

LOWER CRITICAL SOLUTION POINTS IN HYDROCARBON MIXTURES

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It is common for the mutual solubility of a pair of liquids to increase with temperature until miscibility is complete at a critical solution point. Perhaps the best known systems of this kind are mixtures of hydrocarbons with polar liquids such as aniline and nitrobenzene, in which the upper critical solution temperature (U.C.S.T.) is often used as a check on the identity and purity of the hydrocarbons. The explanation of this phase behaviour is simple. The mean energy of interaction of a pair of molecules of one of the pure components is large because of their polarity. It is therefore energetically difficult to dilute such a liquid with a non-polar one. As the temperature is raised, considerations of energy become less important, and those of entropy become more important. Thus the miscibility increases with temperature. There are, however, a few systems in which the mutual solubility decreases with rising temperature and which are completely miscible only below a lower critical solution temperature (L.C.S.T.). Such systems are strongly hydrogen-bonded and, almost always, water is one of the two components. The energy of interaction of a pair of molecules in these systems depends strongly on their mutual orientation. At low temperatures a sufficiently high proportion of neighbouring molecules are able to adopt the orientations of low energy for the liquids to be miscible. These favourable alignments are broken up when the temperature is raised, and complete miscibility ends at a L.C.S.T.

It is the object of this paper to describe a second class of systems in which L.C.S.T. are observed, but in which the mutual orientations of the molecules are not of great importance. Ethane is completely miscible with ethanol, n-propanol and n-butanol at 25°C, but Kuenen and Robson¹ showed in 1899 that two liquid phases are formed in each of these systems over a small range of temperature near the critical point of pure ethane. *Figure 1* shows schematically two projections of the phase diagram of one of these systems. It is seen that the range of liquid immiscibility is small. It is bounded below by the L.C.S.T. and above by a critical point at which the gas phase and the liquid phase rich in ethane become identical. An increase of pressure raises the L.C.S.T. and increases the critical mole fraction of the alcohol. This line ends eventually at the gas-liquid critical point of the pure alcohol. These systems differ in two respects from the better-known class of L.C.S.T. First, only one of the components is polar, and not both, and secondly, the immiscibility is confined to a short range of temperature

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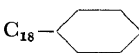
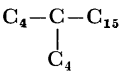
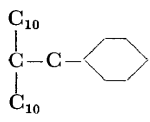
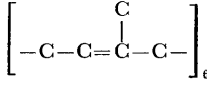
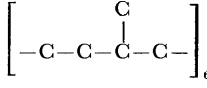
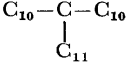
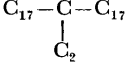
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close to the critical point of the more volatile component. A few other systems which resemble these three have been discovered in the last sixty years: carbon dioxide (T_c 31°C) + *o*-nitrophenol^{2, 3} (liquids immiscible at 26–40°C); carbon dioxide + nitrobenzene⁴ (30–40°C); ethylene (T_c 9°C) + *p*-dichlorobenzene⁵ (26.0–26.5°C); ethane (T_c 32°C) + 1,3,5-trichlorobenzene⁶ (40.3–46.8°C); and propane (T_c 97°C) with many long-chain organic acids and esters⁷.

In some of these systems the L.C.S.T. lies above the critical point of the volatile component. In every system the less volatile component is either polar or of a different chemical type from the volatile component. However, it seemed to us that this polarity or chemical difference was not an essential feature of such systems, and we have therefore examined a range of hydrocarbon mixtures. Our starting point was the observation^{8, 9} that the addition of propane to lubricating oils, which is made in order to precipitate the asphalt, sometimes gives rise to two liquid hydrocarbon layers if the temperature is above 70°C. Our first studies were therefore of solutions in propane of a series of pure liquid hydrocarbons with between 24 and 37 carbon atoms.

EXPERIMENTAL

Seven hydrocarbons, chosen, from those most readily available, for their large molar volumes and low melting points, were used as solutes.

| | | |
|-----|--|---|
| I | n-octadecylcyclohexane (m.p. 40°C) $C_{24}H_{48}$ |  |
| II | 5-n-butyleicosane (m.p. < 0°C) $C_{24}H_{50}$ |  |
| III | 11-cyclohexylmethyleneicosane (m.p. - 4°C) $C_{28}H_{56}$ |  |
| IV | Squalene (m.p. < 0°C) $C_{30}H_{50}$ |  |
| V | Squalane (m.p. < 0°C) $C_{30}H_{62}$ |  |
| VI | 11-n-decyldocosane (m.p. 1°C) $C_{32}H_{66}$ |  |
| VII | 18-ethylpentatriacontane (m.p. 28°C) $C_{37}H_{76}$ |  |

Hydrocarbons I and II were supplied by the British Petroleum Company and were stated to contain less than 1 per cent impurity. III and VI were supplied by the American Petroleum Institute Research Project 42 as pure

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samples sealed in nitrogen. IV was purified from 90 per cent squalene by passing a 3 per cent solution in petroleum ether through a Grade H alumina column. The infra-red spectrum was free from OH and CO bonds. V was prepared by D. Mangaraj by reducing the purified IV with hydrogen at 100 atm over a platinum-black catalyst. The infra-red spectrum was free from C=C bonds. VII was prepared from stearic acid. This was converted into stearone¹⁰ by heating with iron filings at 300°C. The stearone was converted into a Grignard compound (with ethyl magnesium iodide) which was hydrolysed to the alcohol by ethanol. The alcohol was dehydrated with tolyl-*p*-sulphonic acid to give an unsaturated hydrocarbon which was finally reduced to VII by hydrogen with a catalyst of platinum black. The hydrocarbon was passed through a column of Grade H alumina. The infra-red spectrum was free from OH and C=C bonds. The melting point was 27.5°C.

Propane and ethane were supplied by the National Chemical Laboratory and had purities between 99.93 and 99.98 per cent.

Solutions were made in "Veridia" precision-bore glass tubes of 2.00 mm internal diameter and 9 mm external diameter. The lower end was sealed to give an internally square end. The involatile component was added first and weighed in air. The second component was added by distillation *in vacuo*; the tube was then sealed and re-weighed. The density of the mixture was calculated from the length of tube, with a small correction for the conical shape of the final seal. A water thermostat was used at 0–35°C and a vapour thermostat at 35–150°C. The tubes were shaken occasionally and the phase changes were observed with a travelling microscope.

RESULTS

Hydrocarbons II, III and VII were dissolved in propane to give mixtures in which the weight fraction of the heavy component was between 0.1 and 0.6. The specific volumes of the mixtures were varied between 4 cm³/g and 12 cm³/g and the temperature between 20° and 150°C. No liquid–liquid phase separation was found in any of the tubes.

All seven hydrocarbons were dissolved separately in ethane to give mixtures in which the weight fraction of the heavy component was between 0.01 and 0.5. The specific volumes and the temperature were varied between 1 and 5 cm³/g and 0° and 35°C. Every system was found to have a L.C.S.T. and a gas–liquid critical point of the type shown in *Figure 1*. The critical temperatures are listed in *Table 1*.

Table 1

| <i>System</i> | <i>L.C.S.T. (°C)</i> | <i>Gas-liquid C.T. (°C)</i> |
|---------------|----------------------|-----------------------------|
| Ethane | — | 32.3 |
| Ethane + I | < 17 | 33.4 |
| Ethane + II | 27.7 | 34.5 |
| Ethane + III | 13.4 | 33.4 |
| Ethane + IV | 3.7 | 33.3 |
| Ethane + V | 22.6 | 33.6 |
| Ethane + VI | 10.6 | 32.6 |
| Ethane + VII | < 15 | 32.5 |

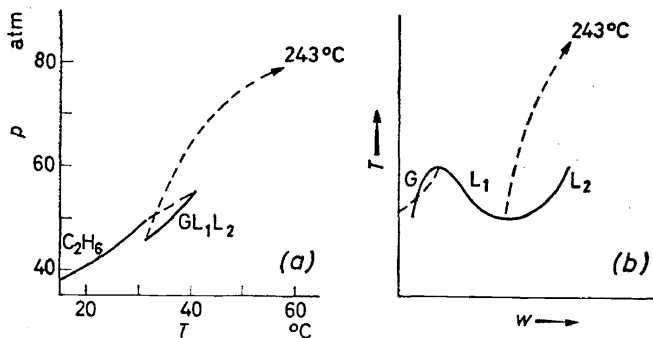


Figure 1. Graphs of pressure (p) and temperature (T) and of temperature and weight fraction (w) for ethane + ethanol: — vapour pressures and compositions of the univariant systems; --- critical states of the mixtures; L_1 and L_2 , the liquid phases rich and weak in ethane, respectively. Graph (b) is not to scale

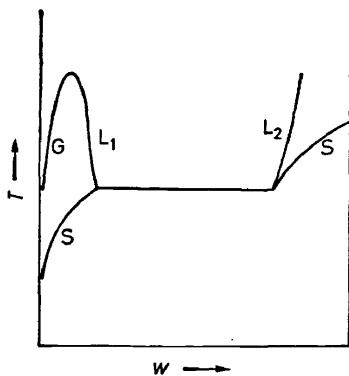


Figure 2. Graph of temperature (T) as a function of weight fraction (w) for a system in which the L.C.S.T. is not realized because of the solidification of the involatile component

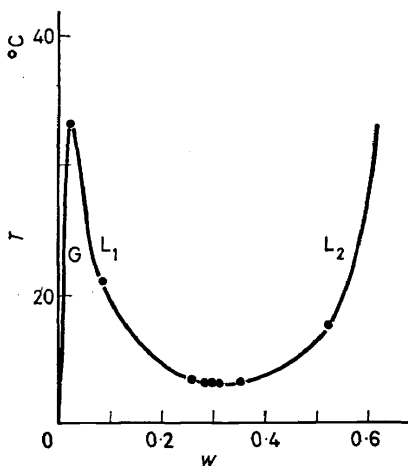


Figure 3. The (T, w) graph of ethane + hydrocarbon III. The critical point of pure ethane is at 32.3°C

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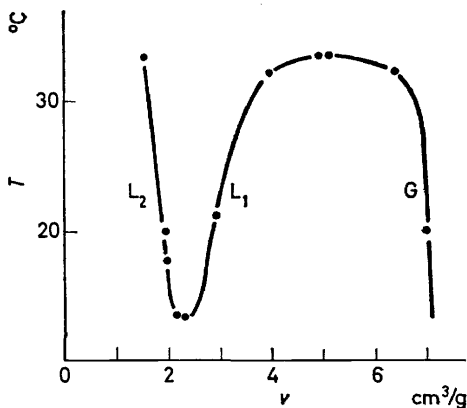


Figure 4. The graph of temperature (T) and specific volume (v) for ethane + hydrocarbon III

Two of the systems could not be cooled to the L.C.S.T. as the heavy component solidified. Here the temperature of the quadruple point (solid + liquid + liquid + gas) is shown as an upper limit of the L.C.S.T. The phase diagrams of these two systems are shown schematically in *Figure 2*. One system, ethane + III, was studied in greater detail than the others in order to establish beyond doubt that the phase behaviour is of the type shown in *Figure 1*. *Figure 3* shows the (T,w) and *Figure 4* the (v,T) projections of the (v,T,w) surface. They confirm that the system is of the type shown in *Figure 1*.

DISCUSSION

The results obtained here establish beyond doubt that this type of immiscibility is found even in mixtures of non-polar molecules of the same chemical type if the molecular sizes and energies of interaction of the two components are very different. The immiscibility is clearly caused by the approach of the volatile component to its own critical point.

A comparison of the results for the hydrocarbons without rings or double bonds, II, V, VI and VII, shows that the greater the number of carbon atoms in the heavier component the lower are both the L.C.S.T. and the gas-liquid critical temperature. That is, the larger the heavy component, the less is its miscibility with liquid ethane and the less its solubility in the critical phase of ethane. This low solubility in the critical phase leads to gas-liquid critical temperatures that differ little from that of pure ethane. It is probable that all paraffin hydrocarbons below about C_{20} are miscible in all proportions with liquid ethane at all temperatures up to the gas-liquid critical point of the mixture. It is known from the work of Kay¹¹ that this is so for hydrocarbons up to C_7 . The results above show that the first paraffin hydrocarbon that is immiscible with propane must lie above C_{37} .

A comparison of I with II and of III with V shows that hydrocarbons with saturated rings ("naphthenic hydrocarbons" to the petroleum chemist) are less miscible with ethane than those without rings. A comparison of

IV with V shows that an unsaturated hydrocarbon is considerably less miscible than the corresponding saturated hydrocarbon. Roof and Crawford¹² have shown recently that isobutane and phenanthrene are immiscible in the liquid phase at 101°C. They have not studied the change of miscibility with temperature but have shown that the system has an upper critical solution pressure at this temperature. Their (p,w) section appears to be that of a system of the type shown in *Figure 1*. This temperature is 34°C below the critical temperature of pure isobutane, and so their results suggest that aromatic hydrocarbons are even less miscible with light paraffin hydrocarbons than are cycloparaffins or ethenes. This is in agreement with the known thermodynamic properties of more conventional systems¹³. The original work of Kuenen and Robson¹ shows that the miscibility of polar substances is even less than that of an aromatic hydrocarbon.

Gunst, Diepen and Scheffer^{5, 14} have studied the phase diagram of ethylene with each of the following hydrocarbons: n-octacosane ($C_{28}H_{58}$), n-hexatriacontane ($C_{36}H_{74}$), diphenyl, naphthalene, anthracene, stilbene and hexamethylbenzene. In every case the melting point of the heavy component is too far above the critical temperature of ethylene (9°C) for liquid phases to be formed, but the course of the gas-liquid critical lines in (p,T,w) space suggests that the liquids would be immiscible were it not for the solidification of the heavy component.

Finally, we have shown that this type of immiscibility is very widespread in polymer solutions. Almost all solutions of high hydrocarbon polymers in solvents such as n-pentane, n-hexane and cyclohexane separate into two phases on heating above the normal boiling point of the solvent. This work has been published separately¹⁵.

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