Some Thermodynamic Aspects of Organic Eutectics; Succinonitrile-Phenanthrene System

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Phase diagram and heat of fusion of succinonitrile-phenanthrene system have been studied. Enthalpy of mixing and excess thermodynamic functions such as $h^E$, $s^E$ and $g^E$ have also been calculated. The results have been explained on the basis of interaction among the components forming the eutectic melt.

The chemistry of eutectic1-3 and monotectic4 systems has been a field of active investigation in the recent past due to their unusual physical properties not normally shown by the parent components. The metallic eutectics constitute interesting systems in metallurgy and materials science. Due to low transformation temperature, ease in purification, transparency, lack of convection and wider choice of materials, organic eutectics have drawn the attention of a number of research groups5-8. Succinonitrile (SCN) is a material of low entropy of fusion, which simulates the metallic solidification, and phenanthrene (Ph) melts with high entropy of fusion. As such, SCN-Ph system is a suitable analogue of Al-Si (metal-nonmetal) system for direct observation on solidification. Further, SCN-Ph constitutes an interesting system for the micro-gravity experiments because of equal density of both components at their melting temperatures. The results of linear velocity of crystallization, diffusion coefficient measurement and microstructure of SCN-Ph system were reported by Singh and coworkers9. In the present note, the data on phase diagram and heats of fusion have been discussed. Using heats of fusion some excess thermodynamic functions such as $g^E$, $s^E$ and $h^E$ and heat of mixing have been calculated. The results have been analysed in the light of interaction among the components forming the eutectic melt.

The phase diagram of SCN-Ph system was determined by thaw melt method10,11. Heats of fusion for SCN, Ph and their eutectic were determined using a Perkin-Elmer DSC-2 with computer aided data requi

Table 1—Enthalpies and Entropies of Fusion of SCN, Ph and Their Eutectic

<table>
<thead>
<tr>
<th>Component</th>
<th>Enthalpy of fusion (kJ/mol)</th>
<th>Entropy of fusion (kJ mol⁻¹ K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SCN</td>
<td>3.704</td>
<td>0.0111</td>
</tr>
<tr>
<td>Ph</td>
<td>18.627</td>
<td>0.0499</td>
</tr>
<tr>
<td>SCN-Ph eutectic</td>
<td>10.071</td>
<td>0.0306</td>
</tr>
<tr>
<td>(Experimental)</td>
<td>(4.076)*</td>
<td>(0.0122)*</td>
</tr>
</tbody>
</table>

*Values calculated on the basis of mixture law are given in parentheses.

The phase diagram of SCN-Ph system (Fig. 1) clearly shows that Ph forms a monotectic (0.225 mol fraction of SCN) and one eutectic (0.975 mol fraction of SCN). The consolute temperature is 49°C above the monotectic horizontal. At the monotectic temperature, $L_2$ (liquid rich in Ph) is in equilibrium with $L_1$ (liquid rich in SCN) and solid Ph. In the upper region shown as $L_1 + L_2$, the two liquids $L_1$ and $L_2$ are immiscible. At the boundary line between ($L_1 + L_2$) and L (vide Fig. 1), the two liquids $L_1$ and $L_2$ are in equilibrium with a third liquid phase containing solutions of $L_1$ and $L_2$. In the region indicated as Ph(s) + SCN(L₁), Ph remains in the solid form while $L_1$ in the liquid state. Below eutectic temperature Ph and SCN solidify in the region shown as SCN(s) + Ph(s) in Fig. 1.
The heats of fusion and entropies of fusion of pure components and eutectic are reported in Table 1. For comparison, the heat of fusion of eutectic was also calculated, using mixture law, and is given in Table 1. In order to assess the nature of interaction between the components forming the eutectic melts, the activities of components and their excess thermodynamic functions were also calculated. The calculated value of heat of fusion of the eutectic is lower than the experimental value. This violation of mixture law may be attributed to the formation of quasieutectic structure in the eutectic melt. During cluster formation by weak intermolecular forces, there may be liberation of heat which consequently lowers the actual value of heat content of the eutectic.

The entropies of fusion of eutectic and pure components, calculated from their enthalpies of fusion, are included in Table 1. Making use of eutectic temperature, of the component i, respectively. The entropies of fusion of eutectic and pure components of the eutectic. The present system is non-ideal since the activity coefficients of components (1) and (2) are not equal to unity.

The heat of mixing of eutectic in the present system was calculated using Eq. (7) and was found to be 6.0 kJ/mol.

\[ \Delta H_m = (\Delta_h)_\text{exp} - \Sigma (x_i \Delta h_i^0) \]  ... (7)

In Eq. (7) \((\Delta_h)_\text{exp}\) is the heat of fusion of the eutectic, determined experimentally, \(x_i\) and \(\Delta h_i^0\) are the mol fraction and heat of fusion of end components respectively, at the eutectic temperature. In the present system eutectic composition is far from equimolar and enthalpy of mixing is reasonably high. The eutectic point is shifted towards the component of lower melting temperature. Recently Singh and co-workers have reported that eutectic composition is connected with enthalpy of mixing in a definite manner. This type of behaviour was observed by Zalkin in the metallic systems and he explained the eutectic structure on the basis of colloidal theory. On the basis of thermochemical studies it was speculated that structure of eutectic melts depend on the sign and magnitude of enthalpy of mixing, \(\Delta H_m\). Based on the above observations, three different structures have been suggested: quasieutectic for \(\Delta H_m > 0\); clustering of molecules for \(\Delta H_m < 0\); and molecular solution for \(\Delta H_m = 0\). In the present system, the value of \(\Delta H_m\) is highly positive which suggests that (i) the eutectic is on one side of the phase diagram and there is miscibility gap in the system, and (ii) the structure is of quasieutectic type.

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References
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