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F. Brochard, J. Jouffroy, P. Levinson. Phase diagrams of mesomorphic mixtures. *Journal de Physique*, 1984, 45 (7), pp.1125-1136. 10.1051/jphys:019840045070112500 . jpa-00209848

HAL Id: jpa-00209848

<https://hal.science/jpa-00209848>

Submitted on 4 Feb 2008

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Classification
 Physics Abstracts
 64.70M

Phase diagrams of mesomorphic mixtures

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(Reçu le 21 novembre 1983, accepté le 23 mars 1984)

Résumé. — Nous avons combiné la théorie de la transition isotrope-nématique de Maier Saupe [1] et la théorie des mélanges de Flory-Huggins, pour décrire les diagrammes de phases de deux nématogènes A + B. Les deux composants peuvent avoir des paramètres d'ordre différents S_A , S_B dans le mélange. On prévoit la morphologie du diagramme en fonction de quatre paramètres seulement. Les calculs numériques sont limités au cas où les points de transition isotrope-nématique des deux composants sont voisins (c'est le cas des corps chimiquement voisins). Pour certaines valeurs des paramètres nous trouvons un diagramme de phases remarquable avec deux points critiques de démixtion : l'un à haute température dans la phase isotrope et un second dans la phase nématique. Nous discutons aussi l'effet de la longueur des chaînes quand l'un des composants est un polymère nématogène avec des groupes latéraux mésogènes, et quand les deux composants sont des polymères.

Abstract. — We have combined the Maier Saupe theory [1] of the nematic-isotropic transition and the Flory Huggins theory of mixtures to describe the phase diagrams of two nematogens A + B. The two components can have different order parameters S_A , S_B in the mixture. We can then predict the morphology of the phase diagrams in term of a relatively small number (4) of interaction parameters. The final numerical calculations are restricted to cases where the clearing points of the two components are nearly equal (cases of chemical similarity). For certain sets of parameters we find a rather remarkable phase diagram with *two* consolute points — one at high temperatures in the isotropic phase and a second one at lower temperatures in the nematic phase. We also discuss the effects of chain length on the phase diagrams : when one component is a nematogenic polymer [2] with mesogenic side groups ; and when the two components are polymers.

1. Introduction.

1.1 NEMATIC MIXTURES. — Nematic mixtures of *small* thermotropic molecules A + B have been extensively studied experimentally. A current way to identify a new nematic phase is to study the mixture with a known nematic. The phase diagrams of these mixtures have been discussed mainly in terms of nearly ideal solutions [3]. In connection with solutions of non nematogenic polymers in nematic solvents, we have set up a description involving *two* interactions parameters [4]. More recently, Warner and Flory have studied the phase diagrams of a mixture of rods in a solvent [5]. A detailed lattice model for thermotropic nematic mixtures has been constructed by Sivardièrre [6]. In this model, each molecule occupies one lattice site, and can be aligned into three separate directions (X, Y, Z). This choice of three possibilities ensures that the nematic-isotropic transition for a pure species is first order, as it should, and predicts an order parameter at transition $S_c = 0.5$ (slightly too large but not unpalatable). The model requires four

interactions parameters, and this, indeed, appears to be the minimal number for a realistic description. Operating in this way, Sivardièrre generates a broad, and interesting classification of phase diagrams.

The aim of the present work is to enlarge the Sivardièrre description keeping four interactions parameters as in reference [6].

a) We use a Maier Saupe model rather than the three positions model, and this improves slightly the predictions on the order parameters.

b) More important, we do *not* assume the same order parameter for both components (as was done by Sivardièrre [6] and Warner and Flory [5]) but we allow for two independent values $S_A(T, \Phi)$, where T is the temperature and Φ the volume fraction of B. This distinction between S_A and S_B may be important in practice, when the two components are chemically very different.

c) We do not restrict our attention to small molecules A and B, but we also consider the case where one (or both) component is a polymer. This generates very dissymmetric phase diagrams, which are quite different from those of reference [6].

1.2 NEMATIC POLYMERS. — Polymers exhibiting mesomorphic behaviour have been extensively studied during the past ten years. One can distinguish three classes [5, 6] :

a) lyotropic systems of rigid chains + solvents found with certain polypeptides [7] and synthetic polyamides [8] (e.g. Kevlar + sulfuric acid) ;

b) flexible or partly flexible chains with mesogenic units incorporated into the *backbone* of the polymer [9] ;

c) polymers with mesogenic *side groups* [2] attached to a polymeric backbone by an aliphatic chain called the « spacer ». Side groups polymers may become useful for liquid crystal display devices because of their high stability and their relatively rapid response to electrical fields ;

d) semi-flexible polymers, namely the « neat » polyethylene type melts considered recently by G. Ronca and D. Y. Yoon [17].

Thermotropic LC polymers « P » can sometimes be dissolved in a nematogenic solvent « M », if the chemical structure of M is similar to the mesogenic group in the polymer. Various studies on this type of polymer-solvent mixture are currently under way (viscosities, elastic constants, neutrons, X-rays). The experimental phase diagrams of such binary mixtures are often rather complex and very sensitive to small changes in the nematogenic units [10]. One of our aims is to reduce this complexity by a suitable mean field description. Thus we shall finally describe the phase diagrams of mixtures

$$\begin{aligned} & (M_A, M_B) \\ & (M_A, P_B) \\ & (P_A, P_B) \end{aligned}$$

where M = monomer, P = polymer. Apart from the interaction parameters discussed in section 2, we shall need to specify the degrees of polymerization (N_A, N_B) of the polymer species (P_A, P_B). We believe that this analysis will be applicable mainly to *side chain thermotropic polymers* for the following reason : if the spacer between the mesogenic group and the backbone is not too small, one can assume an effective decoupling between the mesogen and the polymer backbone. On the other hand, for group (b) mesogenic units in the backbone, the persistence length of the polymer may be strongly enhanced by the appearance of a nematic order [11, 12]. This case has then certain similarities with the case of rigid polymers forming a nematic solution [(case a), studied in particular by Flory and Abe [13]], and is less well treated by the present theory.

2. Mean-field model for binary mixtures.

We always assume that the basic mesogenic units of A and B are of similar size, and think of them as described on a Flory Huggins lattice. The basic object is then

the free enthalpy of mixing (per site). This may always be split as follows :

$$G = G_{\text{iso}} + G_{\text{nem}} \quad (1)$$

where $G_{\text{iso}} = G(S_A = S_B = 0)$ describes a situation without nematic order.

2.1 FREE ENTHALPY G_{iso} OF THE ISOTROPIC MIXTURE. — For this part we use the Flory Huggins theory [14] for two polymers A, B of degrees of polymerization N_A, N_B , Φ being the volume fraction of B, G_{iso} is then given by :

$$G_{\text{iso}} = kT \left[\frac{\Phi}{N_B} \text{Log } \Phi + \frac{1 - \Phi}{N_A} \text{Log } (1 - \Phi) \right] + U_0 \Phi(1 - \Phi). \quad (2)$$

The two first terms represent the entropy of mixing and U_0 is the monomer A-monomer B pair interaction in the isotropic phase. In the following, we assume $U_0 > 0$ (positive enthalpy of mixing), this being the most usual case, at least when van der Waals interactions are dominant. We define a reduced temperature by $\theta = kT/U_0$; U_0 controls the miscibility of the two species in the isotropic phase. The isotropic consolute point deduced from [2] is given by :

$$\begin{aligned} \Phi_c &= \frac{N_A^{1/2}}{N_A^{1/2} + N_B^{1/2}} \\ \theta_c &= \frac{kT_c}{U_0} = \frac{2 N_A N_B}{[N_A^{1/2} + N_B^{1/2}]^2}. \end{aligned} \quad (3)$$

We have solved three typical cases for our numerical studies :

$$\begin{aligned} a) \quad N_A = N_B &= 1 & \Phi_c &= 1/2 & \theta_c &= 0.5 \\ b) \quad N_A = N_B &= 100 & \Phi_c &= 1/2 & \theta_c &= 50 \\ c) \quad N_A = 1, N_B &= 100 & \Phi_c &= 0.1 & \theta_c &= 1.65. \end{aligned}$$

2.2 FREE ENTHALPY G_{nem} DUE TO THE ALIGNMENTS (S_A, S_B). — In a mean-field (Maier Saupe) model, G_{nem} is given by :

$$\begin{aligned} G_{\text{nem}} &= - T \Sigma(S_A) (1 - \Phi) - T \Sigma(S_B) \Phi - \\ &\quad - \frac{1}{2} U_{AA} S_A^2 (1 - \Phi)^2 - \frac{1}{2} U_{BB} S_B^2 \Phi^2 - \\ &\quad - U_{AB} S_A S_B \Phi (1 - \Phi). \end{aligned} \quad (4)$$

Here $\Sigma(S)$ is the decrease in entropy due to the alignment of the molecules. The last three terms describe the gain in energy by molecular alignment and involve three nematic interaction parameters U_{AA}, U_{BB}, U_{AB} . We assume a) that all three parameters U_{ij} are positive (a negative U_{AB} would probably correspond to a mixture of disc-like and rod-like molecules and does not correspond to our problem), b) that U_{ij} para-

meters are independent of degree of polymerization N_A, N_B . This assumption is valid for polymers with mesogenic *side groups*.

We set $u_{ij} = U_{ij}/U_0$ to define *dimensionless* interaction energies.

2.2.1 *Pure nematic* « A » ($\Phi = 0$) or « B » ($\Phi = 1$). — For $\Phi = 0$ (or $\Phi = 1$), we recover the standard Maier Saupe free enthalpy

$$G = - T \Sigma(S_A) - \frac{1}{2} U_{AA} S_A^2. \quad (5)$$

We now recall briefly the mean-field calculation of $S_A(T)$, which is extended later to the mixture.

We choose a trial distribution function $f(\alpha)$ for the molecular alignment given by

$$f(\alpha) = \frac{1}{Z} \exp\left(m \frac{3 \cos^2 \alpha - 1}{2}\right) \quad (6)$$

with

$$Z(m) = \int \exp\left(m \frac{3 \cos^2 \alpha - 1}{2}\right) d\Omega$$

m is a dimensionless measure of the quadrupolar field aligning one monomer. The conjugate nematic order $S(m)$ is related to Z by

$$S_A(m) = \int f(\alpha) \frac{3 \cos^2 \alpha - 1}{2} d\Omega = \frac{1}{Z} \frac{dZ}{dm}. \quad (7)$$

The entropy $\Sigma(m)$ is given by

$$\begin{aligned} \Sigma(m) &= - k \int f \text{Log } 4 \pi f d\Omega \\ &= - k \left(\text{Log } \frac{4 \Pi}{Z(m)} + m S_A \right). \end{aligned} \quad (8)$$

From [7, 8], we can deduce $\Sigma(S_A)$. The derivative of Σ with respect to S_A is simply

$$- \frac{d\Sigma}{dS_A} = km \quad (9)$$

S_A is calculated by minimizing G with respect to S_A :

$$- T \frac{d\Sigma}{dS_A} - U_{AA} S_A = 0. \quad (10)$$

This leads to

$$S_A(m) = \frac{kT}{U_{AA}} m \quad (11)$$

$S_A(m)$ is calculated from (7). Apart from the solution $S_A = 0$, equation (11) has one or two other solutions. When T is below T_A , defined by

$$\frac{kT_A}{U_{AA}} = \frac{1}{\alpha_c}, \quad \alpha_c = 4.54, \quad (12)$$

(or $\theta_A = u_{AA}/\alpha_c$ in dimensionless units)

the nematic phase is the stable phase ($G_{nem}(S_A) < 0$).

At higher temperatures, the isotropic phase ($S = 0$) is the stable phase. At $T = T_A$, there is a first order transition and the order parameter has a universal value $S_A(T_A) = 0.429$.

Conclusion : U_{AA} and U_{BB} are related to the NI transition temperature of pure A and pure B respectively by the relation

$$\frac{kT_A}{U_{AA}} = \frac{kT_B}{U_{BB}} = \frac{1}{\alpha_c}. \quad (13)$$

As mentioned in section 1, a nematogenic polymer can be mixed with a nematogenic solvent only if the two basic units are very similar. This in turn implies $T_A \simeq T_B$ (assumption of chemical similarity). Thus in the following we shall consider mostly the symmetrical case

$$U_{AA} = U_{BB} = U. \quad (14)$$

2.2.2 *Mixture of A and B.*

2.2.2.1 Nematic interaction parameter U_{AB} . — Let us start by the case of ideal mixtures. If $U_{AB} = U$, it is obvious that $S_A = S_B$ whatever the composition Φ of the mixture. If we now go to a more realistic case, with $U_{AB} \neq U$, S_A and S_B are usually different. They become equal only for $\Phi = 1/2$. For $\Phi = 1/2$, one can define a « pseudo transition » temperature $T_p(\Phi = 1/2) = T_M$. T_M is the temperature of a hypothetical nematic-isotropic transition at the fixed composition $\Phi = 1/2$. From the result (12), T_M is defined by

$$\frac{kT_M}{\frac{1}{2}(U + U_{AB})} = \frac{\theta_M}{\frac{1}{2}(u + u_{AB})} = \frac{1}{\alpha_c}. \quad (15)$$

Note that T_M is not usually observable as a real transition temperature. For the (first order) nematic isotropic transition, the composition of the two equilibrium phases are generally different : the constraint $\Phi = 1/2$ cannot be imposed simultaneously on the two phases. However we shall see that, for an « azeotrope », symmetry considerations allow for an equilibrium with $\Phi = 1/2$ in both phases, and then T_M becomes observable. But more generally T_M is simply a useful parameter for the classification of phase diagrams when $N_A = N_B$.

If $U_{AB} < U$, $T_M < T_A$: the mixture disfavors the appearance of a nematic phase.

If $U_{AB} > U$, $T_M > T_A$: the nematic order is increased by mixing.

Remark : If $N_B \gg N_A$, the useful parameter is the « pseudo transition » temperature $T_p(\Phi_c)$, where Φ_c is the critical composition (3). For N_B large, $\Phi_c \simeq 0$ and $T_p(\Phi_c) \simeq T_A$.

2.2.2.2 Calculation of the nematic order S_A and S_B .

— S_A and S_B are derived by minimization of G_{nem} (Eq. (4)). This gives

$$\begin{aligned} -T \frac{d\Sigma(S_A)}{dS_A} - U_{AA} S_A (1 - \Phi) - U_{AB} S_B \Phi &= 0 \\ -T \frac{d\Sigma(S_B)}{dS_B} - U_{BB} S_B \Phi - U_{AB} S_A (1 - \Phi) &= 0. \end{aligned} \quad (16)$$

We calculate $\Sigma(S)$ through the « field parameter » m . The angular distribution functions of monomers A and B are given by equation (6) with $m = m_A$ for « A » and $m = m_B$ for « B ». $\Sigma(m)$ and $S(m)$ are tabulated. We choose a pair m_A, m_B and calculate $\Sigma(m_A), S_A(m_A)$ and $\Sigma(m_B), S_B(m_B)$ respectively.

The equilibrium condition (16) becomes :

$$\begin{aligned} kTm_A &= U_{AA} S_A(m_A) (1 - \Phi) - U_{AB} S_B(m_B) \Phi \\ kTm_B &= U_{BB} S_B(m_B) \Phi - U_{AB} S_A(m_A) (1 - \Phi). \end{aligned} \quad (17)$$

In dimensionless units and for the symmetrical case, equation (17) becomes

$$\begin{aligned} \theta m_A &= u S_A(m_A) (1 - \Phi) - u_{AB} S_B(m_B) \Phi \quad (a) \\ \theta m_B &= u S_B(m_B) \Phi - u_{AB} S_A(m_A) (1 - \Phi) \quad (b) \end{aligned} \quad (18)$$

From equation (18), it is clear that S_A and S_B depend upon three parameters : $\theta/\theta_A, u_{AB}/u$ and Φ . In practice, we choose a value of u_{AB}/u and then calculate S_A and S_B as a function of θ/θ_A and Φ . From (18) (a), we draw S_A as a function of S_B . From (18) (b), we draw $S_B = f(S_A)$. The intersections give the solutions. We have always the isotropic solutions $S_A = S_B = 0$. We may have one or several intersections. For a solution $S_A(\theta, \Phi), S_B(\theta, \Phi)$, we calculate G_{nem} . If $G_{nem}(S_A, S_B) < 0$, we retain the lowest energy anisotropic solution. We show on figure 1 the calculation of $S_A(\theta, \Phi), S_B(\theta, \Phi)$ for two values of u_{AB}/u . On figure 1 (a), the ratio u_{AB}/u is larger than one and, at fixed temperature, S_A and S_B are maximum for $\Phi = 1/2$. On figure 1 (b), u_{AB}/u is smaller than one and the nematic order is depressed near $\Phi = 1/2$. From these curves one can draw the variation of S_A and S_B as a function of θ for a given composition (Fig. 2).

2.2.3 Miscibility of A/B in the nematic phase.

— In the isotropic phase, the miscibility of A and B is controlled by U_0 . The resulting consolute temperature θ_c is a function of U_0, N_A, N_B (Eq. (3)). In the nematic phase, the effective AB interaction is modified by the alignment parameters S_A, S_B . From equations (2, 4), we find an effective interaction parameter

$$\tilde{U}_0 = U_0 - U_{AB} S_A S_B + \frac{1}{2} U_{AA} S_A^2 + \frac{1}{2} U_{BB} S_B^2. \quad (19)$$

If $\tilde{U}_0 < U_0$, the consolute temperature in the nematic

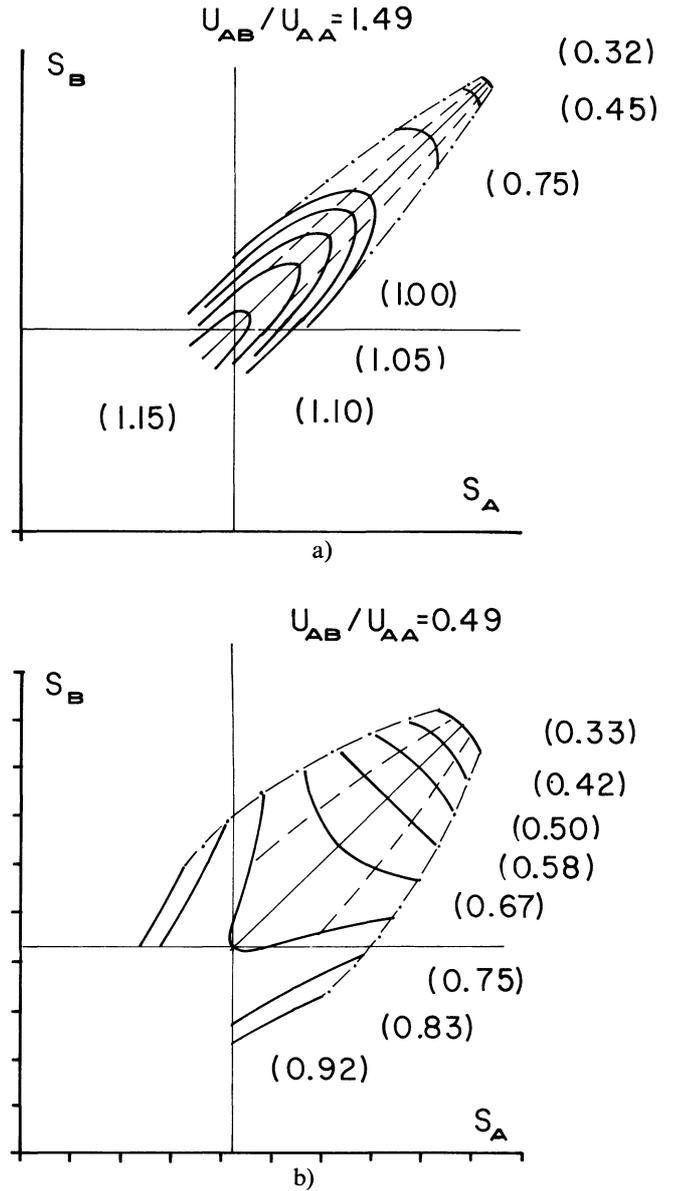


Fig. 1. — Nematic order parameters S_A, S_B as functions of the reduced temperature (θ/θ_A) and composition (Φ) with the assumption of chemical similarity (equal clearing points for A and B). The full lines are the isothermal curves ($\theta = \text{constante}$) and the dotted lines the curves $\Phi = \text{constante}$. a) $U_{AB}/U_{AA} = 1.5$; the nematic order is increased by mixing; b) $U_{AB}/U_{AA} = 0.5$; the nematic order is depressed by mixing.

phase is reduced. From equation (3), one can easily find that

$$\theta_c^{nem} = \theta_c \frac{\tilde{U}_0}{U_0}. \quad (20)$$

If $U_{AA} = U_{BB} = U_{AB}$, $\tilde{U}_0 = U_0$ and the consolute temperature is not modified by the molecular alignment.

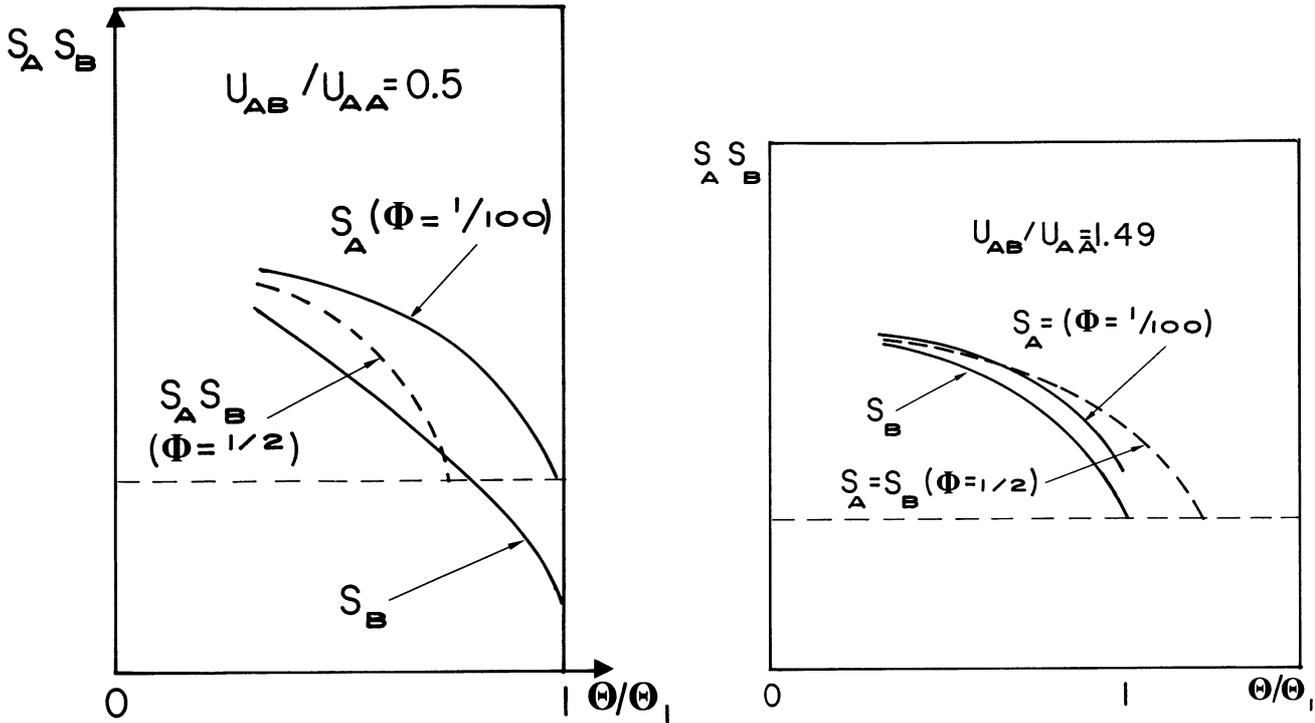


Fig. 2. — Explicit plot of the order parameter S_A, S_B as a function of the reduced temperature θ/θ_A deduced from Fig. 1. a) $U_{AB}/U_{AA} = 1.5$, b) $U_{AB}/U_{AA} = 0.5$. The data are given for two volume fractions of B. i) $\Phi = 1/2, S_A = S_B$; the « pseudo clearing point » corresponds to $S_A = S_B = 0.429$, ii) $\Phi = 0.01$; the « pseudo clearing point » coincides practically at $\theta = \theta_A$.

For $\Phi = 1/2$, if $U_{AA} = U_{BB} = U$ but $U_{AB} \neq U, U_0$ is simply given by

$$\tilde{U}_0 |_{\Phi=1/2} = U_0 + (U - U_{AB}) S^2. \quad (21)$$

Thus $\tilde{U}_0 < U_0$ if $U_{AB} > U$: if mixing favours the nematic order, this in turn increases the miscibility of the two compounds. Then for the symmetrical case

$$\begin{aligned} \theta_c^{nem} < \theta_c & \text{ for } U_{AB} > U \\ \theta_c^{nem} > \theta_c & \text{ for } U_{AB} < U. \end{aligned}$$

We shall see in the next section that the morphology of the phase diagrams is controlled by 3 parameters : $\theta_c^{iso} = \theta_c, \theta_c^{nem}$, and $T_p(\Phi_c)$, the « pseudo » nematic transition at the critical concentration of the isotropic mixture (note that for $N_A = N_B, \Phi_c = 1/2$ and $T_p(\Phi_c) = T_M$).

It may be useful at this point to insist on the following (classical but important) property : *two nematics need not be miscible in all proportions*. If a certain phase β is continuously miscible with a nematic phase α , β is also a nematic. But if β is not miscible with α , β may still be nematic phase.

3. Phase diagrams.

3.1 DEFINITION OF THE EQUILIBRIA. — The equilibrium between two phases (I and II) is described by the

equality of the chemical potentials of A and B

$$\begin{aligned} \mu_A^I &= \mu_A^{II} \\ \mu_B^I &= \mu_B^{II}. \end{aligned} \quad (22)$$

For our model, it is more convenient to use a different pair of fields :

i) the exchange chemical potential

$$\mu = \mu_A - \mu_B = \partial G / \partial \Phi$$

ii) the osmotic pressure

$$\Pi = \mu_A + \mu_B = -\Phi^2 [\partial(G/\Phi) / \partial \Phi]. \quad (23)$$

The equilibrium between two phases is then given by

$$\begin{aligned} \mu_I &= \mu_{II} \\ \Pi_I &= \Pi_{II}. \end{aligned} \quad (24)$$

In practice, to derive the phase equilibria, we calculate $G(\Phi)$ at θ fixed by inserting in equation (3) the values of $S_A(\theta, \Phi), S_B(\theta, \Phi)$ calculated in paragraph (2.2.2.2). The condition (24) corresponds graphically to the existence of a common tangent — which specifies the composition Φ^I and Φ^{II} of the two phases in equilibrium. They are four possibilities :

a) a homogeneous phase (no common tangent) either isotropic or nematic ;

- b) two isotropic phases (I, II) in equilibrium ;
 c) two nematic phases (I, II) ;
 d) equilibrium between an isotropic phase (I) and a nematic phase (II).

In the following section (4), we calculate numerically various phase diagrams for (M_A, M_B) , (M_A, P_B) , (P_A, P_B) pairs varying the interaction parameters (but keeping $U_{AA} = U_{BB}$). On the other hand, for dilute solutions ($\Phi \rightarrow 0$ and $\Phi \rightarrow 1$) and for azeotropic mixtures we can use exact thermodynamic formulas and relate the slopes of the phase diagram to the interaction parameters : this helps to understand some important features of the phase diagrams and is discussed below.

3.2 GENERAL FEATURES.

3.2.1 *Dilute solutions near T_A .* — For $\Phi \rightarrow 0$, equations (16) for S_A and S_B become

$$\begin{aligned} T_A \frac{d\Sigma(S_A)}{dS_A} + U_{AA} S_A &= 0 \\ T_A \frac{d\Sigma(S_B)}{dS_B} + U_{AB} S_A &= 0. \end{aligned} \quad (25)$$

The solution for S_A is the usual threshold $S_A = S_c = 0.429$. The value of S_B is calculated from equations (25). If $U_{AB} < U_{AA}$, $S_B < S_c$. In that limit, $-T\Sigma \simeq 4.47 S^2/2$. Equations (25) lead to $S_B = u_{AB} S_A/4.47 \theta_A$. If $u_{AB} = u_{AA}$, $S_B = S_c$. If $u_{AB} > u_{AA}$, $S_B(u_{AB})$ has to be calculated numerically.

For $\Phi \ll 1$, $T \simeq T_A$, we calculate the composition Φ_N and Φ_i of the nematic and the isotropic phase in equilibrium.

i) the ratio of the two compositions is given in terms of a free enthalpy of transfer ΔG for one B molecule migrating from i to N

$$\frac{\Phi_N}{\Phi_i} = \exp\left(-\frac{\Delta G}{kT}\right) = \exp\left\{-\frac{N_B}{kT} \left[\frac{1}{2} U_{AA} S_c^2 - T\Sigma(S_B) - U_{AB} S_c S_B \right]\right\}. \quad (26)$$

Here S_B is the order parameter for $\Phi \rightarrow 0$ given by equations (25). For $S_B < S_c$, $\Sigma(S) \sim S^2$ and

$$\Delta G \simeq N_B \left[(1/2) U_{AA} S_c^2 - (1/2) U_{AB} S_c S_B \right].$$

ii) The equality of the osmotic pressure leads to

$$\Phi_i - \Phi_N = \frac{N_B}{kT} \Delta H_A \frac{T_A - T}{T_A} \quad (27)$$

where ΔH_A is the latent heat of the pure A compound at the NI transition (if ΔH_A is known, $\Phi_i - \Phi_N$ allows for a derivation of N_B).

From (26), (27), we find that :

- a) $\Phi_N/\Phi_i < 1$ if $U_{AB}/U_{AA} < 1$ and $\Phi_N/\Phi_i > 1$ if $U_{AB} > U_{AA}$;

- b) $\Phi_N \simeq \Phi_i$ if $U_{AB} \simeq U_{AA}$;
 c) Φ_N/Φ_i varies exponentially with the degree of polymerization N_B . When N_B is large, Φ_N tends to zero exponentially.

For $\Phi \simeq 1$, $T \simeq T_B$ we find similarly :

$$\frac{1 - \Phi_N}{1 - \Phi_i} = e^{-N_A/kT} \left[\frac{1}{2} U_{BB} S_c^2 - T\Sigma(S_A) - U_{AB} S_c S_A \right] \quad (28)$$

$$\Phi_N - \Phi_i = N_A/kT \Delta H_B \frac{T_B - T}{T_B}. \quad (29)$$

Conclusion : The measure of T_A and T_B gives the nematic interaction parameters U_{AA} , U_{BB} . From the values of the composition $\Phi_N(T)$, $\Phi_i(T)$ of the nematic and isotropic phases in equilibrium, it is possible to derive N_A , N_B and U_{AB} . But the derivation of U_{AB} is not straightforward. We show now, however, that if the phase diagram presents an azeotrope, U_{AB} is easily obtained.

3.2.2 *Azeotropes.* — An azeotropic mixture (see for instance Fig. 4 (K, L)) has a clearing point T_Z somewhat similar to the clearing point of a pure compound : the isotropic phase and the nematic phase have the same composition Φ_Z . We shall now show the following theorem : at the point (Φ_Z, T_Z) the two components A and B have *the same order parameter* $S_A = S_B$. To prove this, note that since $G_N = G_{iso} + G_{nem}$, we can write the exchange chemical potential as the sum of two terms :

$$\mu_N = \frac{G_N}{\Phi} = \mu_{iso} + \mu_{nem}. \quad (30)$$

Similarly

$$\Pi_N = G - \Phi \frac{G}{\Phi} = \Pi_{iso} + \Pi_{nem}. \quad (31)$$

The equality of μ and Π in the two phases for the *same* Φ leads to the azeotrope conditions :

$$\begin{array}{l|l} \mu_{nem} = 0 & \frac{G_{nem}}{\Phi} = 0 \\ \Pi_{nem} = 0 & G_{nem} = 0. \end{array} \quad (32)$$

We must add to equations (32) the two equations (16) for S_A , S_B . This leads to :

$$\begin{aligned} \left(\Sigma_A - \frac{d\Sigma_A}{dS_A} \frac{S_A}{2} \right) (1 - \Phi) - \left(\Sigma_B - \frac{d\Sigma_B}{dS_B} \frac{S_B}{2} \right) \Phi &= 0 \\ \left(\Sigma_A - \frac{d\Sigma_A}{dS_A} S_A \right) - \left(\Sigma_B - \frac{d\Sigma_B}{dS_B} S_B \right) &= 0. \end{aligned} \quad (33)$$

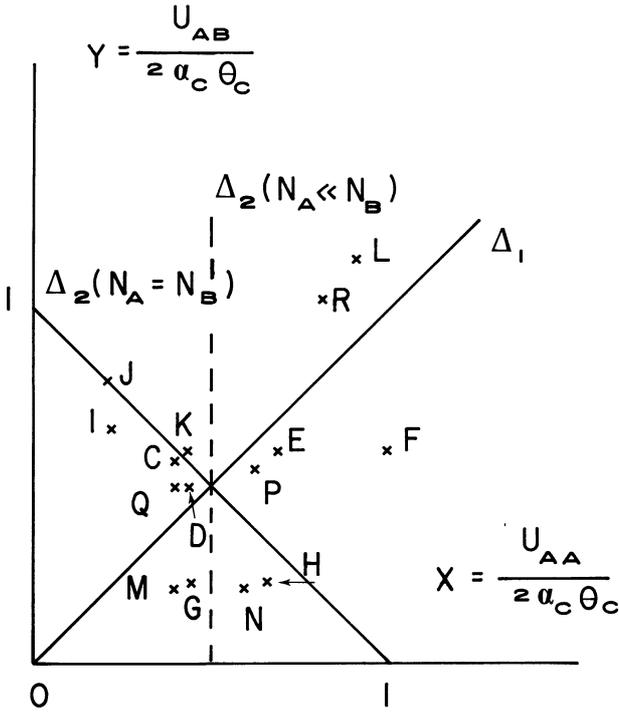


Fig. 3. — Classification of the phase diagrams based on the two dimensionless parameters of equation (37). Above (below) the line Δ_1 nematic order is favored (reduced) by mixing. To the right (left) of the line Δ_2 the isotropic consolute point θ_c is below (above) the « pseudo clearing point » $\theta_p(\Phi_c)$ at the same concentration Φ_c . The position of Δ_2 depends upon N_A/N_B . We display Δ_2 for two simple limits $N_A = N_B$ and $N_A \ll N_B$. The points I, J... correspond to phase diagrams which have been computed numerically and which are displayed on figures 4, 5, 6.

For these two equations to be satisfied simultaneously, we must have

$$S_A = S_B = S_c \quad (34)$$

Then from equations (16, 34), we can write down explicit formulae for the position of azeotropes :

$$\Phi_Z = \frac{U_{AA} - U_{AB}}{U_{AA} + U_{BB} - 2 U_{AB}} \quad (35)$$

$$kT_Z = \frac{1}{\alpha_c} \left(\frac{U_{AA} U_{BB} - U_{AB}^2}{U_{AA} + U_{BB} - 2 U_{AB}} \right) \quad (36)$$

Remark : In our model, for the azeotrope composition ($\Phi = \Phi_Z$) the order parameter $S_A(T, \Phi_Z)$ and $S_B(T, \Phi_Z)$ are equal not only at $T = T_Z$, but also at all lower temperatures : this can be seen from equation (16) with $\Phi = \Phi_Z$.

Inserting the condition $0 < \Phi_Z < 1$ and $T_Z > 0$ in equations (35, 36) gives the condition for the existence of an azeotrope in the phase diagram.

i) If $U_{AA} + U_{BB} - 2 U_{AB} > 0$ (mixing tends to destroy the nematic order) an azeotrope will occur only if $U_{AB} < U_{AA}$ and $U_{AB} < U_{BB}$.

ii) If $U_{AA} + U_{BB} - 2 U_{AB} < 0$, the azeotrope occurs only if $U_{AB} > U_{AA}$ and $U_{AB} > U_{BB}$.

These conditions are obeyed in the symmetrical case $U_{AA} = U_{BB}$. The other requirement to observe the azeotrope is $T_Z > T_c$, the demixing temperature.

To summarize : In our model an azeotrope behaves exactly like a pure compounds, with a fixed composition at transition and a single order parameter in the nematic phase. Note that when an azeotrope is found in the phase diagram, one can derive immediately the interaction parameter U_{AB} from T_Z and Φ_Z : this may be useful in practice. We also predict that the position (T_Z, Φ_Z) of the azeotrope is entirely independent of the degrees of polymerization (N_A, N_B) : this may provide a useful check on the model.

4. Types of diagrams for cases of chemical similarity.

We give now a general discussion of the phase diagrams, within the assumption of chemical similarity ($U_{AA} = U_{BB} = U$). This is supported by numerical calculations for the following examples :

- a) monomer-monomer $N_A = N_B = 1$
- b) polymer-polymer $N_A = N_B = 100$
- c) monomer-polymer $N_A = 1, N_B = 100$.

The basic parameters for our discussion are :

θ_c = isotropic consolute temperature (dimensionless) defined in equation (3).

$\theta_p(\Phi_c)$ = pseudo clearing point at the composition Φ_c (dimensionless) defined at the end of section 2 (recall that $\theta_p(\Phi_c) = \theta_M$ for $N_A = N_B$ and $\theta_p(\Phi_c) = \theta_A$ for $N_A \ll N_B$). It is particularly convenient to choose as our control parameters

$$x = \frac{u_{AA}}{2 \alpha_c \theta_c} \quad y = \frac{u_{AB}}{2 \alpha_c \theta_c} \quad (37)$$

where α_c is defined in equation (12). This choice allows us to cover simultaneously the three cases (a, b, c) defined above. A first line of importance Δ_1 in the (x, y) representation (see Fig. 3) is the bisector $x = y$. Whenever $x > y$, the mixtures have lower clearing points than the pure compounds, while for $x < y$ they have higher clearing points.

The second line of importance Δ_2 corresponds to $\theta_p(\Phi_c) = \theta_c$.

- i) if $N_A = N_B$ this is the line $x + y = 1$;
- ii) if $N_B \gg N_A$ ($\theta_p(\Phi_c) \rightarrow \theta_A$) this becomes a vertical $x = 1/2$.

The two lines Δ_1, Δ_2 divide the allowed region in the xy plane into four sectors (Fig. 3), which correspond to the main types of diagrams.

4.1 MONOMER-MONOMER MIXTURES : $N_A = N_B = 1$.

— We have calculated the phase diagrams corresponding to the points (K, L, J, C, I, D) (E, F, G, H) of figure 3. They are pictured on figure 4.

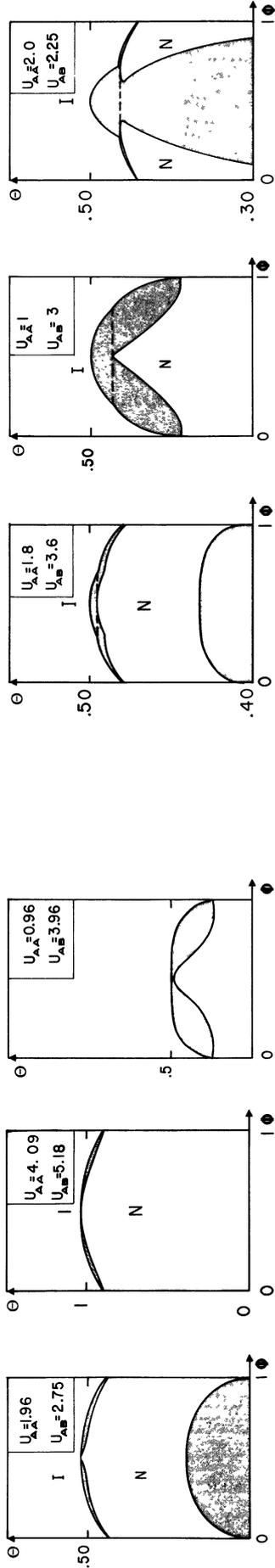


FIG 4(K)

FIG 4(L)

FIG 4(J)

FIG 4(C)

FIG 4(I)

FIG 4(D)



FIG 4(E)

FIG 4(F)

FIG 4(G)

FIG 4(H)

Fig. 4. — Phase diagrams for monomer-monomer mixtures ($N_A = N_B = 1$) corresponding to the points (K, L, J) (C, I, D) (E, F) (G, H) of figure 3. K, L, J $\theta_c^{nem} < \theta_c < \theta_M$. C, I, D $\theta_c^{nem} < \theta_c < \theta_M$. E, F $\theta_c^{nem} > \theta_c$, $\theta_M > \theta_c$. G, H $\theta_c^{nem} > \theta_c$, $\theta_M < \theta_c$.

C, I « Chinese hat » $\theta_c^{nem} < \theta_M$ and $\theta_c^{nem} < 0$, D « Napoleon » $\theta_c^{nem} > \theta_M$, E, F « Napoleon » $\theta_c^{nem} > \theta_c$, $\theta_M > \theta_c$. E $\theta_c^{nem} < \theta_M$, F $\theta_c^{nem} > \theta_M$ « Donkey ».
 G, H $\theta_c^{nem} > \theta_c$, $\theta_M < \theta_c$. G « Ghost » ($\theta_c \gg \theta_M$), H « Owl » ($\theta_c \gtrsim \theta_M$).

4.1.1 $\theta_c > \theta_c^{nem}(y > x)$.

At point « K », $\theta_M > \theta_c > \theta_c^{nem}$. One notices an azeotrope (at $\Phi_Z = 1/2$). The mixture is stabilized by the nematic order and demixes only at a very low temperature ($\theta_c^{nem}/\theta_c = 0.4$).

At point « L », θ_c^{nem} becomes negative : AB are miscible at all temperatures in all proportions.

Point « J » is topologically identical to point « L », but the coexistence region is large because $U_{AB} \gg U_{AA}$. The size of the coexistence region gives an estimate of U_{AB}/U_{AA} . For $U_{AB}/U_{AA} \simeq 1$, the NI coexistence zone tends to a thin line.

Point « C » is very close to point « L » in the parameter space, but the diagram is qualitatively different because $\theta_c > \theta_M$. This case « C » is interesting : the upper biphasic region (« Chinese hat ») corresponds to a demixing in the isotropic phase and to a nematic-isotropic equilibrium. The lower biphasic region corresponds to a demixing in the nematic phase. We have then two consolute points !

One goes from « C » to « I » by increasing $U_{AB} - U_{AA}$: when $\theta_c^{nem} < 0$, one reaches type « I » (pure « Chinese hat »).

For « D », $\theta_c^{nem} > \theta_M$ and the two compounds are never miscible in the nematic state. We call « D » the « Napoleon » type (« hat »).

4.1.2 $\theta_c < \theta_c^{nem}(y < x)$.

At point « E » the upper (thin) biphasic region corresponds to the NI equilibrium. This is an azeotrope at $\Phi_Z = 1/2$. The miscibility is now reduced by the nematic order.

At point « F » the two coexistence regions of « E » become connected (« Donkey » diagram) $\theta_c^{nem} > \theta_M$.

At point « G » a demixing appears in the isotropic phase ($\theta_c > \theta_M$). We call G the « Ghost » type.

At point « H » the biphasic isotropic region disappears even for $\theta_c > \theta_M$ (« owl » type).

Conclusion : The miscibility of two compounds can be completely modified by molecular alignments. For instance, if $U_{AB} > U \gg U_0$, the miscibility is total in the nematic phase. On the other hand, the two species demix if $|U_0| < |U_{AB} - U|$ when $U_{AB} < U$.

4.2 POLYMER-POLYMER MIXTURES : $N_A = N_B = 100$. — We have represented on figure 5 the phase diagrams corresponding to the points (L, J, D) (E, G, H) of figure 3. It is interesting to compare the results to case (a) pictured on figure 4.

4.2.1 $\theta_c > \theta_c^{nem}(y > x)$.

At point « L », the biphasic NI region is now increased, as expected from the discussion of paragraph III.2 ($\Phi_N/\Phi_i \rightarrow 0$ as $N_{A,B}$ become large).

At point « J » one observes the same effect.

The structure at point « D » is completely modified. For $N = 1$, it was « Napoleon » type. For $N = 100$, it becomes « Chinese hat ». The reason is simple : as soon as a nematic order appears, the mixture becomes

miscible at all temperatures : $\theta_c^{nem}/\theta_c = 1 + (U - U_{AB})S^2$. Since U and U_{AB} are of the order of 100, θ_c^{nem} is always negative.

4.2.2 $\theta_c < \theta_c^{nem}(y < x)$.

For $U > U_{AB}$, $\theta_c^{nem}/\theta_c \simeq 100$. This property is well displayed at point « E » : the miscibility is suppressed by the nematic order. Note also the large thickness of the NI region.

At point « G », we find almost complete immiscibility in the nematic phase.

At point « H », the one nematic phase is restricted to extremely small Φ .

Conclusion : At large N , one notices two effects :

1) the thickness of the NI coexistence zone becomes very large ;

2) in the nematic state, the mixture becomes completely miscible for $U_{AB} > U$ or completely *immiscible* if $U_{AB} < U$. This is typical of polymer systems, where a slight incompatibility is enough to provoke complete phase separation.

4.3 MONOMER-POLYMER MIXTURES : $N_A = 1$, $N_B = 100$. — We have represented on figure 6 the phase diagrams corresponding to the points (Q, R) (M, N, P) of figure 3. In this case (C), one must compare θ_c , θ_c^{nem} and $\theta_p(\Phi_c) \simeq \theta_A$. In the space of the parameters (x, y), it corresponds to four regions limited by the bisector $\Delta_1(\theta_c = \theta_c^{nem})$ and the line $\Delta_2(x = 1/2$ or $\theta_c = \theta_A)$.

4.3.1 $\theta_c > \theta_c^{nem}(y > x)$. — We have chosen the points Q and R, one above and one below $x = 1/2$.

At point « Q », $\theta_A < \theta_c$: one first observes a demixing in the isotropic phase ($\theta_c = 1.65$, $\Phi_c \simeq 0.1$) corresponding to the top of the distorted « hat » shape biphasic region. In the nematic-isotropic part, one notices a large dissymmetry : for $\theta \simeq \theta_A$, the ratio of the thickness for the coexistence zone is of order $N_B/N_A = 100$. We also find an azeotrope for $\Phi = 1/2$, $\Phi_Z = \theta_M = 1.48$ (as predicted by our general theorem of section III). We observe no demixing in the nematic phase because $\theta_c^{nem} < 0$.

At point « R », $\theta_A > \theta_c$ and $\theta_c^{nem} < 0$. We have just a NI biphasic region, thin on the B side and thick on the A side. The two polymers are completely miscible.

4.3.2 $\theta_c < \theta_c^{nem}(y < x)$.

At point « M », $\theta_c > \theta_A$. This diagram is a deformed « Ghost » derived from point G of figure 4.

At points « N », « P », the demixing in the isotropic phase disappears because $\theta_c < \theta_A$. These two diagrams correspond to the « Donkey shape » case F of figure 4.

On « P », the asymmetry of the two phases region is clear-cut because $U_{AA} \simeq U_{AB}$. One expects a very thin zone on B side and a large zone on A side.

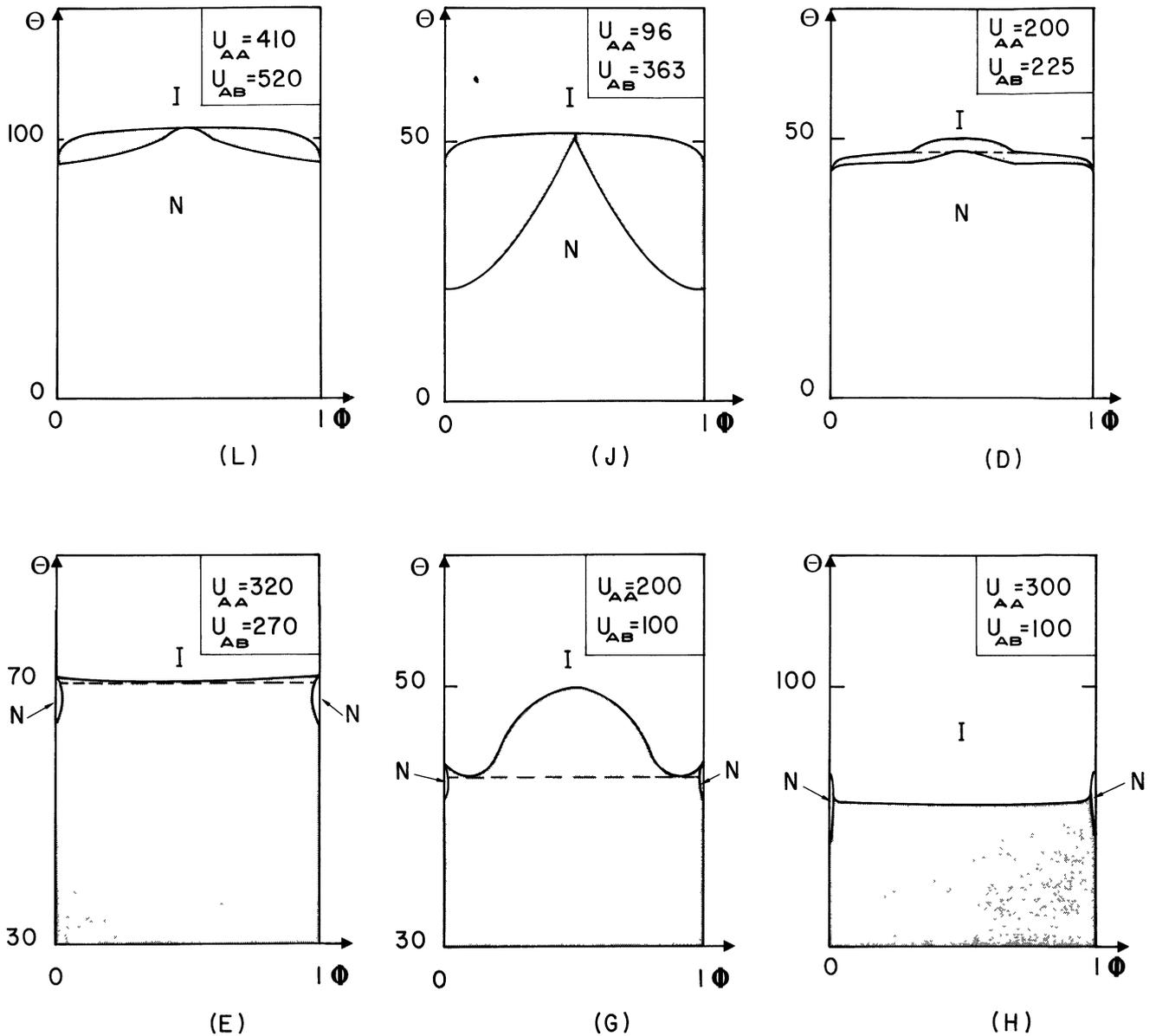


Fig. 5. — Phase diagrams for polymer-polymer mixtures ($N_A = N_B = 100$) associated to the points (L, J) (D) (E) (G, H) of figure 3. Compare with the monomer-monomer case and notice the thickening of the (N/I) coexistence zone. At point « D » (« Chinese hat ») : the demixing in the « N » phase has disappeared. The diagram « E » is transformed in a « Donkey ». At point « G » and « M », we find almost complete immiscibility in the « N » phase.

(On « N », the dissymetry is less because $U_{AB} \ll U_{AA}$).

Conclusions : This case is intermediate between case (a) and (b). The miscibility of the polymer chain in the nematic phase is very small as soon as $U_{AB} < U_{AA}$. This is related to the most familiar case of a non-nematogenic polymer polymer solute (PS, PE...) in a nematic solvent [15, 4]. One can dissolve only a small fraction of P chains. On the other hand, if $U_{AB} > U_{AA}$, the miscibility of a polymer and a small monomer is largely increased by the nematic alignment.

5. Conclusion.

1) We have established a certain catalog of allowed phase diagrams for mixtures of nematogens, showing the effects of interactions and of molecular weight.

2) The catalog is restricted however by a certain number of constraints :

a) we have taken the enthalpy of mixing in the isotropic phase as positive ;

b) we have mainly concentrated our discussion on $U_{AA} = U_{BB}$ (cases of chemical similarity). This res-

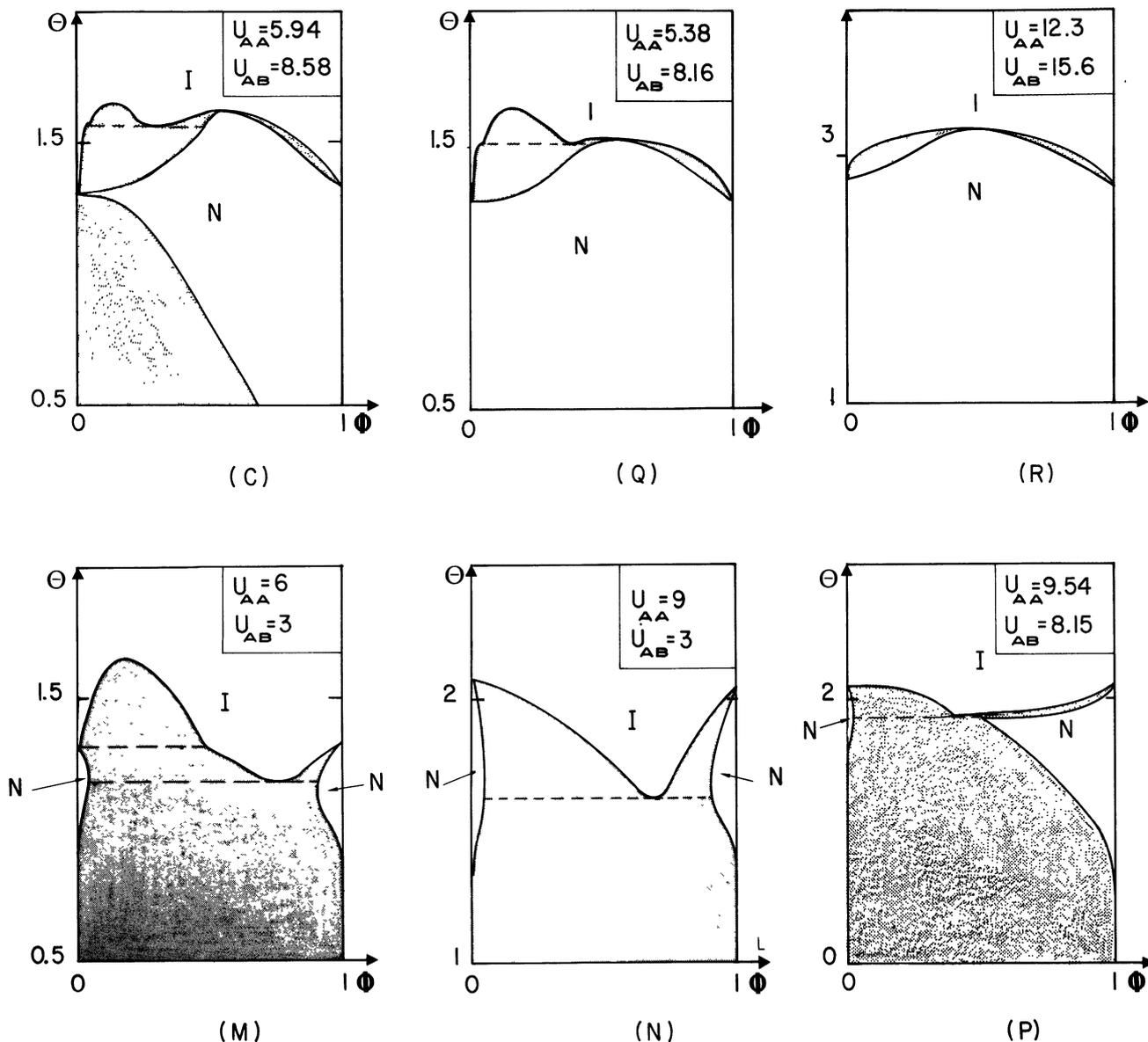


Fig. 6. — Phase diagrams for monomer-polymer mixtures ($N_A = 1, N_B = 100$) associated with the points R, Q, M (N, P) of figure 3.

triction is probably not too serious for qualitative purposes;

c) we have not include persistent length change effects : it seems a good approximation for polymer with mesogenic side groups where the main chains are decoupled from alignment of mesogenic units by the spacers ;

d) all crystal phases (or smectic phases) have been omitted from the discussion.

On the whole, we feel that our choice of constraints is reasonable at the present stage.

3) The inverse problem is of course of major

interest. From measurements on dilute solutions (A in B and B in A) we can extract four slopes giving the two heats of transformation of the pure compounds plus two free energies of transfer $\Delta G_A, \Delta G_B$. From T_A, T_B and the four slopes, using equations (26), (27), (28), (29) we can derive the three interactions constants U_{AA}, U_{BB}, U_{AB} , and the ratio N_A/N_B . Thus our choice of phenomenological parameters appears rather well adjusted.

4) Of course, in the more distant future, it may be necessary to improve on various features — e.g. : to distinguish between a nematogenic portion and a

spacer portion in side group polymers, allowing for different order parameters in both parts, etc... It may also be necessary to improve on the Maier Saupe theory to reconcile the transition points T_A , T_B and the latent heat ΔH_A , ΔH_B : but they are clearly problems of the second generation.

Acknowledgments.

We are grateful to P. G. de Gennes, M. Veysié, C. Casagrande and C. Noël for numerous discussions and comments.

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