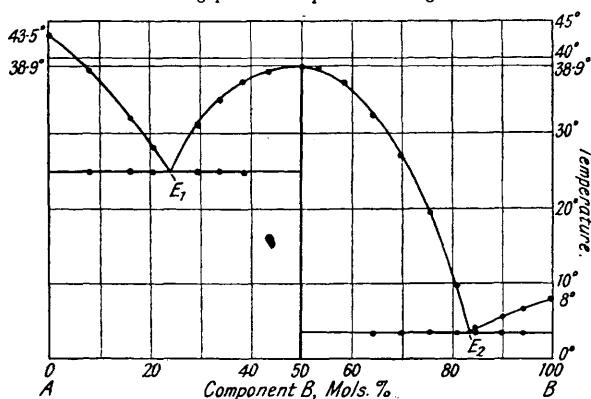


### 181. Some Binary Systems of Organic Compounds. Thermal Analyses and Specific Refractivities.

By W. R. BURNHAM and W. M. MADGIN.

As a preliminary to further studies of equilibrium constants in terms of activities (Glass and Madgin, J., 1934, 1292 and earlier), six binary systems (Figs. 1, 2, and 3), not hitherto reported, have been investigated by the methods of thermal analysis. Baud (*Bull. Soc. chim.*, 1913, 13, 435) has reported the f. p.'s of mixtures of acetic acid with chlorobenzene

FIG. 1.  
Freezing point-composition diagram.



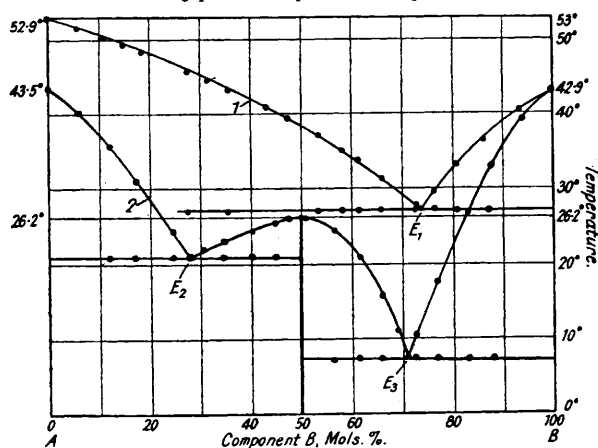
A. *p*-Toluidine :  $E_1 = 24\%$  (mol.) of B ( $25.2^\circ$ ).  
B. *o*-Chlorophenol :  $E_2 = 83.6\%$  (mol.) of B ( $3.6^\circ$ ).

(covering a range of composition from 100% to 65% of acetic acid by weight), but his results are insufficient to show the type of the system. Pushin and Matavulj (*Z. physikal. Chem.*, 1931, 158, 290, and subsequently) have studied the variation of refractive index with composition in binary systems as a means of typifying the systems, and similar studies have been included in the present investigations.

#### EXPERIMENTAL.

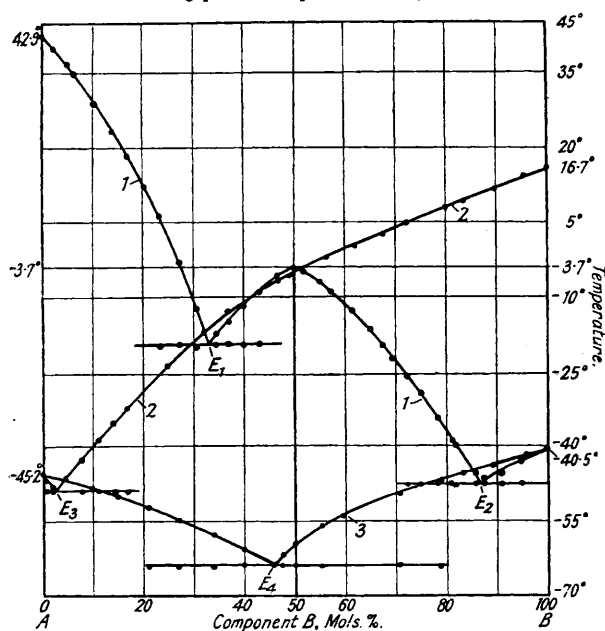
The starting materials were "Purified" reagents. Their further purification has been described previously (Glass and Madgin, *loc. cit.*); except that acetic acid was purified by freezing and fractional distillation (Bousfield and Lowry, J., 1911, 99, 432), chlorobenzene was dried over phosphoric oxide and fractionally distilled, and *p*-chlorophenol was fractionally frozen (down to a f. p.  $42.5^\circ$ ) and the solid phase was separated and fractionally distilled, b. p.  $216^\circ/740$  mm. : all operations upon the last substance were carried out in a current of dried air.

FIG. 2.  
Freezing point-composition diagrams.



1. 2.  
A. p-Dichlorobenzene. p-Toluidine.  
B. p-Chlorophenol. p-Chlorophenol.  
 $E_1 = 73.4\%$  (mol.) of B ( $27.2^\circ$ ).  
 $E_2 = 28\%$  (mol.) of B ( $21^\circ$ ).  
 $E_3 = 71\%$  (mol.) of B ( $7.4^\circ$ ).

FIG. 3.  
Freezing point-composition diagrams.



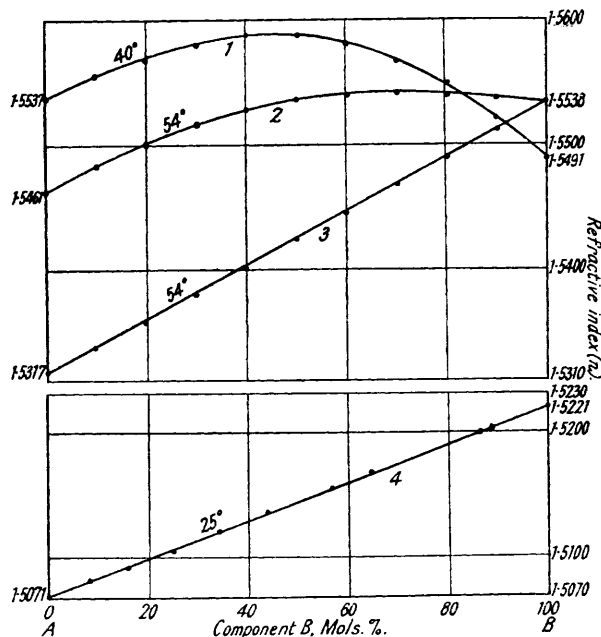
1. 2. 3.  
A. p-Chlorophenol. Chlorobenzene. Chlorobenzene.  
B. Pyridine. Acetic Acid. Pyridine.

$E_1 = 33.4\%$  of B ( $-19.5^\circ$ );  $E_2 = 86.5\%$  of B ( $-47.3^\circ$ );  $E_3 = 3\%$  of B ( $-48.5^\circ$ );  
 $E_4 = 46\%$  of B ( $-63.5^\circ$ ).

The thermal analyses of the binary systems now reported were carried out as previously described (Glass and Madgin, J., 1934, 260), but with the system pyridine-chlorobenzene it was necessary to cool with liquid air in the determination of f. p.'s below  $-55^{\circ}$ .

Of the six systems now reported (Figs. 1, 2, and 3), three are of the simple eutectic type, viz., *p*-dichlorobenzene-*p*-chlorophenol, pyridine-chlorobenzene, and acetic acid-chlorobenzene. The other three systems (*p*-toluidine-*o*-chlorophenol, *p*-toluidine-*p*-chlorophenol, and *p*-chlorophenol-pyridine) definitely indicate the formation of stable equimolecular compounds. When possible this was confirmed by isolating solid phases from numerous melts during the thermal analyses. The contaminating solutions were removed by pressing on porous plates, and the resulting solids had the f. p.'s of the corresponding compounds.

FIG. 4.  
Refractive index-composition diagrams.



- |                            |                         |                            |                |
|----------------------------|-------------------------|----------------------------|----------------|
| 1.                         | 2.                      | 3.                         | 4.             |
| A. <i>p</i> -Toluidine.    | <i>p</i> -Toluidine.    | <i>p</i> -Dichlorobenzene. | Pyridine.      |
| B. <i>o</i> -Chlorophenol. | <i>p</i> -Chlorophenol. | <i>p</i> -Chlorophenol.    | Chlorobenzene. |

Pushin and Matavulj (*Z. physikal. Chem.*, 1933, 164, 80) state that the system *p*-chlorophenol-pyridine cannot be determined by thermal analysis, owing to the persistence of supercooling in most mixtures, but their refractive-index determinations show the existence of an equimolecular compound. When an equimolecular mixture of *p*-chlorophenol and pyridine is prepared at the ordinary temperature, considerable heat is developed and a homogeneous liquid formed. This liquid becomes excessively viscous when cooled below  $-20^{\circ}$  but it shows no tendency to solidify; however, when kept at about  $-8^{\circ}$  for several hours, it solidifies and the solid then has a definite m. p., viz.  $-3.7^{\circ}$ . A mobile liquid is formed on melting.

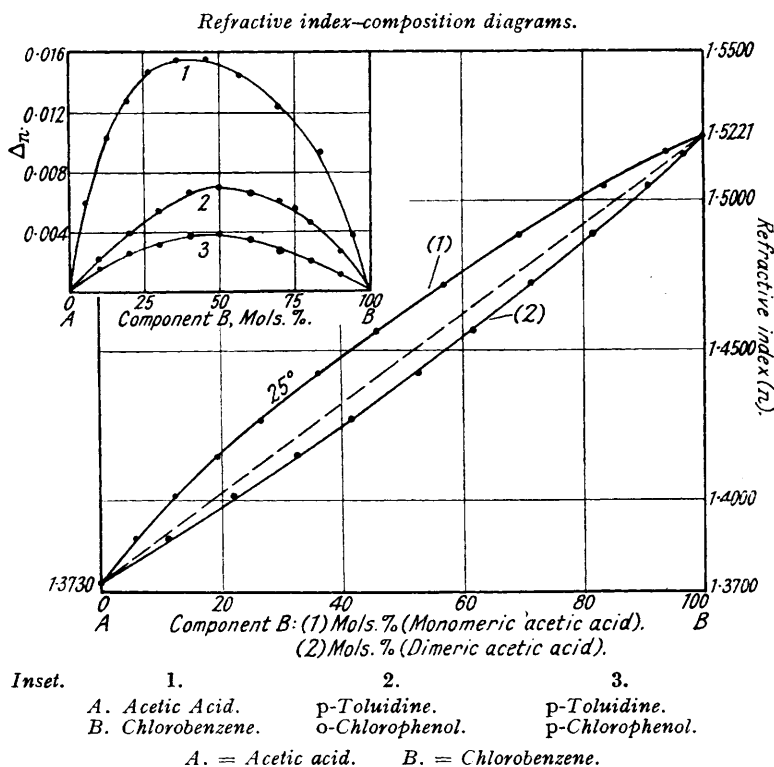
With mixtures containing 0–30% or 90–100% of pyridine the f. p.'s were readily determined, generally by inoculation with pure components, but no eutectic arrests were observed even on cooling to quite low temperatures. By using the solid equimolecular compound (cf. above) as inoculating phase, it was possible to determine eutectic arrests and to investigate the complete diagram (Fig. 3).

The two systems illustrated in Fig. 2 support Kendall and Booge's conclusion (*J. Amer. Chem. Soc.*, 1916, 38, 1712) that, when a compound is formed (*p*-toluidine with *p*-chlorophenol), the f. p. of a pure component (*p*-chlorophenol) is depressed more than when a simple eutectic system is formed.

*Refractive Indices.*—The variation of refractive index with composition has been examined

for the different systems, over a range of temperature, by means of an Abbé refractometer. Sodium light was employed. Apart from a general decrease of refractive index with rising temperature, no notable variations with temperature were found. Representative results are shown in Figs. 4 and 5, but no significance attaches to the particular temperatures selected.

FIG. 5.



#### DISCUSSION.

The thermal analyses seem to point definitely to the conclusions already stated, but the system acetic acid–chlorobenzene merits comment. This is a eutectic system, and the form of the curve (Fig. 3) is the same as that reported by Kendall and Booge (*loc. cit.*) for the system chloroacetic acid–benzene. These authors consider such curves to indicate an ideal solution.

The refractivity results shown in Fig. 4 accord with the views of Pushin and Matavulj (*loc. cit.*), *viz.*, that in systems where compound formation occurs, the refractivity curve shows positive deviations from the mixture law (cf. curves 1 and 2), but with eutectic systems, the refractivity curves follow the mixture law or show negative deviations. Curves 3 and 4 show no deviations. The results in Fig. 4 are similar if weight or volume compositions are used instead of molecular compositions.

When refractivity is plotted against simple molecular composition (monomeric) for the system acetic acid–chlorobenzene (Fig. 5), positive deviations are observed although this is a eutectic system. The inset of Fig. 5 shows the deviations in this system compared with those in two systems involving compound formation. Baud (*loc. cit.*) considers that acetic acid exists as double (dimeric) molecules in chlorobenzene, and, by using molecular compositions of mixtures in terms of dimeric acetic acid, curve 2 of Fig. 5 is obtained. The curves for both weight and volume compositions practically coincide with this, and Pushin and Matavulj (*Z. physikal. Chem.*, 1932, **162**, 415) anticipated that curves for molecular

and for weight compositions should be similar. The mixture-law curve (broken line, Fig. 5) evidently corresponds to molecular compositions in terms of mixed monomeric and dimeric acetic acid. This probably represents the statistical average of the compositions, and the relative proportions of each form will vary continually with dilution. The possibility of higher polymerides is not excluded, and pure acetic acid is no doubt a complicated mixture of various polymerides: its vapour is widely regarded as composed largely of dimeric molecules at the ordinary temperature.

Further work on similar eutectic systems is needed.

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