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Gerald R. Hecke Van [a]

[a] Department of Chemistry, Harvey Mudd College Claremont, California, 91711

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ON THE OBSERVATION OF LIQUID-LIQUID IMMISCIBILITY IN BINARY MIXTURES OF LIQUID CRYSTALS

GERALD R. VAN HECKE
DEPARTMENT OF CHEMISTRY
HARVEY MUDD COLLEGE
CLAREMONT, CALIFORNIA 91711

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ABSTRACT: Liquid-liquid immiscibility or phase separation that is often observed in non-mesogenic systems is suggested to account for the phase behavior exhibited in several binary mixtures of mesogens. A brief qualitative thermodynamic description of the phase separation in mesogenic systems is presented.

Liquid-liquid immiscibility of the type shown in *Figure 1* is well known in mixtures of non-mesogenic materials. Our purpose here is to suggest that such liquid-liquid immiscibility has been observed in mesomorphic systems in at least two separate types of cases. Further we will suggest qualitative thermodynamic explanations for such behaviors.

In *Figure 2* are two phase diagrams redrawn from the

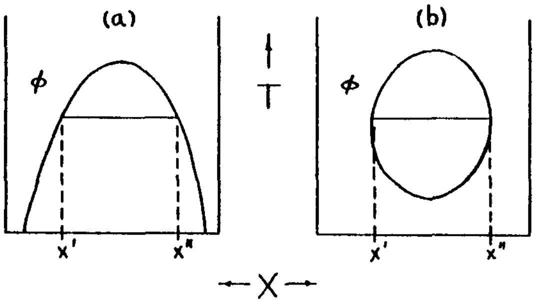

FIGURE 1. Common liquid-liquid immiscibility or demixing of phase ϕ into two phases whose compositions at any temperature are given by the termini of tie lines x' and x". (a) is simple demixing; (b) is closed loop demixing.

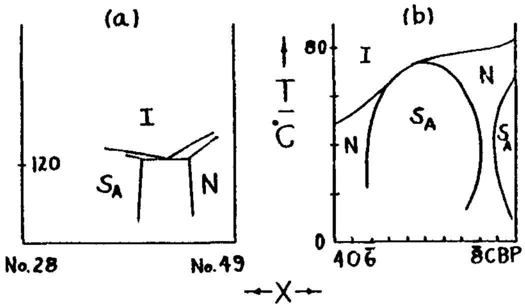

FIGURE 2. Phase diagrams redrawn from literature (a) reference 1a; (b) reference 1b. Compound no. 28 is p,p'-di-*n*-dodecyloxyazoxybenzene; no. 49 is *p*-methoxybenzoic acid -4'-*n*-hexyloxyphenyl ester; 40 $\bar{6}$ is 4-*n*-butylbenzoic acid-4'-*n*-hexyloxyphenyl ester; $\bar{8}$CBP is 4-cyano-4'-*n* -octyloxybiphenyl.

original papers.[1] Consider the case represented in *Fig 2a* first. If we write the total isobaric Gibbs energy of a phase ϕ as

$$(1)\quad \bar{G}_\phi(T,x) = (1-x)\mu^*_{1\phi}(T) + x\mu^*_{2\phi}(T) + RT\,[(1-x)\ln(1-x) + \ln x] + \bar{G}^E_\phi(T,x)$$

where x is the mole fraction of the 2nd component and $\mu^*_{i\phi}(T)$ is the chemical potential of pure i in ϕ phase, it can be easily shown that the cause of phase separation, henceforth called demixing, is the relative magnitudes of the ideal mixing term $[(1-x)\ln(1-x) + x\ln x]$ and the excess Gibbs energy $\bar{G}^E_\phi(T, x)$. If, for example, $G^E_\phi(T, x)$ has enough influence to change $\bar{G}_\phi$ from case (i) in *Figure 3a* to case (ii) demixing of ϕ will be predicted with the common tangent construction showing that a phase of composition x is equilibrium with a phase x'. Moreover, if $\bar{G}^{E}_{\phi}(T, x)$ has a particular temperature dependence, then the demixing region can close as illustrated in Figure 1b.

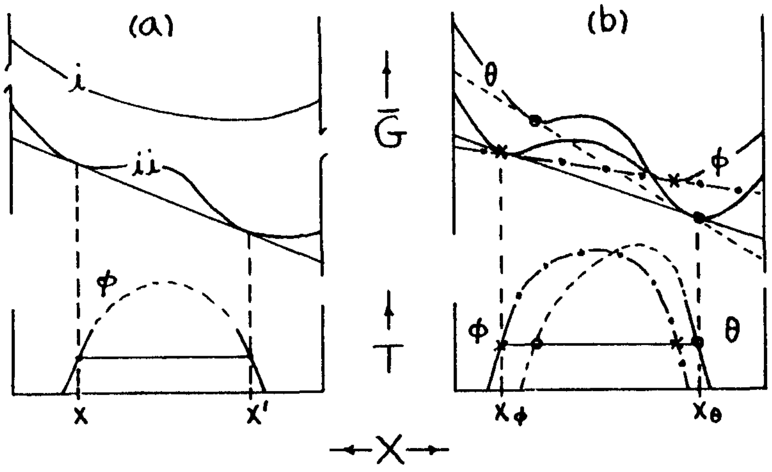

FIGURE 3. Upper portion shows plot of total Gibbs energy of phase ϕ at two temperatures case i and ii. (a) Lower portion shows the compositions in equilibrium at the temperature corresponding to case ii. Case i corresponds to temperature where phase separation is not possible. (b). Upper portion shows plot of total Gibbs energy for two phases ϕ and θ at the same temperature. Phase separation is predicted for both ϕ and θ phases but because the curves cross the lowest Gibbs energies are achieved by phase ϕ being in equilibrium with phase θ. Lower portion shows the expected temperature-composition diagram where the solid lines show stable phases while broken lines show metastable phases.

Now suppose *Figure 2a* is an example of this type of demixing, only in this case the top of the dome is interrupted by other phase equilibria, for example, I-S_A and I-N which are more stable at those temperatures and compositions. In terms of $\bar{G}$ vs x diagrams that the $\bar{G}_{tot}$ for these other phases would be lower in energy but not shown in *Figure 3a* for clarity. Consider now the meaning of this type of demixing. If this explnation of the phase diagram were correct, then the S_A and N phases are just the same phase demixed. Further such behavior would predict a S_A/N critical point at the maximum temperature of the virtual dome (the upper consolute point). Since it seems more likely from many experiments that the S_A and N phases are truly different phases, a different explanation of the phase diagram is required. Such an explanation is provided by considering the total Gibbs energies shown in *Figure 3b*. Here it is supposed that two different phases ϕ and θ, each capable of demixing, are in equilibrium. The composition of stable phases as well as the metastable ones can be found from the $\bar{G}$ vs x diagram in the upper part of *Figure 3b*. To achieve correlation with *Figure 2a*, again the domes of the now <u>two</u> demixed phases are interrupted by some other, more stable, phase equilibria. Thus we suggest here that the phase equilibria of the type shown in *Figure 2a* represents a double demixing phenomena.

Figure 2b illustrates what looks like two types of reentrant behavior. Clearly the reentrant behavior for compositions close to pure 8CBP is just that, "classic" reentrant behavior. However, our purpose here is to suggest that the other type of reentrant behavior is really a consequence of either closed loop demixing or unusual azeotropic type behavior but not "classic" reentrant behavior. Thus we suppose that the non-classical reentrant behavior in the phase diagram of *Figure 2b* is one of the cases shown in *Figure 4*. *Figure 4a* illustrates a closed loop demixing, the most commonly discussed example of which is the nicotine-water system.[3] *Figure 4b* illustrates closed loop azeotrophy which is possible in principle but not yet found in vapor-liquid systems or alloys.[4] In either case, the "reentrant" behavior shown in *Figure 4* and thus by supposition *Figure 2b* as well is caused entirely by non-zero excess Gibbs energies.

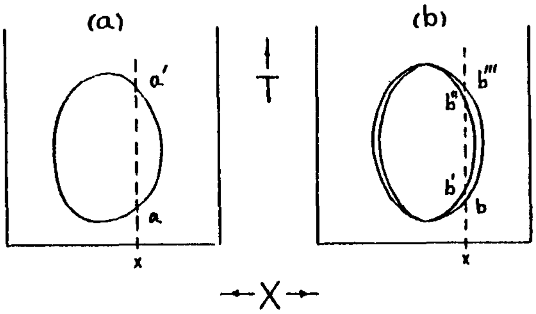

FIGURE 4. a. Closed loop demixing of single phase. b. Closed loop azeotropy showing finite two phase coexistance regions at all temperatures between maximum and minimum values.

To distinguish between these types of behavior would be experimentally difficult. Differential scanning calorimetry could not distinguish between the two cases for, if, in the azeotropic case, the two phase coexistance region were very narrow in composition, then all that would be observed experimentally would be some enthalpy change at the temperature and composition of the transition. (See the paths at composition x labeled a-a', b-b'-b"-b''' in *Figure 4* for example.) The magnitudes of the enthalpy change for a demixing (a-a' *Figure 4a*) as opposed to an azeotropic two phase separation (b-b''' *Figure 4b*) would in principle be different but not predictable a priori. To distinguish the two cases by polarized light microscopy would require recognition of the textural features characteristic of a S_A/N two phase mixture as opposed to recognition of the textural appearance of two coexisting demixed N phases, whatever those might be. Thus the question of which type of "reentrant" behavior shown in the mid-composition region of *Figure 2b* is still open. It should be pointed out that the answer is not exclusive, that is, some mixtures might exhibit closed loop demixing while others exhibit closed loop azeotropy.

Why is it important to offer a different explanation for the "reentrant" behavior in the middle of *Figure 2b*? It is important because the origins of the two reentrant behaviors are quite different. The "classic" reentrant behavior close to pure 8CBP (*Figure 2b*) has its origin in properties of pure 8CBP, and, from a thermodynamic point of view, here heat capacity effects are important, if not dominant, in determining such behavior.[5] The "reentrant" behavior in the mid-composition range depends only, again from a thermodynamic view point, on excess Gibbs energies and not on the fact that one or both of the components are themselves reentrant. In brief then, closed loop demixing or azeotropy which have the appearance of reentrant behavior, can occur with or without pure component reentrant behavior, but "classic" reentrant behavior can only occur if at least one pure component is reentrant.

What we have suggested here, whether or not the explanations apply to the specific systems illustrated in *Figure 2*, is that liquid-liquid immiscibility may have indeed already been observed in binary phase diagrams of liquid crystals and any discussion of phase diagrams of the type illustrated in *Figure 2* should take into account such possibilities. A quantitative treatment of such immiscibility via the equal Gibbs energy analysis will be forthcoming in a future communication.

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