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PREVIEW

**PROPERTIES OF THE BINARY SYSTEM ALCOHOL-
BENZENE AND THE VARIATIONS DUE
TO THE PRESENCE OF WATER**

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PROPERTIES OF THE BINARY SYSTEM ALCOHOL- BENZENE AND THE VARIATIONS DUE TO THE PRESENCE OF WATER

INTRODUCTION

The problems concerned with solubilities and with the nature of solutions are of fundamental importance in chemistry. The dissociation theory of Arrhenius is being modified as studies of concentrated solutions of electrolytes are being carried out. The generalizations of Van't Hoff, Raoult, Nernst and Henry concerning dilute solutions of non-electrolytes are now in general use. However, the nature of concentrated solutions is little understood and general relationships are simply approximations and often untrustworthy. The properties of large numbers of liquid systems have been studied by investigators in order to obtain a physical or chemical viewpoint of these problems.

Many of these studies have been concerned with chemically unrelated substances and so they have led to few important generalizations. In this laboratory, a rather ambitious program has been laid out, involving the study of the physical properties of closely related compounds, as of the members of homologous series, and the changes in these properties as related to the mutual solubilities of these compounds. The lower alcohols and the lower molecular weight aromatic hydrocarbons and mixtures of these with and without water have been studied.¹⁻⁶

In one of these studies,¹ an anomalous behavior of ethyl alcohol-benzene mixtures was noted. Contractions in volume in the alcohol-rich mixtures and expansions in the benzene-rich mixtures were observed. Other workers⁷⁻⁸ have called attention to this same phenomenon. However, J. Barbaudy⁹ found no contraction in the entire composition range from pure alcohol to pure benzene. Schreder¹⁰ and Kowalski and Modzelewski¹¹ report the same results as Barbaudy although Kowalski and Modzelewski did not include the temperature at which their work was carried out so no satisfactory check could be made. The presence of water in the alcohol was shown to be a possible explanation of these apparent contradictions, since alcohol with 10% water in it showed no contraction and a greater expansion throughout the entire composition range. It was thought that if very dry alcohol were used, a contraction throughout the whole range might be obtained. The work of Baker on very dry substances has led to results which are even more surprising. Part of the aim of this work was to test this conjecture and also to find what relationships could be found between the nature of the solution and the properties of the solution and of its components.

Various properties of the binary system alcohol-benzene have been previously measured. Vapor pressures,¹² freezing points,² and solubilities¹³ have been studied quite completely. The heats of mixing, the specific heats, and the fluidities of mixtures have been the subjects of the experimental study here as these have been used as indications of molecular complexity in solution. Heats of mixing should be evidence of some process occurring in the solution and its magnitude should be of importance in estimating reactivity. Fluidity or viscosity studies have been used by several investigators^{14,15} as an indication of the size and complexity of the molecules making up the solution. Bramley¹⁶ gives evidence of a relationship between viscosity and compound formation although he points out that that evidence alone is quite untrustworthy.

Because of the widely different properties of water, alcohol and benzene, it was expected that the presence of water in the alcohol might exaggerate certain properties and in this manner might shed some light on the problems of concentrated solutions of non-electrolytes.

MATERIALS

The benzene was of the C. P. quality obtainable from Mallinkrodt Chemical Company. It was first washed with concentrated sulfuric acid, then with a dilute solution of sodium carbonate and finally with water. The benzene was next dried with metallic sodium and distilled. The initial and final tenths of the distillate were discarded. The middle fraction of the distillate was fractionally crystallized and kept dry over sodium. The product had a freezing point of 5.4° C., a boiling point of 80.4° C., and the density of the different samples used at 25° C. compared favorably with the value, .8734 gm/cc. given by the International Critical Tables.

The ethyl alcohol was refluxed over calcium oxide for periods of time varying from 50 to 75 hours. It was distilled into an all-glass distilling apparatus. When working with very dry alcohol, it was distilled from this all-glass apparatus and its density determined immediately preceding the measurements.

The dry alcohol to which reference is made throughout this paper refers to alcohol whose density corresponded to 99.99% -100.00% alcohol as given by the tables of alcoholimetry of Osborne, McKelvy and Bearce.¹⁸ The percentage of the water in the wet alcohol was determined by a comparison of the densities with the compositions given by these tables of alcoholimetry.

The water used in the mixtures and for calibration purposes was laboratory distilled water which was redistilled from an alkaline permanganate solution. The still was a pyrex flask fitted with a block tin condenser.