Characterization of Organic Compounds in the Liquid State by Means of Vapour-Liquid Equilibria of Added Test Substances

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This note describes a general method for the characterization of organic liquids by measuring the vapour-liquid equilibria of a number of volatile test substances simultaneously added to the organic liquid. The result is obtained in the form of a set of partitions, or a partition spectrum, which constitutes a characterization of the liquid compound.

Obviously, this characterization is based on weak matter-matter interactions between the test substances and the compound under investigation. A variety of intermolecular interactions are involved among others van der Waals forces, dipole-dipole interactions, hydrogen bonding, and complex formation.

In order to obtain the partition spectra the following has to be considered:

(i) The selection of the test substances is of importance for the specificity of the characterization, and it seems convenient to include test substances of a highly different polarity and with different active groups.

(ii) The interaction between the test substances and the organic liquid should not involve any reactions leading to new compounds.

(iii) Generally, it would be possible to select among a very large number of test substances but in practice this number is reduced by the actual facilities for measuring the concentration of each test substance without any disturbing interference, especially from the liquid compound under study.

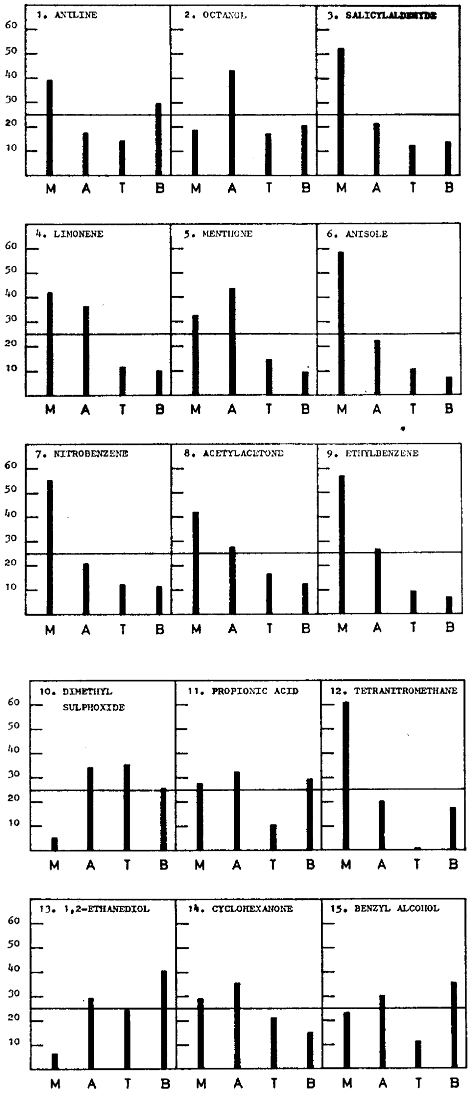
(iv) In order to avoid saturation effects and obtain the vapour-liquid equilibria of the individual test substances with a minimum of mutual interference, the amount of test substances should be kept as low as possible relatively to the amount of the compound under study.

(v) The temperature of the system has to be controlled, and it must be ensured that the vapour-liquid equilibria have been established before the analysis of the test substances is performed.

The partition spectra can be obtained by measuring the concentration of the test substances either in the vapour, in the liquid phase, or in both of them. In the experiments here described the relative concentrations of the test substances were measured in the vapour phase by the technique of gas chromatography. The experiments were performed with a test set composed as follows: methanol:acetone: tetrahydrofuran:benzene, 2:1:1:1 by weight. 5 μl of this test solution was incubated with 1.0 ml of the liquid organic compound (1:200) in a 100 ml Erlenmeyer flask equipped with Teflon valves and previously flushed with dry nitrogen. The mixture was magnetically stirred for a certain time at controlled temperature. A small amount of the vapour was then transferred by the aid of a gas sampling valve to the column of a gas chromatograph equipped with a flame ionization detector, and analyzed for the relative concentration of the four test substances (column: 1.5 m × 1/4″ O.D. Stationary phase: Chromosorb 102 at +180°C, Carrier gas: N_2). The area under the peaks was measured by an electronic integrator. The composition of the test mixture in the vapour state was also analyzed and measured without the presence of any organic liquid compound and the result normalized to 4 × 25 per cent. The results obtained with different organic liquids are given relative to this normalization (the horizontal line in the diagrams is at 25 %).

In order to ensure that the partition of the test substances between the vapour phase and the liquid under study had reached an equilibrium, two samples were prepared for each liquid: (a) one starting with the test solution dissolved in the liquid, and (b) one with the test solution completely vapourized in the Erlenmeyer flask before the introduction of the liquid. Generally, it was found that the relative composition of the test substances in the vapour phase of samples (a) and (b) was equal within the experimental error after about 2 h at +20°C.

With the column and the test substances so far used the method could be applied to liquid compounds with boiling points above about +120°C without any disturbing overlaps on the chromatogram of the test substances by the vapour of the compound under study.



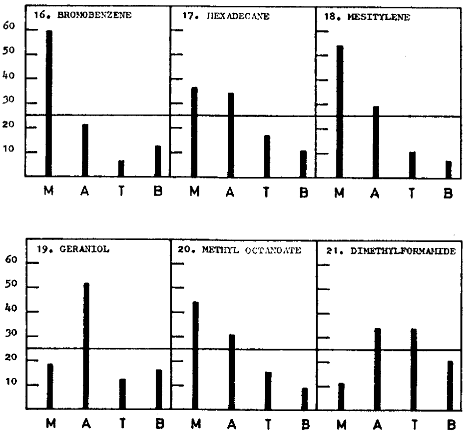


Fig. 1. **Partition spectra of the indicated liquid compounds. Test substances: M = methanol, A = acetone, T = tetrahydrofuran, B = benzene. The rectangles give the percentage amount of the test substances present in the vapour phase above the liquids after equilibration at +20°C. The horizontal line at 25 % indicates the composition of the set of test substances in the vapour phase in the absence of any liquid organic compound.**

The results obtained with some different organic liquids at +20°C are shown in the diagrams of Fig. 1. In this rather arbitrarily selected collection of compounds the relative concentration of the four test substances, *i.e.* the partition spectra, are all different from each other. However, closely related spectra were obtained with anisole (6) and nitrobenzene (7), and with ethylbenzene (9) and mesitylene (18), respectively.

Some characteristic patterns could be recognized among the partition spectra. Thus, aromatic compounds such as ethylbenzene (9) and mesitylene (18) exhibited a very high relative concentration of methanol in the vapour phase corresponding to a very low relative absorption of this substance by the organic liquid. On the other hand, tetrahydrofuran and benzene were absorbed to a great extent, leaving only a small concentration in the vapour phase. These findings reflect an interaction between test substances and liquid compounds of low polarity. The introduction of substituents on the benzene ring such as CH_3O (6), NO_2 (7), and Br (16) changed the pattern by exhibiting a somewhat larger absorption of acetone. Benzene derivatives with substituent groups such as NH_2 (1), CHO+OH (3) and Br (16) gave rise to partition spectra exhibiting a lower absorption of benzene compared with the other derivatives of benzene.

Alcohols showed partition spectra characterized by a relatively large absorption of methanol compared with that of acetone (2, 13, 15, 19). A similar pattern was also shown by propionic acid (11), menthone (5), and cyclohexanone (14). A very high absorption of methanol was observed with dimethyl sulphoxide (10) and dimethyl formamide (21). Obviously, a common feature of these cases is an interaction of the polar hydroxyl group of methanol with polar groups of the liquid compound.

A number of compounds such as limonene (4), acetylacetone (8), hexadecane (17), and methyl octanoate (20) showed partition spectra of a type rather similar to that observed with ethylbenzene (9) and mesitylene (18).

Tetranitromethane (12) gave rise to a very characteristic partition spectrum exhibiting a highly selective absorption of tetrahydrofuran. This finding is consistent with the formation of an electron-donor-acceptor complex between tetrahydrofuran and tetranitromethane.

The influence of the temperature on the partition spectra was also studied for some of the organic liquids of this series. As expected, the deviation from the 4×25 per cent composition of the test vapour was found to increase at lower temperatures, and decrease at higher ones, as compared with the results obtained at $+20°C$.

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Optical Activity Developed by Preferential Racemization of One Enantiomer in Racemic Cr(III) $(ox)_3^{3-}$ Induced by Irradiation with Circularly Polarized Light

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The idea of using *circularly polarized light* in photolysis to produce optical activity is not new. In 1925 Zocher and Coper[1] reported that on exposing a colloidal silver halide, they obtained a "circular double refractive" colloid of silver. In 1929 Kuhn[2] showed that a partial activation could be obtained by photodecomposition of racemic 2-bromopropanoic acid ethylester with circularly polarized light. A few similar experiments were performed at about the same time.[3–5] The reaction mechanism was not investigated, however, in any of these studies, and especially in the last mentioned case,[5] in which "an asymmetric catalysis" is proposed to take place in a mixture containing only *non*-dissymmetric species, the effect seems dubious.

In this laboratory a generator for circularly polarized light has been built, and a series of photolyses using this type of light have been performed on oxalates of iron(III), cobalt(III), and chromium(III) and on diamine complexes of cobalt(III).[6] The intention of the experiments has been to find a photodecomposition which could be studied at a wavelength where the actual compound has a high circular dichroism (and a low absorption) giving higher light-absorption for circularly polarized light for one of the two diastereomers in a racemic mixture. For several reasons reactions involving a net change (decomposition, ligand exchange, *etc.*) are not very suitable for this purpose. One reason is that the resolution yield reaches its maximum at a conversion of about 50 % and then decreases. Another reason is the change in absorbance due to the decrease in concentration of the reacting species or to a high absorptivity of the product. Thus it was found when repeating the experiment of Kuhn in this laboratory, that the absorbance (270—300 nm) first decreased indicating indeed a decomposition of the