

stigated in detail, should be given by the change in melting point of ethylene with pressure<sup>8</sup> and with dilution.<sup>10</sup> With pentane (Fig. 6), the critical locus can be followed down to the upper critical end point (UCEP), or the lower critical solution temperature (LCST) on the vapor pressure curve, where two liquid phases and a gas phase coexist.<sup>3</sup> This point lies at 91°C. at a pressure indistinguishable from the vapor pressure of the pure solvent by the present method of measurement. Freeman and Rowlinson<sup>3</sup> did not attain complete miscibility in the system polyethylene-*n*-pentane, probably because they operated with lower temperatures, intersecting the critical locus above the LCEP. It is clear that a LCEP of high molecular weight polyethylene exists only for *n*-alkanes with five carbons and greater because of an increase in the UCEP with size of the solvent molecule and because of the increase in melting point of the polymer with pressure.

### DISCUSSION

All systems reported are characterized by a large free volume and by large density differences between the components. There also should be a negative volume change of mixing  $\Delta V$  along a critical locus of the type described. Every point on this locus, denoted by subscript *c*, may be considered as LCST with  $(dP/dT)_c > 0$  or as UCST with  $(dP/dT)_c < 0$ . Certain inequalities involving the second derivatives with respect to composition of the thermodynamic mixing functions must be satisfied along the locus and, if there are no points of inflection, one has at an LCST  $\Delta H < 0$ ,  $\Delta S < 0$  and at an UCST  $\Delta H > 0$ ,  $\Delta S > 0$ .<sup>4</sup> These latter conditions have been verified near an LCST in several cases.<sup>11,12</sup> In addition,  $(dP/dT)_c$  is given by

$$\frac{\partial^2 \Delta S}{\partial x_2^2} / \frac{\partial^2 \Delta V}{\partial x_2^2}$$

where  $x_2$  refers to the mole fraction of solute.

Clearly, all lattice treatments of polymer solutions seem here less satisfying physically than under ordinary conditions and violate one or more of the inequalities which must be met along the critical locus, particularly where  $(dP/dT)_c > 0$ . One objection to the use of the results obtained from lattice treatments is removed, when it is realized that expressions for the free energy of mixing formally identical to that of the Flory-Huggins equation have been obtained by considerations not requiring the lattice assumption.<sup>13,14</sup> In order to allow for negative, as well as positive, heats of mixing the Flory-Huggins interaction parameter  $\chi$  must be considered as a free energy,<sup>11</sup> as indeed required by the more general lattice treatments<sup>15</sup> and by the theory of Longuet-Huggins.<sup>13</sup> Patterson<sup>11</sup> has suggested further that  $\chi$ , although no longer a heat term, may still be identified with Hildebrand's solubility parameter term, which then becomes