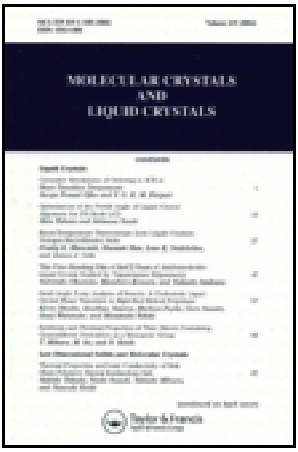

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Equal G Analysis of Unusual Binary Phase Diagrams†

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The equal G analysis recently introduced to the field of liquid crystals is used to fit some extraordinary phase diagrams. In binary systems of highly polar components non-linear phase transitions are observed, which give rise to reentrant behaviour. We show, that in spite of the complex phase behavior, it is possible to describe such systems in terms of the ideal mixture. To this end we take into account the heat capacity, as was already done by Oonk[7] and van Hecke[8] to explain binary phase diagrams. We generalize their approach and get an expression for the chemical potential up to the fifth order in the temperature. That means, the chemical potential difference of the pure component possesses up to five zeros, i.e. transition points between the two phases under discussion.

Unfortunately, up to now there is a lack of experimental data to verify such a behaviour of the heat capacity.

Keywords: reentrant, smectic, heat capacity, Gibbs free energy

INTRODUCTION

Since the discovery of reentrant phases several theories[1,2,3,4] were developed to explain the phenomenon.

The equal G analysis recently introduced to the field of liquid crystal research has proved to be a powerful tool for the quantification of binary phase diagrams. Van Hecke[8] applied this simple thermodynamic approach to ideal and non-ideal systems. Continuing our present efforts in that field, we apply the equal G method to some unusual diagrams investigated by Pelzl *et al.*[6] and Hardouin *et al.*[5]

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Pelzl *et al.*[6] found in binary systems of homologues of 4-(β-cyanethyl)-phenyl 4-n-alkyloxycinnamates reentrant behaviour although the pure components were non-reentrant.

Hardouin *et al.*[5] found in a binary mixture of DB_8ONO_2 and DB_9ONO_2 even triply reentrant behaviour.

The observed phase transition lines are clearly non-linear although the constituent components belong in both cases to a homologous series. In the following we show, that it is possible to get a surprisingly good fit of the observed diagram without the use of excess terms. To this end, it is necessary to generalize the customary ansatz of the chemical potential difference at the transition point. This was already done by Oonk[7] in order to explain the phase diagrams of iron and its alloys.

We must go behind that approach to fit the above mentioned diagrams.

The general idea is the following: The maximal number of points of intersection of the phase transition curve with a line parallel to the temperature axis is related with the number of zeros of the chemical potential difference of the phases of the components.

Analyzing reentrant phase behaviour in mixtures we have to consider two cases:

(i) At least one constituent component shows reentrant behaviour.

(ii) Neither component is reentrant.

In the first case the reentrant component must show a complicated temperature dependence of the chemical potential difference allowing for so many zeros like transition points between the two phases occur. For simple reentrant behaviour a second order temperature dependence of the chemical potential difference (Δc_p = const.) allows for two transition points T^+ and T^- between the phases of interest. In the case of higher order reentrance we have to take into account the temperature dependence of the heat capacity difference Δc_p (T). This is done in section II.

If neither of the components of the mixture is reentrant the origin of the phenomenon is not clear. Excess terms may be of importance. But, in the chosen example[6] the reentrant region is close to one of the pure components. Therefore we believe *the properties* of this component to be responsible for the occurrence of the reentrant phenomenon in the mixture. We take into account the temperature dependence of the heat capacity. But, the values of the coefficients of the series expansion have to be determined in view of the non-reentrant character of the pure component.

Here we deal with a thermodynamical model. The phases are characterized by entropies, heat capacities and their derivatives. The existence of different phases is assumed "a priori" and their order doesn't come into play.

Derivation of the chemical potential difference

The customary ansatz for the chemical potential difference of the pure component is derived in the following way

$$\left.\frac{\partial \Delta\mu}{\partial \mathrm{T}}\right|_{p} = -\Delta \mathrm{S} \tag{1}$$

and

$$\Delta\mu(\mathrm{T}) = \Delta\mu(\mathrm{T}^{+}) - \int_{\mathrm{T}^{+}}^{\mathrm{T}} \Delta S(\mathrm{T}')\,d\,\mathrm{T}' \tag{2}$$

where ΔS is the entropy difference and $\Delta\mu(\mathrm{T}^{+}) = 0$ at the transition temperature T^{+}.

Assuming the entropy to be temperature independent, we get the well-known result

$$\Delta\mu(\mathrm{T}) = -\Delta S\,(\mathrm{T} - \mathrm{T}^{+}). \tag{3}$$

The Δ symbol here refers to the difference of thermodynamic quantities between the phases of interest.

The difference of the heat capacities of both phases must vanish because of the temperature independence of the entropy

$$\left.\frac{\partial \Delta S}{\partial \mathrm{T}}\right|_{p} = \frac{\Delta C_p}{\mathrm{T}} = 0$$

Following Oonk[7] we must assume non-zero heat capacity to explain reentrant behaviour. Here, in contrast to Oonk, we assume not only the heat capacity but also its derivatives up to the third order to be non-zero. Performing out the corresponding integrations we get a 5.

order expression for the temperature dependence of the chemical potential difference of the pure component

$$\Delta\mu(T) = -\Delta S(T^+)(T - T^+) - \Delta C_p(T^+)\left(T^+ - T + T\ln\frac{T}{T^+}\right)$$
$$- \Delta C_p'(T^+)\left[\frac{1}{2}(T - T^+)(T + T^+) - TT^+\ln\frac{T}{T^+}\right]$$
$$- \Delta C_p''(T^+)\left[\frac{1}{12}(T - T^+)(T^2 - 5TT^+ - 2T^{+2}) + \frac{1}{2}TT^{+2}\ln\frac{T}{T^+}\right]$$
$$- \Delta C_p'''(T^+)\left[\frac{1}{12}(T - T^+)(T^3 - 5T^2T^+ + 13TT^{+2} + 3T^{+3}) - \frac{1}{6}TT^{+3}\ln\frac{T}{T^+}\right] \qquad (4)$$

where $\Delta S(T^+)$ is the transition entropy at T^+ and $\Delta c_p(T^+)$ and $\Delta c_p^{|\cdot|}(T^+)$ are the heat capacity difference and its derivatives.

In general the above formula possesses five zeros, representing possible transition points of the pure component. The number of positiv, real zeros can be smaller, depending on the values of the coefficients of the above series expansion.

Depending on the experimental situation some of the coefficients can be neglected. Supposing the derivatives of the heat capacity to be zero we get the result of Oonk.[7]

Equal G approach to binary phase transitions

The total Gibbs energy of the phase of interest at temperature T and at constant pressure is given by

$$G(T,x) = x_1 \cdot \mu_1(T) + x_2 \cdot \mu_2(T) + x_1 \ln x_1 + x_2 \ln x_2 + G^E(T,x) \qquad (5)$$

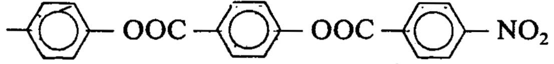
where $\mu_i(T)$ is the chemical potential of pure component (i) and x_i is the mole fraction.

The logarithmic terms represent the Gibbs energy of mixing and the last term is the excess Gibbs energy. The equal G method sets equal the total Gibbs energies of both phases instead of equating the corresponding chemical potentials of each component in each phase.

Therefore the biphasic region degenerates to the so-called equal *G* curve. Neglecting the excess Gibbs energy we get the following equal G equation for two phases α and β in equilibrium

$$\Delta G^{\alpha\beta} = x_1 \cdot \Delta\mu_1(\mathrm{T}) + x_2 \cdot \Delta\mu_2(\mathrm{T}) = 0 \tag{6}$$

Binary system of DB_nONO_2

Now we apply equations (4) and (6) to the phase diagram found by Hardouin *et al.*[5] in binary systems of $C_nH_{2n+1}O$—  or DB_nONO_2 for short. The experimental phase transition curve N-S_{Ad} is shown by the dashed line in Figure 1. The pure component DB_9ONO_2 shows four transition points nematic-smectic A_d at 468 K, 429 K, 411 K and 400 K. Therefore the use of equation (4) is recommended and the last term can be neglected.

We assume the highest transition temperature to be the reference value $T^+ = 468$ K. Moreover, there are transitions to smectic A monolayer and to the smectic C phases, which are outside our present interest. The first component DB_8ONO_2 has no nematic-smectic A_d transition in the region $400 \text{ K} \leq T \leq 468$ K. This is surprisingly because of the structural resemblance between the neighbouring homologues DB_8ONO_2 and DB_9ONO_2. For the sake of simplicity we employ the costumary ansatz (3) to the first component and get a satisfactory fit of the experimental phase boundaries. The application of higher order terms like (4) could achieve further improvements of the fit. But, this will not be investigated here.

Substituting $\Delta\mu_1(\mathrm{T})$ and $\Delta\mu_2(\mathrm{T})$ in equation (6) and we get with $\Delta C_p''' = 0$

$$X_1 \frac{\Delta S_1}{\Delta S_2}(\mathrm{T}_1^+ - \mathrm{T}) + x_2 \Bigg[\mathrm{T}_2^+ - \mathrm{T} + \frac{\Delta C_{p_2}}{\Delta S_2} \left(T - T_2^+ - T \ln \frac{T}{T_2^+}\right) + \frac{\Delta C'_{p_2}}{\Delta S_2}\left(\frac{1}{2}\mathrm{T}_2^{+2} - \frac{1}{2}\mathrm{T}^2 + \mathrm{T}\mathrm{T}_2^+ \ln \frac{\mathrm{T}}{\mathrm{T}_2^+}\right) - \frac{\Delta C''_{p_2}}{\Delta S_2}\left(\frac{1}{12}\mathrm{T}^3 - \frac{1}{2}\mathrm{T}^2\mathrm{T}_2^+ + \frac{1}{4}\mathrm{T}\mathrm{T}_2^{+2} + \frac{1}{6}\mathrm{T}_2^{+3} + \frac{1}{2} T T_2^{+2} \ln \frac{T}{T_2^+}\right)\Bigg] = 0 \tag{7}$$

where all caloric quantities refer to the transition temperatures T_1^+ and T_2^+, respectively.

Knowing the transition temperatures of DB_9ONO_2 the parameters $\Delta c_{p_2}/\Delta S_2$, $\Delta c'_{p_2}T_2^+/\Delta S_2$ and $\Delta c''_{p_2}T_2^{+2}/\Delta S_2$ are determined from the equation (4). These values only depend on the reduced transition temperatures T/T_2^+.

The parameters $\Delta S_1/\Delta S_2$ and T_2^+/T_1^+ are free to fit the experimental shape of the phase boundaries. Experimental data for the entropies and the transition temperature T_1^+ are not available. With respect to

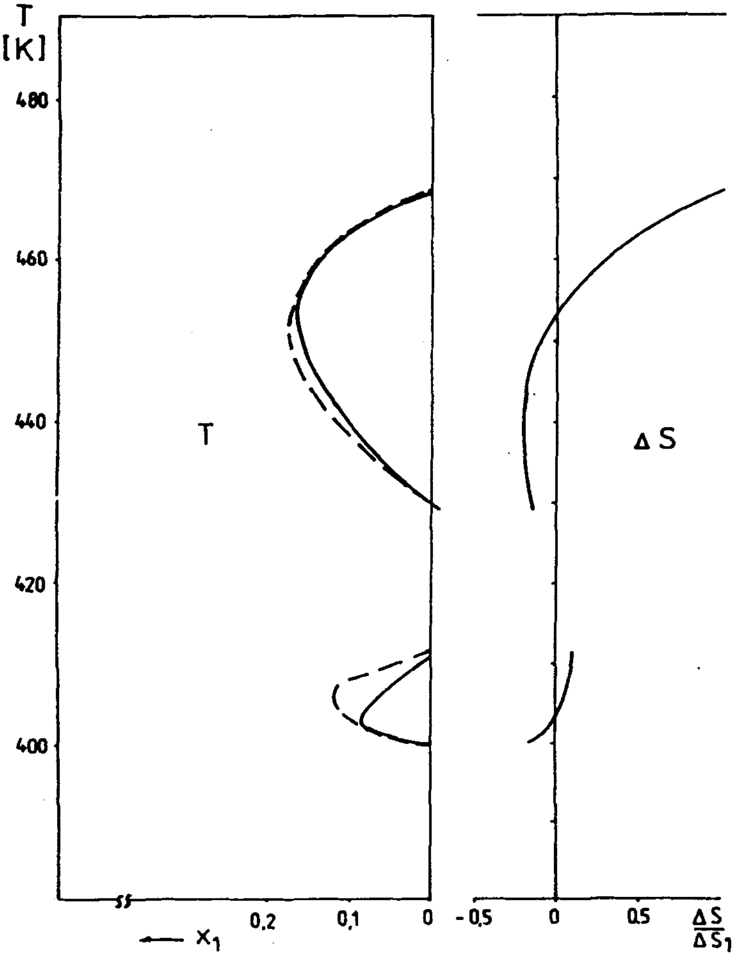


FIGURE 1 Transition temperatures versus mole fraction and transition temperatures versus transition entropy in the binary system of DB_8ONO_2 and DB_9ONO_2.

the temperature T_1^+ we know, that it must be outside the region of the transition temperatures of the second component.

The solid line in Figure 1 represents a fit to the experimental diagram, which was calculated with the following data set

$$\Delta c_{p_2}/\Delta S_2 = 52.97, \quad \Delta c'_{p_2}/\Delta S_2 = 2.951\ \mathrm{K}^{-1}, \quad \Delta c''_{p_2}/\Delta S_2 = 0.071\ \mathrm{K}^{-2}, \quad T_2^+/T_1^+ = 1.18, \quad \Delta S_1/\Delta S_2 = 0.5$$

It is worth noting, that the temperature ratio T_2^+/T_1^+ is very critical and must be in the range

$$1.17 \leq T_2^+/T_1^+ < 1.4$$

otherwise the character of the phase diagram will change dramatically. The calculated phase diagram is represented by the solid line in the left part of Figure 1. In the right part the calculated transition entropies are displayed.

Binary system of 4-(β-cyanethyl)-phenyl *4-n-alkyloxycinnamates*

In case of binary mixtures of 4-(β-cyanethyl)-phenyl 4-n-alkyloxycinnamates[6] the situation is quite different because three phase transitions come into play and none of the pure components is reentrant. The reentrant behaviour occurs only in a limited concentration range.

We deal here only with the C_6–C_{10} binary system of Ref. (6) to show the working principles.

Assuming the experimental transition lines to have metastable continuations throughout the whole concentration range we get virtual transition points of the C_6 component at

$$T_{NA} \sim 264\ \mathrm{K},\ T_{NC} \sim 272\ \mathrm{K}\ \text{and}\ T_{AC} \sim 337\ \mathrm{K}$$

The complete diagram consists now of two meander-like transition curves and a linear one, which all intersect at the NAC-point. The properties of such a critical point are outside the scope of our present interest and will not be discussed here.

The meander-like transition lines show up to three crossing points with a line parallel to the temperature axis. Therefore the use of the 3. order version of equation (4) is suggested. But, in the temperature region under discussion only one zero of $\Delta\mu$ (T) is allowed. We apply this ansatz to the C_{10} component and the customary ansatz (3) to the

C_6 component. We make such a choice because the reentrant region occurs in the vicinity of the pure C_{10} component. Substituting equations (3) and (4) in the equal G equation with $\Delta c_p'' = \Delta c_p''' = 0$ we get the following formula to calculate the meander-like nematic-smectic A transition line

$$x_1 \frac{\Delta S_1}{\Delta S_2}(\mathrm{T}_1^+ - \mathrm{T}) + x_2 \left[\mathrm{T}_2^+ - \mathrm{T} + \frac{\Delta C_{p2}}{\Delta S_2}\left(\mathrm{T} - \mathrm{T}_2^+ - \mathrm{T}\ln\frac{\mathrm{T}}{\mathrm{T}_2^+}\right) + \frac{\Delta C'_{p_2}}{\Delta S_2}\left(\frac{1}{2}\mathrm{T}_2^{+2} - \frac{1}{2}\mathrm{T}^2 + \mathrm{T}\mathrm{T}_2^+ \ln\frac{\mathrm{T}}{\mathrm{T}_2^+}\right)\right] = 0 \qquad (8)$$

Because the second component C_{10} has only one transition point N-S_A the parameters $\Delta c_{p_2}/\Delta S_2$, $\Delta c'_{p_2}/\Delta S_2$ and the entropy ratio $\Delta S_1/\Delta S_2$ are free to fit the experimental phase boundary.

The linear smectic A - smectic C transition can be calculated applying equation (3) to both components.

Since the free enthalpies of all three transitions are correlated according to

$$\Delta G^{\mathrm{NC}}(\mathrm{T}) = \Delta G^{\mathrm{NA}}(\mathrm{T}) + \Delta G^{\mathrm{AC}}(\mathrm{T})$$

the nematic-smectic C transition can easily be calculated from the other ones.

The calculated diagram for the C_6–C_{10} system is displayed in Figure 2. In the inset the applied parameter set is to be seen. To simplify the problem, the isotropic and solid phases are not taken into account. The dashed lines represent metastable branches.

The other diagrams of Ref. (6) can be treated in like manner.[9]

CONCLUSIONS

We apply the equal G method to analyse complex phase diagrams found in binary systems of liquid crystals. Taking into account the temperature dependence of the heat capacity we are able to explain highly non-linear phase diagrams without using excess terms. Such a procedure is justified because the constituent components belong to the same homologous series. The complex temperature dependence of the chemical potential difference is a consequence of the reentrant behaviour of the pure components. Of course, to improve the agreement with the experiment the use of additional excess terms is rec-

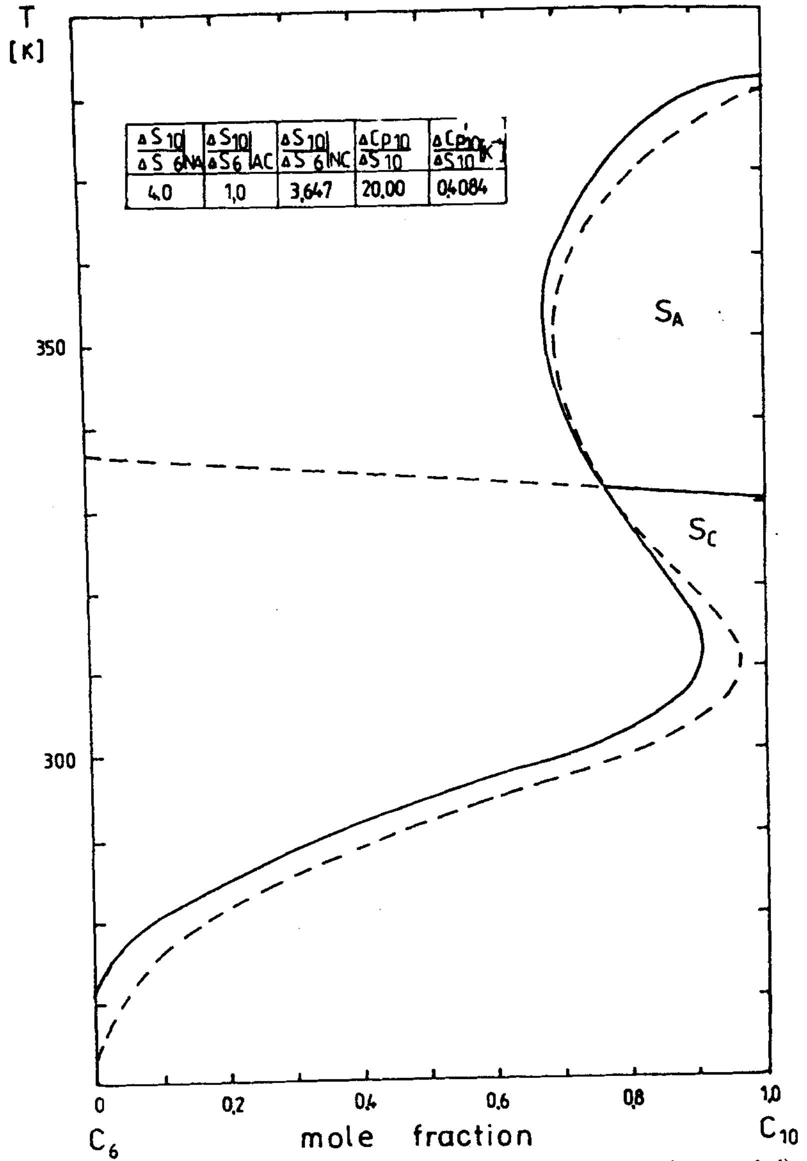


FIGURE 2 Calculated phase diagram of the C_6–C_{10} mixture of 4-(β-cyanethyl)-phenyl 4-n-aklyloxycinnamates redrawn from Ref. 6.

ommended. Even in cases where both components are non-reentrant our model can be used to explain the observed non-linear phase diagrams. In such cases also a complex temperature dependence of the excess term can be employed to account for the reentrant behaviour of the mixture or at least to improve the agreement with the experiment. The physical meaning of the additional excess parameters remains questionably for the time being.

But, the purpose of the present paper is not to find the best fit, but to show the influence of the temperature dependence of the heat capacity on phase transitions.

Our approach relates the phase behaviour of binary liquid crystal mixtures with the number of zeros of the chemical potential differences in the phases of interest.

Unfortunately, up to now there are no systematic measurements of the heat capacity in the vicinity of the reentrant transitions. We need not only knowledge of the heat capacity difference, but also its variation with the temperature to test equation (4).

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