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Thin Layer Chromatographic Separation of the Products of Reaction between Phenol & Acetone

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The products obtained by reacting phenol with acetone have been separated by thin layer chromatography employing kieselguhr plates impregnated with dimethyl formamide [10 per cent (vol./vol.) in acetone] and cyclohexane-ethyl acetate-acetic acid (125 : 25 : 4·5) as the eluting solvent. The purity of bisphenol-A obtained depends on phenol-acetone molar ratio and the amount of hydrogen chloride (condensing agent) used. Bisphenol-A of maximum purity is obtained with phenol-acetone molar ratio 4 : 1 and hydrogen chloride concentration 0·3 mole/litre.

PHENOL condenses with acetone in the presence of strong acids to form bisphenol-A [2,2-bis (4-hydroxyphenyl) propane]. Earlier work[1-3] on bisphenol-A deals mostly with the method of preparation and purification of the product. Formerly the purity of this compound was mostly assessed by its colour and melting point. Only recently thin layer[4,5] and gas liquid[6,7] chromatographic techniques have been used for detecting the individual impurities in bisphenol-A. In the present investigation, the thin layer chromatographic partition technique has been applied for the rapid detection and identification of individual impurities in bisphenol-A produced under different conditions so as to establish the optimum conditions for the production of high purity bisphenol-A.

The separation of bisphenol-A was effected on kieselguhr plates impregnated with dimethyl formamide using cyclohexane-ethyl acetate-acetic acid mixture as the eluting solvent.

For the preparation of the solvent, 30 ml. of ethyl acetate (E. Merck) was added to 150 ml. of cyclohexane (LR; BDH distilled) and the mixture transferred to a 500 ml. separating funnel. To this mixture were added 50 ml. of a 72 per cent (vol./vol.) aqueous solution of dimethyl formamide and the contents were shaken vigorously for 10 min. The contents were allowed to stand overnight. The upper layer (150 ml.) was then taken in a developing jar to which was also added 4·5 ml. glacial acetic acid (E. Merck) for defining the spots and the mixture was kept for saturation of the chamber for about 2 hr.

Kieselguhr plates (20 × 10 cm.) were coated with slurry made from 6 g. kieselguhr (E. Merck), 0·5 g. plaster of Paris (E. Merck) and 14 ml. water, using a laboratory-made applicator to give a layer of 0·3 mm. thickness. The plates were baked at 105-10°C. for 45 min. and then cooled in a desiccator.

The cooled plates were then impregnated in a 10 per cent (vol./vol.) solution of dimethyl formamide in dry acetone and then kept under a fan for a few minutes to remove acetone. The samples were applied as a 1 per cent solution in acetone on impregnated plates with amounts varying from 10 to 15 γ with glass capillaries along a line 2 cm. above the end of the plates and at a distance of 1·5 cm. between the spots. Development was carried out in ascending manner. When the solvent reached a distance of 14-15 cm. in 25-30 min., the plates were taken out and kept in air to evaporate most of the solvent. The phenols were detected by spraying the chromatogram first lightly with diazotized sulphanilic acid[8] and then with a 25 per cent solution of sodium carbonate. The spots were visible for more than 5 min.

The standards used for measuring and comparing R_f values were phenol (I), 2-(4-hydroxyphenyl) propan-2-ol (II), 2-(4-hydroxyphenyl) propene (III), 2-(4-hydroxyphenyl) propane (IV), 2,2-dimethyl 4(*p*-hydroxyphenyl) 4-methyl chroman (V), 2,2-bis-(4-hydroxyphenyl) propane (VI), and 2-(2-hydroxyphenyl), 2(4-hydroxyphenyl) propane (VII). The R_f values were 0·535, 0·535, 0·90, 0·90, 0·64, 0·236 and 0·363 respectively. Phenols II and III could not be detected in a reaction mixture of phenol and acetone because they had R_f values equal to those of I and IV respectively. The formation of these compounds in a reaction mixture of phenol and acetone was, however, assumed by several workers[9,10].

The effect of excess of phenol on the purity of bisphenol-A was studied by condensing phenol with acetone at 45°C. in varying initial molar ratios using dry hydrogen chloride as the condensing catalyst and thioglycollic acid (1 ml. per mole of acetone) as promoter. Dry hydrogen chloride was first dissolved in acetone (1 mole) to saturation and then added to the requisite amount of phenol; the mixture was kept saturated with acid by passing through it dry hydrogen chloride from time to time. After 24 hr, samples were collected for chromatographic analysis. The excess of phenol was removed by steam distillation and the product isolated by the method of Vladimir[11]. The yield of the product (m.p. 153-57°C.) varied from 80 to 85 per cent.

Chromatographic analysis of the product showed that when the phenol-acetone molar ratio was 2:1, the number of spots was 10 (m.p. 153-55°C.) and they were due to I, IV, V, VI and VII and unidentified compounds with R_f values 0·99, 0·97, 0·78, 0·48 and 0·16 respectively. When the ratio was 3:1, the number of spot was 9 (m.p. ~155°C.) and they were due to I, IV, V, VI and VII and unidentified compounds with R_f values 0·99, 0·78, 0·48 and 0·16; when the ratio was 4:1, the number was 6 (m.p. ~156-57°C.) and the spots were due to I, IV, V, VI, VII and a compound with R_f 0·48; when the ratio was 5:1, (m.p. 156-57°C.), the number of spots was the same as with 4:1 ratio; with 10:1 ratio (m.p. 156-57°C.) the spots were again the same as with 4:1 ratio. It follows that the use of higher molar ratio of phenol to acetone gives high purity bisphenol-A, the optimum ratio being 4:1. This substantiates the observation of Aurenge *et al.*[5].

To investigate the effect of the amount of hydrogen chloride as condensing agent, 0·3, 0·78 and 1·0 mole respectively of hydrogen chloride per litre of the phenol-acetone mixture were used. The condensation was carried out in the presence of thioglycollic acid as promoter whose concentration was kept constant at 0·078 mole/litre. The details of the procedure have been reported in another communication[12]. From the chromatogram of the products, it was found that with 0·3 molar acid concentration, the spots (4) were due to I, V, VI and VII; at 0·78 molar acid concentration, the spots (8) were due to I, IV, V, VI, VII and products with R_f values 0·99, 0·48 and 0·16; and at 1·0 molar acid concentration the spots (9) were due to I, IV, V, VI, VII and products with R_f values 0·99, 0·78, 0·48 and 0·16 respectively.

A total time of 45 min. is needed for the detection and identification of impurities by this technique.

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