Universality of the reentrant-nematic–smectic-C–smectic-A and nematic–smectic-A–smectic-C multicritical points

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(Received 11 June 1986)

It is shown that by tuning the experimentally observable critical region, singularities of the phase boundaries can be observed in the immediate vicinity of the reentrant-nematic–smectic-C–smectic-A multicritical point. The exponents evaluated from these singularities are found to be identical to the universal exponents associated with the nematic–smectic-A–smectic-C multicritical point.

Since the discovery of the nematic–smectic-A–smectic-C multicritical point (N-A-C point) in binary liquid-crystal mixtures,[1,2] there have been several experimental as well as theoretical studies to understand the nature of this multicritical point.[3-8] The universality of the topology of the phase diagram near the N-A-C point was established experimentally both in the temperature-concentration $(T$-$X)$[9] and pressure-temperature $(P$-$T)$ planes.[10] A second type of multicritical point, viz., the reentrant-nematic–smectic-C–smectic-A multicritical point (RN-C-A point), has been observed for a single-component system at high pressure[11,12] as well as for a binary mixture in the T-X diagram.[13] Two differences were observed in the case of the RN-C-A point. First, of course, the sequence of transitions (observed at a constant concentration or pressure) was not the same as for the N-A-C point. Second (and more important), singularities were conspicuously absent near the RN-C-A point, so much so that the topology of the phase diagram exhibiting the RN-C-A point did not resemble the universal topology of the N-A-C point. This was somewhat surprising. The symmetries of the different phases which constitute the RN-C-A point and the N-A-C point being the same, it is to be expected[14] that both of them exhibit the same universal behavior although the temperature sequence of transitions are different in the two cases.

In this Rapid Communication we present high-resolution T-X diagrams for two binary systems exhibiting the RN-C-A multicritical point. These diagrams show for first time that by bringing the RN-C-A point and the nematic-isotropic transition into closer proximity in temperature, the experimentally observable critical region can be increased and singularities can be observed in the vicinity of the RN-C-A point. Analysis of these singularities yields exponents which are identical to those obtained for the N-A-C system, showing thereby that these two types of multicritical points belong to the same universality class.

The complete phase diagrams for the two systems are given in Figs. 1 and 2. The transitions were detected optically using a polarizing microscope. In the neighborhood of the multicritical point, data were obtained with much greater precision, viz., ± 0.01 mol% in X and ± 10 mK in T. These high-resolution data are shown in Figs. 3 and 4. These data cover only a very small region of T and X in

the immediate vicinity of the RN-C-A point. (In fact, typically, the size of a circle in the global phase diagram of Fig. 1 constitutes the entire region of T and X shown in the high-resolution diagram of Fig. 2.) Clearly, singularities are seen for all three phase boundaries. These singularities exist over much narrower regions of T and X compared to the singularities seen near the N-A-C point. It may be recalled that in the earlier diagrams which reported the first observation of the RN-C-A point[11-13] such singularities wee not seen. In these systems the RN-C-A point was
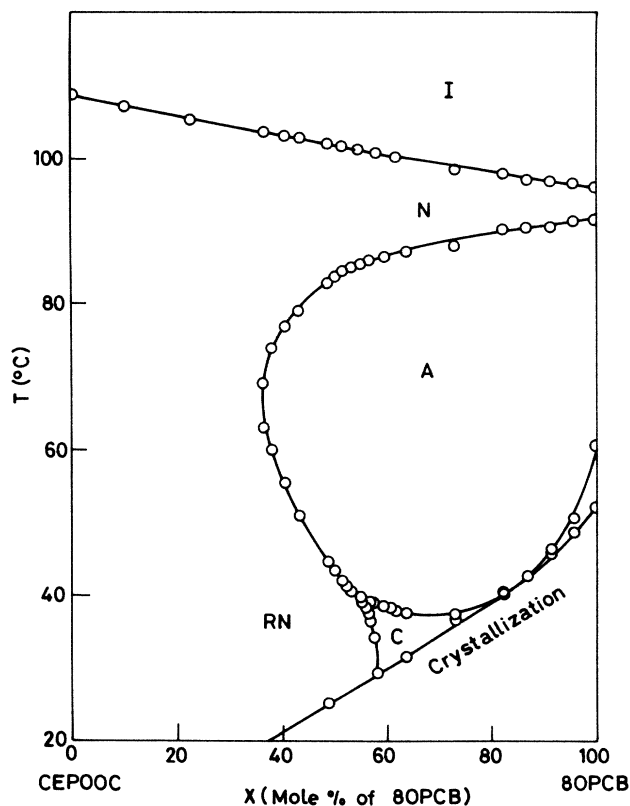

FIG. 1. Complete temperature-concentration $(T$-$X)$ diagram for binary mixtures of 4-cyanoethylphenyl-4'-octyloxycinnamate (CEPOOC) and 4'-octyloxyphenyl-4-cyanobenzoate (8OPCB). X is the mol% of 8OPCB in the mixture. The solid lines are guides to the eye.
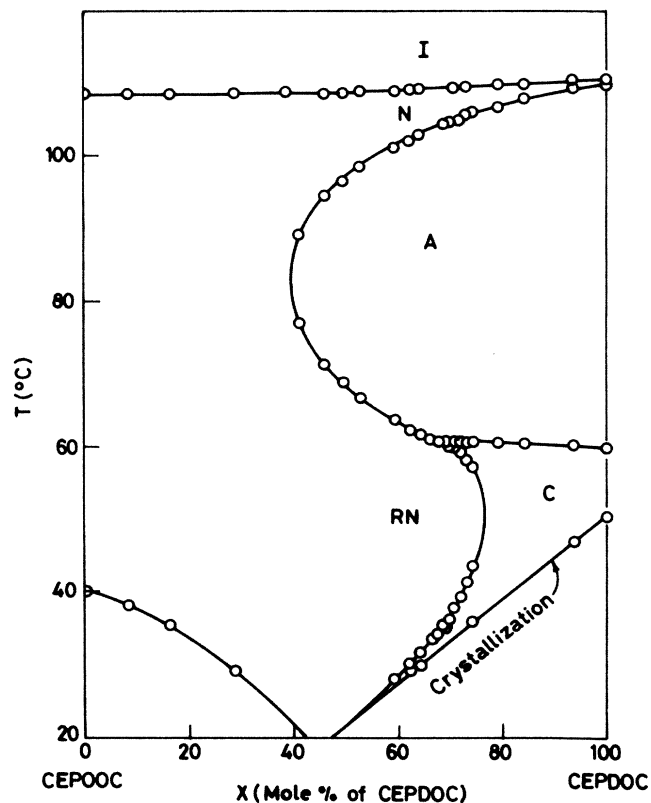
FIG. 2. Complete T-X diagram for binary mixture of CEPOOC and 4-cyanoethylphenyl-4'-decyloxycimnamate (CEPDOC). X is the mol% of CEPDOC in the mixture. The solid lines serve as guides to the eye.
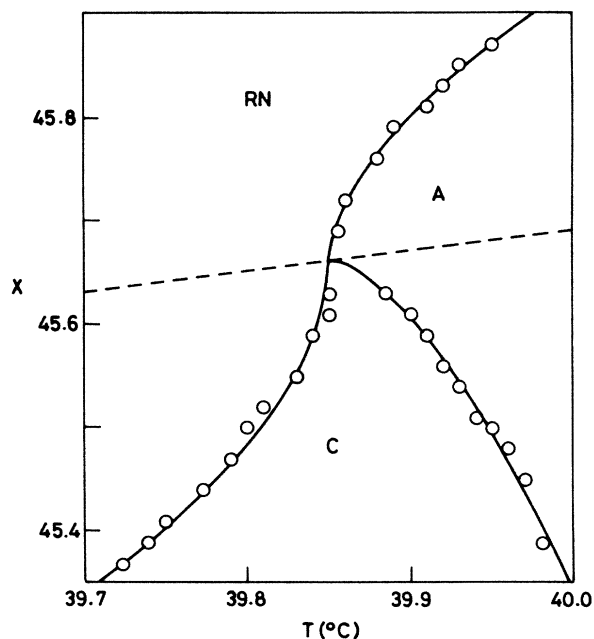

FIG. 3. High-resolution T-X diagram in the vicinity of the RN-C-A multicritical point in the 8OPCB+CEPOOC binary system (X is the mol% of CEPOOC). The solid lines are computer fits of our data to expressions for the A-RN, A-C, and C-RN phase boundaries (see text). The dashed line represents the best-fit B term.
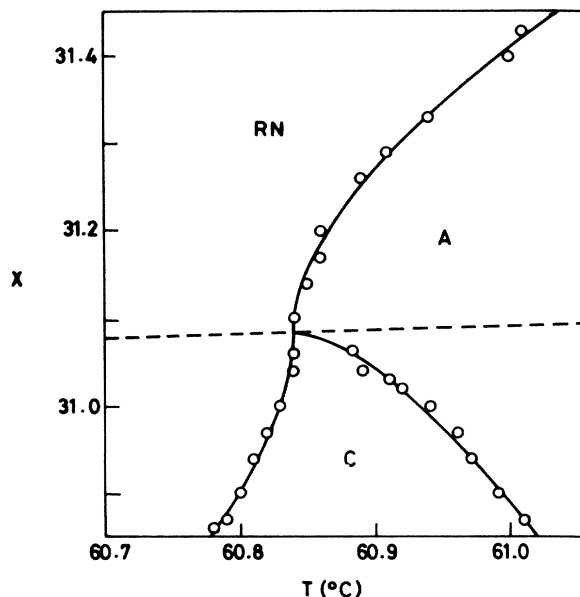

FIG. 4. High-resolution T-X diagram in the vicinity of the RN-C-A point in the CEPDOC+CEPOOC binary system (X is the mol% of CEPOOC). See also legend of Fig. 3.

about 180°C away from the nematic-isotropic transition. In the present case we have chosen the systems such that the RN-C-A point occurs much closer to the nematic-isotropic transition (60°C in Fig. 1 and 48°C in Fig. 2) and in so doing have been able to generate singularities in the vicinity of the RN-C-A point. This can perhaps be attributed to the "tuning" of Brazovskii fluctuations.[15] These fluctuations are believed to induce the smectic-C–nematic transition to be first order.[16] It is conceivable that in the phase diagram wherein the RN-C-A point was nearly 180°C away from the nematic-isotropic transition, the Brazovskii fluctuations were practically absent near the RN-C-A point. This would make the bare correlation length very large and, consequently, the critical region would be too small to be observed experimentally. This situation is similar to the mechanism which causes mean-field behavior in spin-reorientation transitions in magnetic systems.[17] On the other hand, in the present case wherein the RN-C-A point lies much closer to the nematic-isotropic transition, the critical region has probably been made effectively larger and thereby it has been possible to see singularities near the RN-C-A point.

We shall now analyze the singularities quantitatively. It is relevant to recall that the remarkable feature of the results on the N-A-C multicritical point was that the scaling axes were the same as the experimental axes—P and T in the case of a single-component system, T and X in the case of binary systems. In our computations on the RN-C-A point we have used essentially the same expressions as those used by Brisbin, Johnson, Fellner, and Neubert[9] for the N-A-C system but with a simple 90° rotation of the scaling axes. This is necessary because of the differences in the sequences of transitions near the RN-C-A point compared to that near the N-A-C point—the nematic phase is the lowest temperature phase in the case of the former, while it occurs as the highest temperature phase in

the case of the latter. The results of our computations carried out in this manner and with the same universality constraint as was used in previous computations[9,10] (i.e., $\eta_{A\text{-RN}} = \eta_{C\text{-RN}}$), are given in Table I, $\mathcal{A}$ and η being the amplitude and the exponent defined by the scaling relations (see Ref. 9 for details regarding the form of the expressions). The exponents are, within statistical uncertainties, the *same* as the universal exponents associated with the N-A-C point.[9,10] Thus, despite having different temperature sequences of phase transitions, *the RN-C-A and the N-A-C multicritical points exhibit the same universal behavior.*

It will be of interest to study the effect of tuning the critical region near the RN-C-A point in a single-component system at high pressure. High-resolution x-ray and calorimetric experiments on the RN-C transition should also be of much interest. On the theoretical side, although there have been predictions on the x-ray scattering profile and the behavior of elastic constants near the N-A-C point,[18,19] there is no theory which explains the uniqueness in the topology of the phase boundaries near the N-A-C and RN-C-A multicritical points. Also the biaxial nematic phase which is predicted by the renormalization-group theory[7] is yet to be observed experimentally near either of these multicritical points. Further studies, experimental as well as theoretical, are clearly needed to elucidate the nature of multicritical points in liquid crystals.

TABLE I. Best-fit parameters and values of χ^2 obtained from individual fits of our high-resolution T-X data to the expressions similar to those given in Ref. 9 but with a 90° rotation of the scaling axes (see text).

	8OPCB+CEPOOC	CEPDOC+CEPOOC
B	0.20 ± 0.10	0.05 ± 0.15
$T_{\text{RN-}C\text{-}A}$ (°C)	39.85 ± 0.01	60.84 ± 0.01
$X_{\text{RN-}C\text{-}A}$ (mol%)	45.66 ± 0.01	31.085 ± 0.01
$\eta_{C\text{-RN}} = \eta_{A\text{-RN}}$	0.571 ± 0.03	0.569 ± 0.03
$\eta_{A\text{-}C}$	1.531 ± 0.02	1.528 ± 0.03
$\mathcal{A}_{A\text{-RN}}$	0.6976 ± 0.15	0.8942 ± 0.13
$\mathcal{A}_{C\text{-RN}}$	-1.0349 ± 0.20	-1.1688 ± 0.14
$\mathcal{A}_{A\text{-}C}$	-6.3896 ± 0.70	-3.3215 ± 0.50
$\chi^2_{A\text{-RN}}$	1.083	1.058
$\chi^2_{C\text{-RN}}$	0.946	1.079
$\chi^2_{A\text{-}C}$	1.083	0.944

[1]D. Johnson, D. Allender, R. de Hoff, C. Maze, E. Oppenheim, and R. Reynolds, Phys. Rev. B **16**, 470 (1977).

[2]G. Sigaud, F. Hardouin, and M. F. Achard, Solid State Commun. **23**, 35 (1977).

[3]For a review of the work on the N-A-C point until 1982, see D. L. Johnson, J. Chim. Phys. **80**, 45 (1983).

[4]C. R. Safinya, L. J. Martinez-Miranda, M. Kaplan, J. D. Lister, and R. G. Birgeneau, Phys. Rev. Lett. **50**, 56 (1983).

[5]S. Witanachi, J. Huang, and J. T. Ho, Phys. Rev. Lett. **50**, 595 (1983).

[6]J. Shecti, A. Zywocinski, and S. A. Wieczorek, Phys. Rev. A **28**, 434 (1983).

[7]G. Grinstein and J. Toner, Phys. Rev. Lett. **51**, 2386 (1983); **54**, 1732 (1985); see also P. Bak and R. Bruinsma, *ibid.* **54**, 1731 (1985).

[8]Y. Drossinos and D. Ronis, Phys. Rev. A **33**, 589 (1986).

[9]D. Brisbin, D. L. Johnson, H. Fellner, and M. E. Neubert, Phys. Rev. Lett. **50**, 178 (1983).

[10]R. Shashidhar, B. R. Ratna, and S. Krishna Prasad, Phys. Rev.

Lett. **53**, 2141 (1984).

[11]R. Shashidhar, A. N. Kalkura, and S. Chandrasekhar, Mol. Cryst. Liq. Cryst. Lett. **82**, 311 (1982).

[12]R. Shashidhar, S. Krishna Prasad, and S. Chandrasekhar, Mol. Cryst. Liq. Cryst. Lett. **103**, 137 (1983).

[13]G. Sigaud, Y. Guichard, F. Hardouin, and L. G. Benguigui, Phys. Rev. A **26**, 3041 (1982).

[14]L. P. Kadanoff, in *Critical Phenomena, Enrico Fermi Course LI*, edited by M. S. Green (Academic, New York, 1971), p. 100.

[15]S. A. Brazovskii, Zh. Eksp. Teor. Fiz. **68**, 175 (1975) [Sov. Phys. JETP **41**, 85 (1975)].

[16]J. Swift, Phys. Rev. A **14**, 2274 (1976).

[17]See, e.g., J. D. Litster and R. G. Birgeneau, Phys. Today **35** (No. 5), 26 (1982).

[18]J. Chen and T. C. Lubensky, Phys. Rev. A **14**, 1202 (1976).

[19]K. C. Chu and W. L. McMillan, Phys. Rev. A **15**, 1181 (1977).