclusion that the hydrogen in chloroform is more active than both those in methylene chloride.

All maximum boiling mixtures of this type in the literature^{1,6} involve ketones and esters and one aldehyde (furfural) as the electron donor liquid. This paper demonstrates the phenomenon for ethers, several additional aldehydes and two tertiary amines (triethylamine and pyridine), all of which have oxygen or nitrogen atoms with lone pairs of electrons.

This paper demonstrates that methylene chloride and several polychloropropanes, besides chloroform and other liquids listed by Lécat, contain hydrogens capable of forming hydrogen bonds. Such hydrogens will be referred to as active or activated hydrogens, and the chlorines, etc., will be called the activating atoms or groups. Activating atoms or groups attached to the carbon to which the hydrogen is attached will be called alpha, those attached to the next carbon will be called beta, etc.

The hydrogens on chloroform, bromoform, and mixed haloforms such as dichlorobromomethane, dichlorofluoromethane, etc., should be the most active, having three alpha halogens. However, two chlorines in the alpha position activate the hydrogen as in methylene chloride. 1,1-dichloroethane, 1,1-dichloropropane, and 1,1,3-trichloropropane. A single alpha chlorine atom does not seem to be enough for activation since 1-chloropropane, 2-chloropropane, 1-chlorobutane, and 1,3-dichloropropane all failed to give maximum boiling mixtures with esters and ketones boiling only one or two degrees away. However, one alpha and one or more beta chlorines will activate the hydrogen since 1,2-dichloroethane, 1,2-dichloropropane, 1,2,2-trichloropropane, 1,2,3-trichloropropane and 1,2,2,3-tetrachloropropane all formed maximum boiling mixtures with nearby donor liquids. Thus it seems that chlorine atoms in the beta position have some activating effect, but much less than those in the alpha position.

The activating effect of the X groups on the hydrogen in CHX_3 can be placed in the following order: $\text{H} < \text{R} < \text{CH}_2\text{CH}_2\text{Cl} < \text{CH}_2\text{CHCl}_2 < \text{CH}_2\text{CCl}_3 < (\text{CH}_2\text{Cl}, \text{CHRCl}, \text{CR}_2\text{Cl}) < (\text{CHCl}_2, \text{CRCl}_2) < \text{CCl}_3 < \text{Cl}$, where R stands for an alkyl group or chloroalkyl group if there are no chlorines on the first carbon atom. On this basis the chloromethanes could be placed in this order of hydrogen bond forming power: $\text{CH}_3\text{Cl} < \text{CH}_2\text{Cl}_2 < \text{CHCl}_3$, and the chloroethanes in this order: $\text{CCl}_3\text{CH}_3 < \text{CH}_3\text{CH}_2\text{Cl} < \text{CH}_2\text{ClCH}_2\text{Cl} < \text{CCl}_3\text{-CH}_2\text{Cl} < \text{CHCl}_2\text{CH}_3 < \text{CHCl}_2\text{CH}_2\text{Cl} < \text{CHCl}_2\text{-CHCl}_2 < \text{CCl}_3\text{CHCl}_2$. The relative position of 1,1,1,2-tetrachloro- and 1,1-dichloroethane in this list is uncertain, *i. e.*, whether one alpha chlorine or three beta chlorines would have the greater activating effect. Such a list for the chloropropanes would be too complicated to attempt in the light of present data.

Two anomalous minimum boiling mixtures were observed, 1,2-dichloroethane with triethylamine and pentachloroethane with furfural, for which no explanation seems apparent.

The results of this paper delineate the general rules for the formation of maximum boiling mixtures, and literally hundreds of additional examples of this type could be predicted. Lécat⁶ lists a number of maximum boiling mixtures of bromoform, dichlorobromomethane and 1,2,3-tribromopropane with ketones and esters, which would have been expected in the light of the results with the chloroparaffins. While the data on brominated compounds are meager, it seems that chlorine is a more effective activating atom than bromine. This would be expected from general considerations of electronegativity. The hydrogen bond forming power of ethers, ketones, aldehydes and esters appeared to be approximately the same in these experiments, except that cyclic ethers, such as propylene oxide, isobutylene oxide and dioxane, seemed to be exceptionally active.

Besides halogenated paraffins Lécat lists trichloroethylene, chloral, benzal chloride, *p*-dichlorobenzene and 1,3,5-trichlorobenzene as forming maximum boiling mixtures with nearby donor liquids. In all these molecules, there are hydrogen atoms which have chlorine atoms in either the

alpha or beta position so that their activation seems plausible.

One of the points of interest in the formation of maximum boiling mixtures is the possibility of using them to separate difficultly separable mixtures. For example, 1,3-dichloropropane and 1,2,2-trichloropropane are very difficult to separate by distillation since they boil at 120.4 and 122.35°, respectively, and, furthermore, they form a shallow minimum boiling mixture. However, 1,2,2-trichloropropane forms a maximum boiling mixture with *n*-butyl acetate (125.05°), which boils at 126.4° and contains 38% by weight of 1,2,2-trichloropropane (Fig. 2), while 1,3-dichloropropane does not form one. This difference might be used to separate these two chloropropanes by distillation of a suitable ternary mixture. However, the course of distillation in such a system is too complex to make any definite predictions. Other such mixtures are 1,1,1,2-tetrachloropropane (153°) and 1,1,2,2-tetrachloropropane (153°), and 1,1,1,3-tetrachloropropane (165°) and 1,1,3,3-tetrachloropropane (165°), where the second chloropropane in each pair should form hydrogen bonds with a suitable donor liquid much more strongly than the first chloropropane.

Summary

A systematic study has been made of the formation of maximum boiling mixtures of the type exemplified by the system chloroform-acetone, and thirty-five new maximum boiling mixtures are reported. Not only do haloforms exhibit this phenomenon, but also chlorinated paraffins with only two alpha chlorine atoms, such as methylene chloride, 1,1-dichloroethane, 1,1-dichloropropane and 1,1,3-trichloropropane, or with one alpha and one or more beta chlorine atoms, such as 1,2-dichloroethane, 1,2-dichloropropane, 1,2,2-trichloropropane, 1,2,3-trichloropropane and 1,2,2,3-tetrachloropropane. A wide variety of esters, ketones, aldehydes, ethers and tertiary amines are shown to function as donor liquids. These maximum boiling mixtures are attributed to the formation of hydrogen bonds between the active hydrogen atom or atoms of the chloroparaffin and the oxygen or nitrogen of the electron donor liquid.

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