

Interaction Studies in Urea-Phenol and Urea-Resorcinol Eutectics

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The phase interaction studies of urea-phenol (U-P) and urea-resorcinol (U-R) were carried out as a function of their per cent composition in their proportionately prepared solutions. With reference to time ($t = 0$), a thermo-constancy ($\Delta T = 0$) condition of stabilizing interactions for a fixed composition of urea-phenol and urea-resorcinol solutions were observed, thermally constant temperature values determined from cooling statistics of U-P and U-R solutions were plotted against their individual per cent compositions. From these phase diagrams eutectically thermodynamic values were derived and the results were explained in terms of eutectic coordinates.

INTRODUCTION

Some of the physico-chemical aspects of urea-phenol and urea-resorcinol solution systems of different compositions were studied by viewing their physico-chemical state at varying temperature with reference time interval. The phase variation, an important thermodynamic (dispersing) function of miscibly soluble urea-phenol and urea-resorcinol systems was assumed to be a vital tool to investigate their interacting and non-interacting molecular re-orientations in urea-phenol and urea-resorcinol solutions. The observations on the structural interactions and an initiation of crystallization of urea-phenol and urea-resorcinol organic solutions were of current interest for an expertise, in a search of new organic crystalline substances of specific physico-chemical nature. These formulations seem suitable for their use in the field of biotechnology, detergents, dyes, drugs, paints, biomedical science, adsorption techniques, selective separating methods, occulants, insecticides, pesticides, fertilizers, food and fuels. It was indicated to be proved as a model method and an authentic yardstick to look into the various structural formulations (aberrations) undergone in an intermediate step of the compound preparation in organic solutions.

EXPERIMENTAL

The required chemicals were heated for 24 h before use and urea was of BDH grade and phenol and resorcinol were of AnalaR grade of highest degree of purity. A newly designed Man Phavie cell (MPC) was used for phase viewing with

temperature and time of urea-phenol and urea-resorcinol condensed compositions taken into sample container.

A spiral stirrer and a thermometer of $\pm 0.1^\circ\text{C}$ accuracy were inserted into a sample container, a cylindrical vessel. The A vessel fitted with glass hooks was mounted on a perforated supporting thermocouple, its base stuck to a base of B vessel and the vessel B was used as an air cooler, the inner space of which was filled with cooled air currents. The air cooler was kept in ice bath of 20 L capacity.

The urea-phenol and urea-resorcinol samples in different proportions were taken into a sample container, the vessel A.

These solid samples were allowed to melt smoothly before bring them in contact with air cooler B and the vessel A containing melt of samples was fixed into air cooler B and allowed to cool down slowly. The decreasing temperature was measured with time and the data were processed.

TABLE-1
EUTECTIC COORDINATES OF UREA-PHENOL AND UREA-RESORCINOL
CONDENSED SYSTEMS

| S. No. | System | Eutectic I | | Eutectic II | | EQE | |
|--------|-----------------|-------------------------|--------|-------------------------|--------|-------|----|
| | | ET ($^\circ\text{C}$) | EC (%) | ET ($^\circ\text{C}$) | EC (%) | EC | ET |
| 1. | Urea-phenol | 60.0 | 58.5 | 31.0 | 90.0 | 61.0 | 62 |
| 2. | Urea-resorcinol | 84.5 | 23.5 | 83.5 | 78.5 | 101.5 | 50 |

ET = Eutectic temperature, EC = Eutectic composition

EQE = Equilibrated compound formation eutectic

RESULTS AND DISCUSSION

The heat capacity dependent¹ phase formation of U—P and U—R was seen to be attributed to their structural interactions and the results were discussed in terms of eutectic coordinates such as eutectic temperature, eutectic composition for urea-phenol and urea-resorcinol binary phase diagrams.

The drawn graphs between measured temperature data *vs.* time for urea-phenol and urea-resorcinol organic solutions were assumed to show the crystallization² of these solutions of specific structural interactions and of peculiar heat capacity.

The nature and tendency of the graphs (Figs. 1, 2) was seen to be a function of van der Waals and the structural forces governed by urea-phenol and urea-resorcinol proportions and the evaluated structural stabilizing temperature and composition values (Table-1, Figs. 3, 4) were seen to be dependent on interacting³ orientation.

In case of urea-phenol solutions the observed I eutectic composition (Table-1) was seen to be less stable (flat point) (Fig. 3) with respect to intermolecular⁴ forces (observed flat point in urea-phenol eutectic curve, Fig. 3, was assumed to be temporary compound formation⁴) in comparison to I eutectic (Fig. 4) of urea-resorcinol solutions (sharp deep points were assumed to be the result of

X, Y Scales are common for all the graphs
Graphs starting from 0.0 on X axis as a ref. point

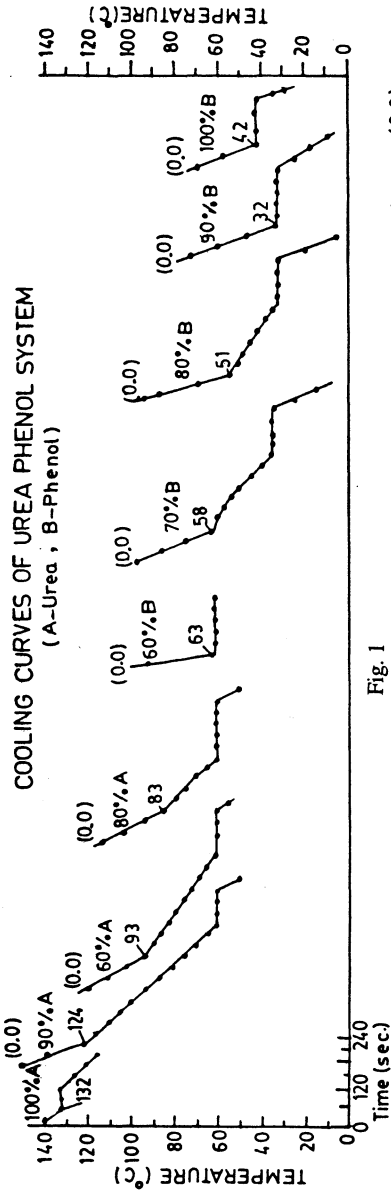


Fig. 1

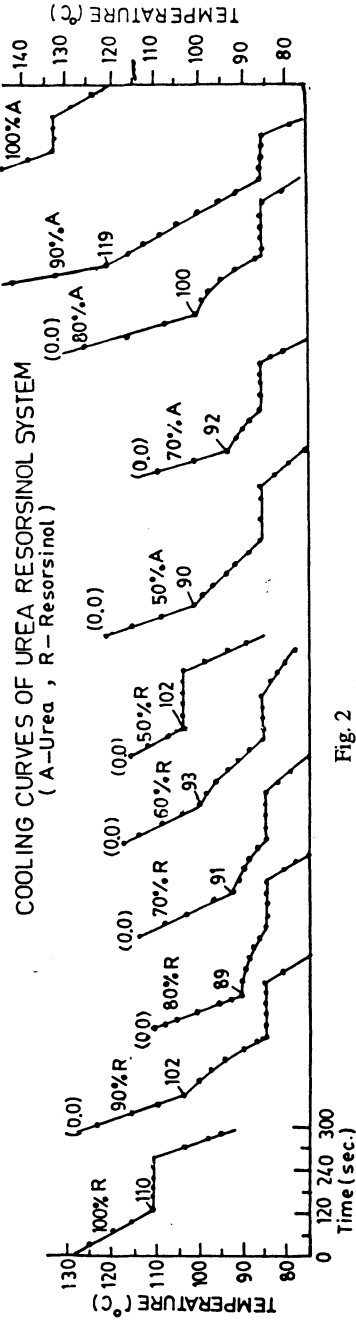
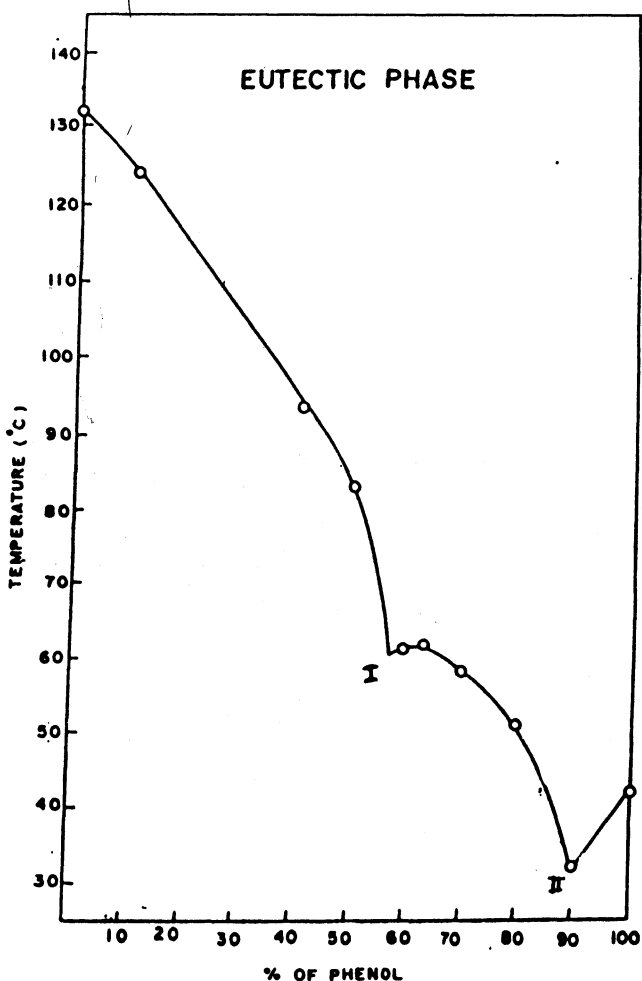


Fig. 2

strong intermolecular interactions between urea and resorcinol molecules in their organic solutions).

The difference in the nature of I eutectic of urea-phenol and urea-resorcinol appeared to depend on the formation of U-P type weakly hydrogen-bonded network between urea (U) and phenol (P) molecules which was further seen to tends towards a more stable eutectic formation between urea and phenol and it was assumed that the urea and phenol proportionate compositions in organic solution were the driving constitutionalising⁵ agencies for the development of the structural interactions resulting in a chemical crystal (eutectic compound) of specific heat content and the II (Figs. 3, 4) eutectic a new structural stability attained at 31°C in 90% phenol in urea-phenol organic solutions was seen to be more stable than that of its I one.

Eutectic temperature at 84.5°C in 23.5% and at 83.5°C in 78.5% resorcinol



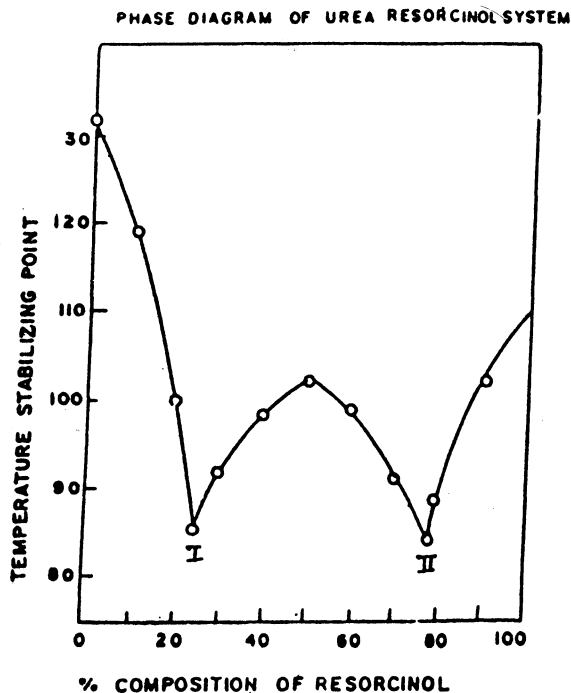


Fig. 4

composition (Fig. 4) in urea-resorcinol was seen to be because of higher heat holding nature of stronger compound formations which were seen to be equilibrated at 101.5°C (Fig. 4). The presence of two eutectic stability points (Figs. 3, 4) in these systems appeared to be attributed to the different heat holding nature of the two structures. Diagram 3 was observed to show the tending shape of I eutectic towards II one and in a state of low temperature it was not seen to be an equilibrated⁶ structure, while for urea-resorcinol I eutectic characteristic coordinates of urea-resorcinol structural formulation were observed to be equilibrated with II eutectic (Fig. 4). The sharp shape of the cooling curves (crystallization curves) of I and II eutectic of U-R was seen to be correlated to the stronger structural interaction between U-R which further go on dissolving in each other under higher temperature and larger proportion of each other in the solution, even in such varied experimental condition, they appeared to maintain their structural identity.

The molecular interactions between U-P were observed to evolve some amount of heat which appeared to counterbalance the solution's molar heat dissipation, a marking temperature halt with time interval. An attained hydrogen bonded network of U-R structural interactions in their organic solutions was observed to oppose the further molecular twisting of the already formed bonds and the continuous cooling operation of the sample solution was marked to search a new

stabilizing molecular interaction (Figs. 1, 2) as a function of their proportions in the solution system.

But the structural stabilization between urea-resorcinol was seen to take place in a state of lower heat content (Fig. 4) and was marked to retain a stability condition for a longer time (Fig. 2) than that of urea-phenol (Fig. 1). It was observed to be attributed to the extra —OH (hydroxyl) functional group in resorcinol which was seen to bring structural stability at low heat content (Fig. 2).

The urea-phenol system was seen to be a model one for its sample structural stabilities as a function of their composition (Figs. 1, 3). The per cent composition (stabilities) of phenol (10%, 20%, 30%, 40%) in 100% urea-phenol mixtures was seen to considerably affect the stabilization of reactions (Figs. 1, 3) while for urea-resorcinol solution systems (Figs. 2, 4) (10%, 20%, 30%, 50%) resorcinol in urea-resorcinol solution systems were observed to have structural stabilities comparatively at lower temperatures (Figs. 2, 3) but at 50% each urea and resorcinol was seen to have got an equilibrium between the critical or eutectic compositions of 60%.

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