ON THE FORMATION OF LAYERS IN MIXTURES OF ACETIC ACID AND BENZENE.

BY C. E. LINEBARGER.

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DUCLAUX[1] states in reference to mixtures of benzene and acetic acid that "at temperatures from 15°–20° these two liquids are soluble in every proportion with each other. If a mixture of equal volumes of the two substances be cooled to about 11°, the mixture, until then homogeneous, becomes troubled all of a sudden and separates into two nearly equal layers; 0.2° of interval of temperature at most separate the two states." Duclaux then proceeds to give the results of his analyses of the two layers, as well as other results and discussions.

This account has been universally accepted, and it has passed into standard text-books that mixtures of benzene and acetic acid present at certain temperatures the phenomenon of layer-formation. This is not, however, according to fact; mixtures of *very pure* acetic acid and benzene do not separate into layers even at temperatures as low as 20°. Duclaux's observations were not made on binary mixtures of acetic acid and benzene, but upon *ternary* mixtures of *water*, acetic acid, and benzene.

A certain theoretic importance attaches itself to this question. In the course of an investigation of the vapor-tensions, both partial and total, published a few months ago in this Journal, the results found with mixtures of benzene and acetic acid were such as to preclude the possibility of layer-formation in this case. Accordingly, I have carried out some experiments on the exposure of mixtures of acetic acid, benzene, and water to varying temperatures to ascertain under what conditions of concentration and temperature, layer-formation takes place.

A cylindrical phial provided with a good cork was filled about two-thirds full of mixtures of acetic acid[2] and benzene.[3] The tube was enclosed in another larger tube, so as to prevent any possible contamination of the contents of the first tube with the baths or freezing mixtures. Several mixtures of different concentrations were exposed to a temperature of —20°, but in no case did there occur a separation into layers.

1 *Ann. chim. phys.* [5], 7, 267, *1876*.

2 Purified by repeated crystallization until melting-point was not perceptibly changed no matter what the relative proportions of solid and liquid acid was.

3 Purified by repeated treatment with strong sulphuric acid, repeated crystallizations and distillation over sodium.

14.6225 grams of a mixture containing 7.6037 grams of acetic acid and 7.0188 grams of benzene were placed in the tube described above and a few centigrams of water were added successively, the mixture being exposed to the temperature of a mixture of ice and salt, *i. e.*, about —20°, after each addition of water. Not until 0.7226 gram of water had been added did there occur a separation into layers, which persisted even at 0°, but disappeared a few degrees above.

Now, Duclaux was fully aware that the presence of water rendered it possible to cause layer formation even at temperatures above 11°, for he writes: "It is indeed not necessary to have recourse to cold to obtain the separation, and the state of unstable equilibrium in which these liquids are, can be destroyed by the addition of a third substance, as, for example, water.

"A single drop of water suffices to cause a mixture of 10 cubic centimeters of benzene and of 10 cubic centimeters of acetic acid to become troubled.

"Acetic acid crystallizing at 14° always gives a limpid solution with benzene. If it crystallizes only at 12° the mixture of equal volumes remains troubled."

Now, acetic acid melting at 14° contains not inconsiderable quantities of water, so that the behavior just described by Duclaux is what is to be expected under the circumstances. If Duclaux had taken the trouble to raise the melting-point of his acid by a few fractional crystallizations, and had employed this purified acid, there would have been one less error and its rectification encumbering the pages of chemical journals.

SCHEME FOR THE IDENTIFICATION OF ACETANILIDE, PHENACETINE, QUININE SULPHATE, ETC.

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THE test made by boiling the substance with caustic potash and chloroform is one of the most important in the scheme given below. It is known as the "carbylamine reaction" or "isonitrile test," and is common to those compounds which are classed as *primary amines* ($R—NH_2$).

$$R-NH_2 + Cl_3HC + 3KOH = R-N \equiv C + 3KCl + 3H_2O.$$