

Notes

Zone Melting Studies of Organic Eutectic Mixtures: Naphthalene-Catechol & Naphthalene-*p*-Chloronitrobenzene Systems

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The effective distribution coefficient, direction of solute transference and the separation efficiency have been determined for the naphthalene-catechol and naphthalene-*p*-chloronitrobenzene eutectic systems using zone melting technique.

ZONE melting was originally developed by Pfann¹ as a refining process taking the advantage of difference in solubilities in the solid and liquid states. Yue^{2,3} has determined the effective distribution coefficient and the effect of various factors, like the number of passes, temperature and the concentration on the effective distribution coefficient for various alloys by means of zone melting technique. Such studies for organic eutectics are limited although many other studies have been made⁴. We report in this note the results of our studies on the naphthalene-catechol and naphthalene-*p*-chloronitrobenzene eutectic systems. Parameters such as direction of solute transference, separation efficiency and the effective distribution coefficient have been determined.

Naphthalene and catechol were purified by repeated distillations and finally by zone melting process. *p*-Chloronitrobenzene was purified by fractional crystallization and finally by zone melting technique. The purity was checked by determining the melting points. The observed melting points were in good agreement with the literature values⁵.

The phase diagrams were studied using thaw-melt method⁶ and the zone melting studies were made using a horizontal single heating zone-melting unit. In this unit the heater is fixed and the tube containing samples moves. A nichrome wire (length = 15 cm, diameter = 0.1 cm) in the form of a circular coil was used as the heater. The diameter and the breadth of the heating coil were 1 and 2.4 cm respectively. A pyrex glass tube filled with the sample (diameter = 0.7 cm, length = 30 cm) rested at V-shaped aluminium grooves (well polished to minimise friction) fitted on a wooden base. Sample tube was moved by a geared motor with a speed of 4 cm/hr. Temperature was controlled by an autotransformer. The zone length was kept 4 and 3 cm for one and four passes respectively.

Naphthalene-catechol system — The phase diagram of this system is shown in Fig. 1. The zone melting

experiment was carried out for naphthalene-catechol mixture containing 10 wt % catechol. Determination of the concentration of catechol at different distances showed that catechol moves towards the direction of zone travel. Concentration ratio C/C_0 was determined for various values of x/l . The results were compared with the empirical Eq. (1) for the region $C/C_0 < 1$,

$$C/C_0 = a \exp\left(\frac{bx}{l}\right) \quad \dots(1)$$

where C is the concentration at the length x , C_0 is the initial concentration, l is the zone length, a and b are constants. k , the effective distribution coefficient, is defined as $C/C_0 = k$ at $x/l = 0$. This was determined by plotting $\log C/C_0$ against x/l (Fig. 2) and noting the value of a at $x/l = 0$. The values of the constants a and b in Eq. (1) are found to be 0.48 and 0.045 respectively and hence the value of the effective distribution coefficient comes out to be 0.48.

Naphthalene-p-chloronitrobenzene system — The phase diagram for this system is due to Rastogi *et al.*⁸. The zone melting experiment was carried out using a mixture of 20% (by wt) of *p*-chloronitrobenzene as an impurity. The results indicated that *p*-chloronitrobenzene travels towards the direction of zone travel. The effective distribution coefficient determined using Eq. (1) is found to be 0.42. The values of constants a and b , as calculated from Fig. 2, are 0.42 and 0.034 respectively.

Equations have been theoretically deduced for zone melting of eutectic systems⁹ for the case of (i) complete mixing and (ii) non-mixing. Eq. (2) is followed in the case of complete mixing:

$$x = l \left(\frac{C}{C_0} - 1 \right) \left(\frac{\rho_1}{\rho_s} \right) \quad \dots(2)$$

Here x is the length of the purified material, l is the zone length, C_e is the eutectic composition, C_0 is the original composition and ρ_1 and ρ_s are the liquid and solid densities respectively.

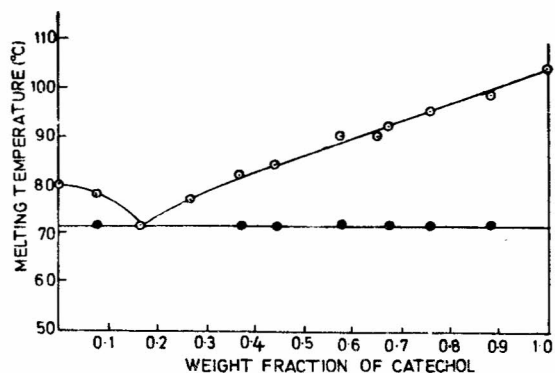


Fig. 1 — Phase diagram of the naphthalene-catechol system (○ melting points; ● thaw points)

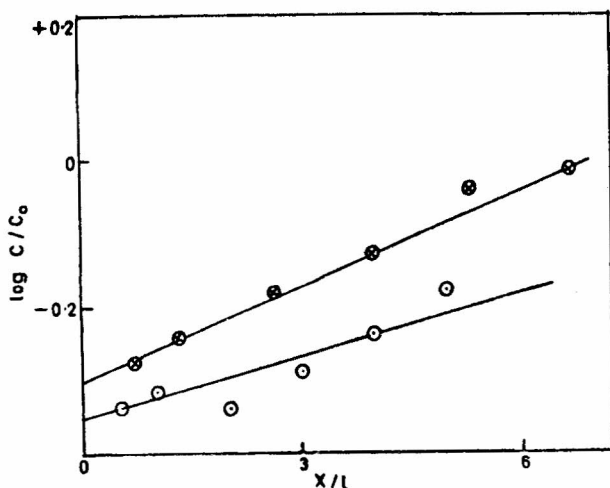


Fig. 2 — Plots of $\log C/C_0$ against x/l [● naphthalene-catechol system; ○ naphthalene-*p*-chloronitrobenzene system]

For the case of non-mixing, Eq. (3) is followed:

$$C = C_0 \left[1 + \left(\frac{C_s}{C_0} - 1 \right) \exp \left(\frac{-xv \rho_s}{D \rho_1} \right) \right] \quad \dots(3)$$

where D is the diffusion coefficient and v is the velocity of zone movement.

From Eq. (2) it follows that for complete mixing there should not be any change in the concentration with change in the value of x . This is not true in the present case. Hence, complete mixing does not take place in the zone melting of the samples studied in the present case. In order to test Eq. (3), $\log (1 - C/C_0)$ was plotted against x . Straight lines were not obtained. Hence it follows that the equation for non-mixing is also not applicable. Since the rate of zone movement is large and Eqs. (2) and (3) do not fit the data, it appears that partial mixing occurs in the present eutectic systems.

Since the value of effective distribution coefficient is less than unity in both the systems, the impurities are preferentially rejected by the solid and pile up in the liquid close to the interface. Further, greater the deviation from unity in the value of k , the greater is the separation efficiency. The separation efficiency in the naphthalene-*p*-chloronitrobenzene system is greater than in the naphthalene-catechol system.

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High Temperature X-Ray Diffraction Study of Barium Pyrophosphate

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High temperature X-ray diffraction study of barium hydrogen phosphate has been undertaken in order to find out whether any phase changes take place in it. It has been observed that this compound gets completely converted into barium pyrophosphate at 550°. On heating the latter to further higher temperatures there is no change in phase but the d -values decrease after 850°. This behaviour is similar to that of UP_2O_7 . X-ray powder pattern of barium pyrophosphate has been indexed. The system is orthorhombic with the following crystal data: $a=9.200 \text{ \AA}$, $b=14.120 \text{ \AA}$, $c=5.420 \text{ \AA}$, $z=4$, $D_m=4.45 \text{ g cm}^{-3}$ and space group symmetry is P_{mmm} or P_{mm2} or P_{222} .

THE effect of heat on barium hydrogen phosphate has been investigated by X-ray methods and the results are described in this paper.

X-ray diffraction patterns were taken on a Philips PW 1010 X-ray diffractometer employing nickel filtered CuK radiation. The samples were heated by means of a high temperature attachment to the diffractometer. Pure barium hydrogen phosphate was heated up to 1000° starting from room temperature, and X-ray patterns were taken at intervals of 100°. The accuracy of temperature measurement and uniformity of temperature have been checked by known lattice spacing-temperature relation of silver. Calibration at room temperature was done from the positions of high angle peaks by extrapolation methods.

It is observed that the conversion of barium hydrogen phosphate into barium pyrophosphate begins at 270° and is complete at about 550°. The X-ray pattern of this pyrophosphate is similar to the pattern of δ -pyrophosphate reported in literature¹ (except for the presence of a few extra weak reflections, which could be located by us because the patterns were taken on a diffractometer and not on a camera). But the temperature of formation of δ -barium pyrophosphate observed here is much less than that reported. The low temperature or α -phase has not been observed at all. The pattern obtained at 550° is completely that of δ -pyrophosphate. It is stable at room temperature and is unaffected by further heating even up to 1400°. Also, there is no indication of the formation of another phase. However an interesting phenomenon has been observed. The values of the interplanar spacings increase when the temperature reaches about 850° and then start decreasing on heating to higher temperatures. This can be seen from the plots in Fig. 1, where the variation in d -spacings with temperature is shown for four strong reflections. This unusual behaviour of barium pyrophosphate is similar to that of uranium pyrophosphate² which expands up to about 400° and then contracts till 1200°. Since the structure of