Anomalous Columns Produced from Non-Hydrogen Bonded Liquids

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Summary Residual columns of an extremely involatile nature have been produced by concentrating liquid columns condensed from the saturated vapours of carbon tetrachloride, benzene, and toluene in microscopic capillaries by a procedure successfully used to produce polywater and residues from other hydrogen-bonded liquids.

ANOMALOUS columns have previously been observed to form in microscopic capillaries exposed to the vapour of water, methanol, propanol, acetic acid, and acetone.[1-6] The formation of these columns may possibly be explained in terms of hydrogen-bonding.[2,4,5,7] We report the formation of anomalous columns using the non-hydrogen-bonded liquids carbon tetrachloride, benzene, and toluene and consider the implication of this work to the current polywater controversy.

The anomalous columns were produced by modifying[8] our basic method[6] in which a bundle of microscopic capillaries is suspended above a sample of normal liquid in a closed, but ungreased, unevacuated desiccator kept at room temperature during the growth process. Precautions were taken to minimize possible surface contamination. The outside surfaces and the bore of the stock Pyrex tubing from which the capillaries were drawn was washed alternately with acetone and distilled water and rinsed thoroughly with distilled water prior to drawing. The desiccator was washed in turn with benzene, acetone, distilled water, hot chromic acid and rinsed with large volumes of distilled water. Since a grease seal was not employed, contamination from vacuum grease[9] was avoided. The capillaries were suspended about 5 cm above the surface of the liquid by clean fine nichrome wires and at no time came in contact with the walls of the container. In order to minimize any contamination of the residual columns by water-vapour, columns of these liquids were grown in an inert water-vapour free atmosphere. This was accomplished in one case (C_6H_6) by placing the desiccator in a dry bag continuously flushed with N_2 dried over $Mg(ClO_4)_2$ and in another case (CCl_4) by placing the desiccator inside another larger one containing P_2O_5, with the whole assembly inside a dry bag filled with Ar dried over $Mg(ClO_4)_2$. Dry spectrophotometric grade liquids were used. Surgical gloves were worn whenever the cleaned apparatus and capillaries were handled.[10] The vacuum system used to pump on the capillaries was equipped with a liquid N_2 trap to prevent backflow of pump oil vapour.

The ultra-dry preparation techniques and the observed high temperature behaviour of these materials indicate that they are not polywater. Columns of polywater discolour and leave dark brown residues when heated *in vacuo* (10^{-2} Torr) to 360 °C. This behaviour, similar to that observed while attempting to take laser Raman spectra,[11] was not exhibited by any of the residual columns obtained from non-hydrogen-bonded liquids. These residual columns appear unchanged when heated *in vacuo* to 300 °C and evaporate cleanly at 360 °C.

Neither hydrogen-bonding nor other commonly accepted types of polymer-bonding explains the formation of anomalous columns of CCl_4, C_6H_6, and C_7H_8. The various impurity explanations[10,12] that have been suggested for polywater are primarily inorganic in origin (*e.g.*, Si or Na) and hardly seem appropriate for these organic liquids. Our results show that the anomalous liquid phenomenon is more general than has been previously supposed. If the explanation lies in dissolved impurities, then a wide variety of substances rather than a specific one must be responsible. An overall understanding of the anomalous liquid phenomenon can only be obtained by investigating the nature of several anomalous liquids, especially including ones obtained from non-hydrogen-bonded and essentially non-polar liquids.

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