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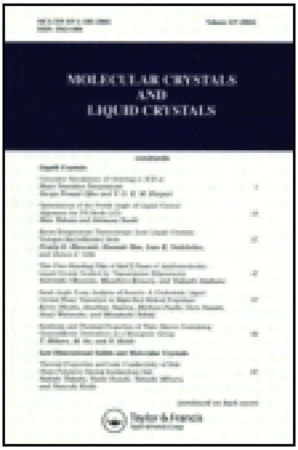

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The Interfacial Free Energy of Nematogen Droplets in an Isotropic Matrix: Determination of its Temperature Dependence from Coalescence Kinetics

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The Interfacial Free Energy of Nematogen Droplets in an Isotropic Matrix: Determination of its Temperature Dependence from Coalescence Kinetics

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We have determined the surface free energy, σ, at the interface between a nematogen and an isotropic liquid by measurement of the time constant for coalescence of nematogen droplets imbedded in the matrix. The basis for this technique is an analysis developed by Frenkel in 1945. The major conclusions of the present work are four-fold: 1) the magnitude of the interfacial free energy is on the order of 10^{-2} to 10^{-1} dyne/cm; 2) the temperature dependence of σ for nematic droplets shows a greater negative slope than for isotropic droplets; 3) the accuracy of the method is insufficient to detect a discontinuity in σ at the nematic to isotropic transition temperature; and 4) the interfacial free energy decreases toward zero as the temperature increases toward that at which the droplets dissolve in the matrix. This last behavior was expected by analogy with the Eotvos expression for ordinary liquid/vapor surface free energies. The droplet coalescence technique shows promise as a means for determining temperature-dependent interfacial free energies for other liquid/liquid systems.

INTRODUCTION

The interfacial free energy, σ, of a liquid crystal (LC) at its boundary with another phase plays a role in determining the surface orientation of the LC molecules. Goosens[1] has discussed the relationship of σ to both order parameter and surface anchoring energy, *W*, of the liquid crystal molecules, pointing out that it is not yet possible to calculate the strength or even the sign of the latter. However, the importance of the anchoring energy to molecular orientation—and hence performance of many liquid crystal devices—has been empirically recognized for a long time. A processing step in the fabrication of many liquid crystal displays (LCDs) has been the chemical or physical treatment of a containment medium (e.g., glass or plastic) to produce a desired LC molecular alignment. Cognard[2] has published an extensive review of mechanisms and techniques for alignment of nematic liquid crystals at surfaces. Surface free energy also presumably determines the molecular orientation in droplets of polymer-dispersed liquid crystal (PDLC)

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films.[3-5] These electro-optic films, in which submicron liquid crystal droplets are dispersed throughout a polymer matrix, are candidates for several applications, including variable transmittance windows and display devices.

Anchoring energy has been measured for the interfaces of a nematic with a solid, with its own vapor, and with its own isotropic phase. Determinations of both W and σ have been made at the nematic-isotropic and nematic-vapor interfaces. For the NI interface, $W \sim 10^{-4}$ to 10^{-3} dyne/cm[6] and $\sigma \sim 10^{-2}$ dyne/cm,[7-10] so that $W/\sigma \sim 10^{-2}$ to 10^{-1}. For the nematic-vapor interface, $W \sim 4 \times 10^{-3}$ to 6×10^{-2} dyne/cm[6] and σ is roughly[2] 30 dyne/cm, giving $W/\sigma \sim 10^{-4}$ to 10^{-3}. Grechko, *et al.*[11] have discussed the magnitude of anchoring energies expected for the nematic-polymer interface in a PDLC; they estimated that W is approximately 10^{-2} dyne/cm, in good agreement with the recent experimental determination of Erdmann, *et al.*[12] These results make the measurement of σ for a similar system particularly intriguing.

Clearly, the interfacial free energy of PDLCs is incompletely understood, Although free energies for ordinary liquid/liquid interfaces have been measured using the pendant drop method,[13] interfacial free energies of nematogen droplets in a matrix have been determined in apparently only a few special cases: liquid crystal droplets in equilibrium with their own isotropic phase at a single temperature.[7-10] Consequently, we have undertaken to determine interfacial free energies of nematogen droplets embedded in two different matrices with moderate viscosities: one a mixture of monomers and oligomers, the other a low molecular weight polymer. Our intent was to determine the interfacial free energy over as wide a temperature range as possible: from just above the crystal-nematic transition temperature, T_{KN}, through the nematic and isotropic ranges, up to the temperature where the isotropic droplets dissolve in the matrix.

By analogy with liquids below their critical temperature, we expected that the surface free energy would exhibit Eotvos-like behavior.[14,15] In such a case σ should decrease monotonically with temperature in a manner like that shown schematically in Figure 1. The temperature dependence of the high temperature portion of the curve might then be given by an expression analogous to the Eotvos equation:

$$\sigma = \text{const } x\ (T_{\text{sol}} - T) \tag{1}$$

where T_{sol} is the critical solution temperature at which the droplets completely dissolve in the matrix. (T_{sol} replaces T_c, the critical temperature, in the Eotvos equation.) The discontinuity seen in Figure 1 at the nematic-isotropic transition temperature, T_{NI}, should be on the order of the nematic-isotropic interfacial free energy, σ_{NI}, which has been shown to be approximately 10^{-2} dyne/cm.[7-10] Whether or not a change this small could be detected would depend on the accuracy of the determination scheme. Another feature seen in Figure 1 is the greater negative slope of the curve for the nematic as compared to the isotropic range. We suggest this behavior in analogy to that for a nematogen-air interface as seen by Schwartz, *et al.*[16]

The method we used to determine the interfacial free energy is based on droplet coalescence, the process whereby two touching liquid drops, embedded in a matrix,

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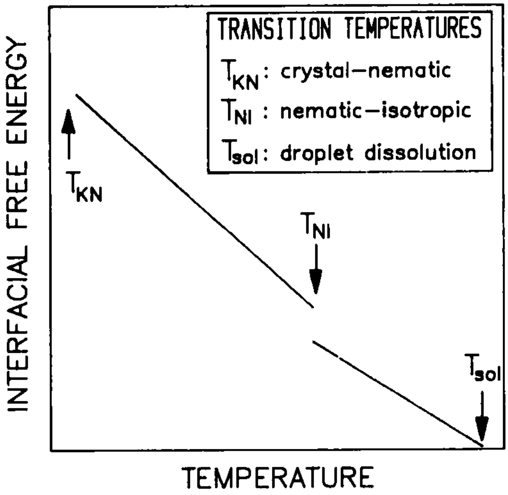

FIGURE 1 Schematic diagram illustrating expected temperature dependence of interfacial free energy for surface between nematogen droplets and polymer matrix. Major features indicated are: steeper negative slope for nematic phase compared to isotropic; discontinuity at nematic-isotropic transition; and decrease to zero at temperature where droplets dissolve in matrix.

flow together to become a single larger droplet. A simple approximate equation for this process was derived by Frenkel[17] and will be described below. Obviously the coalescence technique is applicable only to cases where both matrix and droplets are fluid; hence, the method cannot be used to determine the droplet-matrix interfacial free energy in a PDLC, for which the matrix is rather rigid. Nevertheless, σ values obtained for the uncured system can be regarded as lower limits for a PDLC. It should also be pointed out that the method can usefully be extended to determine interfacial free energies over a wide temperature range for other binary fluid systems.

EXPERIMENTAL ASPECTS

Materials

Two liquid crystals were chosen for these experiments: ROTN-404[18] (a mixture of cyanobiphenyl, cyanoterphenyl, and cyanopyrimidine compounds) and 5CB[19] (a single component liquid crystal, 4′-*n*-pentyl-4-cyanobiphenyl). The mixture has so wide a nematic temperature range (from below room temperature to 105°C) that isotropic droplets could not be formed in the matrix (the nematic material dissolved in N65 at about 36°C). Therefore we used ROTN-404 only in a preliminary experiment to test the measurement methods. The single component liquid crystal has a sufficiently narrow bulk-phase nematic range (24°C to 35°C) for an experiment covering the entire temperature range of interest (from T_{KN} to T_{sol}), provided a matrix with the appropriate solubility behavior is used. Since 5CB contains only a single nematogen, it had the added advantage that no preferential dissolution of components in the matrix could occur.

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Two matrix materials were selected: uncured Norland[20] Optical Adhesive 65 (abbreviated N65, a mixture of monomers and oligomers) and a Polysciences[21] viscosity standard, a polydimethylsiloxane (PDMS) with low molecular weight [M_n = 5970] and viscosity of 100.5 cp at 25°C. PDMS had two additional advantages: 1) Its density (0.982) is comparable to that of 5CB (1.023), so that droplets of 5CB formed in a PDMS matrix do not rapidly settle or rise. 2) The viscosity of PDMS is much closer in magnitude to that of 5CB over the entire temperature range than is that of N65 (e.g., at −10°C the viscosities of N65, PDMS, and 5CB are 13180 cp, 208 cp, and 212 cp, respectively; at 15°C they are 1939 cp, 119 cp, and 40.4 cp). As a result, for a PDMS matrix, computation of the viscosity which controls coalescence is less subject to errors due to assumptions regarding the contributions of droplet and matrix viscosities (see below).

Sample viscosity

As will be seen below, knowledge of the temperature-dependent viscosity of the materials is needed in order to derive the interfacial free energy from measurements of droplet coalescence. We obtained viscosity values for the four components by a variety of means. The temperature dependence of the viscosity, η, is generally assumed to be given by[22–24]

$$\ln \eta = A + B/T, \tag{2}$$

where A and B are constants and T is the temperature in kelvins.

Values of A and B were determined for N65 from viscosity measurements[25] at 40°C and 100°C (313 K and 373 K). The coefficients for the polydimethylsiloxane (PDMS) were obtained in two ways: from the 25°C value and a temperature coefficient[26] provided by Polysciences; and by viscosity measurements[25] at two temperatures. The PDMS coefficients determined from the two methods agreed very well: A to within 10%, B to within 4%. The viscosities calculated from the two sets of coefficients agreed to better than 10% over the entire temperature range of interest, i.e., to within experimental error of the measurements. The PDMS coefficients in Table I are those derived from the Polysciences data.

Values of A and B for the two liquid crystals were determined using published or manufacturer's data at a temperature near ambient and logarithmic slope values for similar systems. As Schadt and Mueller[27] have pointed out, the slopes of similar systems are nearly identical. Magnitudes of the constants for the four components studied are given in Table I.

Sample preparation

Samples were prepared by mixing a liquid crystal with its matrix material in a concentration capable of producing a dispersion of suitably sized (generally a few to 40 μm in radius) LC droplets in the temperature range of interest. The mixtures were placed between a glass slide and cover plate separated by glass fiber spacers. The spacers used were large compared to the droplet diameters so that we could conduct our studies on droplets floating freely in the matrix and not in contact with either glass substrate.

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TABLE I

Viscosity coefficients (For viscosity in centipoise)

SAMPLE	A	B
Liquid crystals		
ROTN-404	−13.58	5383
5CB	−13.75	5027
Matrix materials		
N65	−12.6	5811
PDMS	− 1.07	1686

Temperature control was achieved by placing the slide in the sample chamber of a Mettler FP5 + FP52 thermal microscopy system,[28] a unit which provides stable temperatures with a precision of 0.1°C. Temperatures below −20°C were attainable by circulating precooled nitrogen gas through the chamber, and the temperature was monitored using a thermocouple attached directly to the sample slide. The sample chamber was mounted on the stage of a Reichert Zetoplan microscope.[29] Optical images of droplet coalescence could then be studied by direct visual observation, by video cassette recording using a VCR with stop-action capability, or by high speed electronic recording with a Spin Physics motion analysis system.[30]

Determination of σ from coalescence kinetics

In 1945 Frenkel published a seminal paper[17] describing the kinetics of coalescence of two initially touching droplets of radius R. He derived an approximate equation for the time, τ, required for the two droplets to coalesce:

$$\tau = \eta R/\sigma. \tag{3}$$

This equation is simple but extremely useful. Strictly speaking, the equation applies only during the early stages of coalescence, and a number of other workers have subsequently modified it to extend it to a variety of situations.[31] However, as has been demonstrated in studies of mesophase droplet coalescence,[9–10] the original Frenkel expression yields interfacial free energy values in good agreement with determinations from other methods.

Having accepted the validity of Equation (3), one can easily determine values of both τ and R by frame-by-frame inspection of VCR or Spin Physics recordings. In our studies we selected coalescence events in which the droplet pairs were as similar in size as possible. The mean value of R was used in the Frenkel equation.

CONSIDERATIONS REGARDING VISCOSITIES FOR DROPLET COALESCENCE

In applying Equation (3) the most difficult quantity to assess is the viscosity. There are several reasons why this should be so. First, the temperature-dependent viscosity of the components (i.e., mesogen and matrix) must be measured or otherwise

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evaluated independent of the coalescence studies. This aspect has been discussed above. Second, we must determine the relationship of the viscosity actually controlling the coalescence of the droplets to the viscosities of the components. This relationship may be different from that for a homogeneous mixture or for a bulk dispersion of the two components. Finally, account must be taken of the effect of droplet dissolution on viscosity as T_{sol} is approached. We shall discuss this last aspect after considering how to determine the viscosity which controls coalescence.

Viscosity which controls coalescence

Fortunately, this aspect of the viscosity question has been addressed for a related system, the motion of a liquid droplet in a second fluid at a planar surface. Foister[32] has shown that the viscosity which governs the early stages of the spontaneous displacement of the liquid by the droplet as it coalesces with the planar interface is essentially the geometric mean, $(\eta_1\eta_2)^{1/2}$, of the viscosities of the two components. Although Foister's system is not identical to our own, it is sufficiently similar to justify our use of his expression. Thus, the viscosity controlling the coalescence of two droplets is taken to be

$$\ln \eta = 0.5(\ln \eta_d + \ln \eta_m), \tag{4}$$

where η_d and η_m are the viscosities of the nematogen in the droplets and of the matrix respectively.

The use of the geometric mean (Equation 4) is satisfying since it has been previously pointed out[10] that the flow properties of both droplets and matrix govern droplet coalescence so that a viscosity intermediate to the values of both systems should be used. It is fairly easy to see that, on a local scale, the coalescing motion of two droplets is opposed by viscous forces within both the droplets and the surrounding matrix. Furthermore, the viscous forces in the immediate neighborhood of the two droplets should not be affected by the number of droplets farther away. In other words, the viscosity governing coalescence should be independent of droplet concentration for a fairly wide range of concentrations, as is the case for Equation (4).

Finally, it should be emphasized that the closer η_d and η_m are in magnitude, the smaller should be any error due to the use of Equation (4). Therefore, we expect the σ values for PDMS/5CB to be more reliable than those for N65/5CB.

Effect of droplet dissolution

In addition to the intrinsic temperature dependence of the viscosity, there is a second temperature effect due to the dissolution of the droplets in the matrix as the critical solution temperature, T_{sol}, is approached. Since the ROTN-404/N65 and 5CB/N65 systems were essentially tests, we shall be concerned about dissolution effects only in the case of 5CB droplets in a PDMS matrix. We shall demonstrate that, even in this case, the effect is small.

In order to take account of the effect of droplet dissolution on viscosity, we must modify Equation (4). This can be done by replacing the viscosity of the polymer

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matrix, η_m, by that for a homogeneous nematogen/matrix mixture η_{mix}. The viscosity of such mixtures is commonly described by the Arrhenius mixture rule:[23]

$$\ln \eta_{\mathrm{mix}} = \sum x_i \ln \eta_i \tag{5}$$

where η_i is the viscosity of the i^{th} component in the mixture and x_i is usually the corresponding mole fraction. However, it has been shown that in polymer systems x_i should be taken to be the *volume* fraction instead of the mole fraction.[23,33] Since the 5CB/PDMS system contained only one part of LC to five parts of matrix, the maximum attainable volume fraction of liquid crystal in the matrix was 0.167.

Rowlinson[34] has pointed out that, for partially miscible liquids near the critical point, the temperature dependence of the coexistence curve is cubic, which would yield a LC solubility, x, with a cube root temperature dependence:

$$x \propto \text{const.} - (T - T_{\mathrm{sol}})^{1/3}. \tag{6}$$

If the maximum volume fraction of LC dissolved in the matrix does not exceed 0.167, Equation (6) becomes

$$x = 0.167\{1 - [(T - T_{\mathrm{sol}})/(T_{NI} - T_{\mathrm{sol}})]^{1/3}\}, \tag{7}$$

where we have normalized x by assuming that no liquid crystal is dissolved in the matrix at the nematic-isotropic transition temperature. (This seems to be a valid assumption, based on the experimental observation that droplets do not appreciably shrink in size until the temperature has been increased to within a few degrees of T_{sol}.)

Substitution of Equation (5) into Equation (4) then yields an expression for the controlling viscosity which takes account of both the intrinsic temperature dependence and the dissolution of LC in the matrix:

$$\ln \eta = 0.5[(1 + x) \ln \eta_d + (1 - x) \ln \eta_m], \tag{8}$$

where x is given by Equation (7). We recall that η_d and η_m are the viscosities of the pure nematogen in the droplets and of the pure matrix. It is evident that the closer η_d and η_m are in magnitude, the smaller will be any error due to use of Equation (8) since the homogeneous mixture will have a viscosity close to that of dispersion. (Actually, we expect that any reasonable viscosity model would give a fairly small error if droplets and matrix have equal viscosities.)

We have compared the viscosities calculated with correction for dissolution (Equation 8) and without (Equation 4), finding that there is a small (<13%) decrease of η just below T_{sol}. This is not too surprising since the system contained only 16.7% 5CB, which would not decrease η_m significantly by dilution. In the remainder of this paper we shall ignore the effects of dissolution, keeping in mind that for large LC concentrations, such an effect could become appreciable.

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RESULTS

In this section we present results of three different coalescence experiments. The first was a feasibility test in which the coalescence of ROTN-404 droplets in uncured N65 was observed at a single temperature. In the second, dispersions of 5CB in uncured N65 were studied over a temperature range from −10°C to +15°C. For this system we were unable to obtain droplets in the isotropic phase since dissolution occurred while the droplets were still nematic. Therefore, we conducted a third experiment using a PDMS matrix for which it was possible to obtain 5CB droplets in both the nematic and isotropic phases. For this system coalescence of 5CB droplets was observed from just above the crystal-nematic transition temperature through the nematic range to just below the temperature at which the droplets dissolved in the matrix.

ROTN-404 droplets in uncured N65

The coalescence of nematic droplets of ROTN-404 (50 volume percent) in uncured N65 was observed at a single temperature (32.6°C). The temperature of observation was only a few degrees below T_{sol} (~36°C). This low value of T_{sol} obviously precluded the use of this system for studies in the isotropic range.

Coalescence events for a range of droplet sizes were recorded using the video cassette recorder described above. Coalescence time versus droplet size is plotted in Figure 2. The good linear fit strengthened our confidence in the validity of the Frenkel equation.

The controlling viscosity for use in the Frenkel equation was determined from

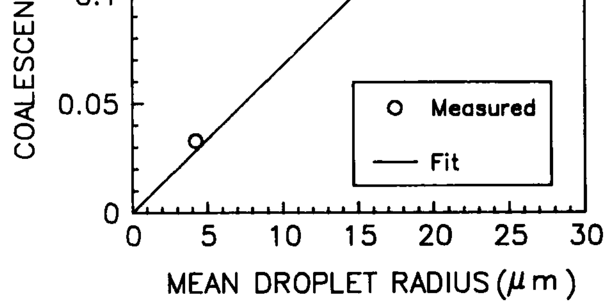

FIGURE 2 Dependence of coalescence time on droplet size for nematic ROTN-404 in uncured N-65 matrix at 32.6°C. The good linear fit supports the Frenkel model for coalescence; the interfacial free energy derived from the Frenkel expression is 0.026 dyne/cm.

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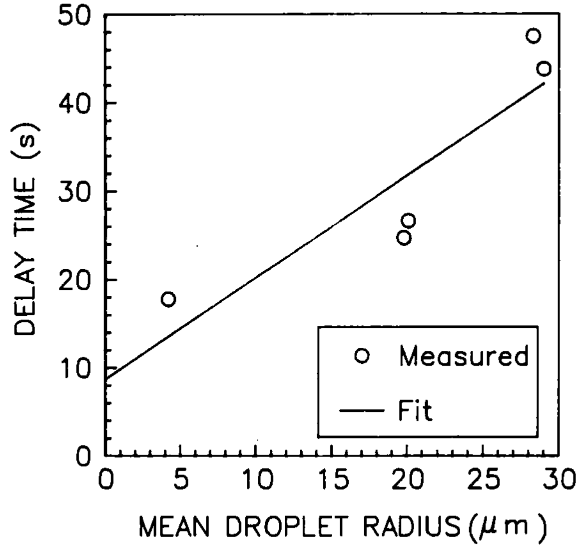

FIGURE 3 Dependence of delay time on droplet size for nematic ROTN-404 in uncured N-65 matrix at 32.6°C. The long delay time between droplet contact and start of coalescence is incompletely understood (see text).

the viscosities of the components by means of Equations (2) and (4) which gave $\eta = 1.8$ poise. (Measurements of η for the homogeneous mixture at 40°C and 100°C and extrapolation by means of Equation 2 yielded a viscosity of 1.7 poise, in fortuitously good agreement with the calculated value.) With $\eta = 1.8$ poise, a best fit of the Frenkel equation to the data of Figure 2 yielded an interfacial free energy of 2.6×10^{-2} dyne/cm, a value coincidentally close to the nematic-isotropic interfacial free energy.[7-10] This low value of σ may have resulted from the proximity of the measurement temperature to T_{sol}. (It should be kept in mind that the large difference in viscosities of ROTN-404 and N65 could represent an appreciable source of error if our model for the controlling viscosity is only approximate. This possibility reinforces the need to use a matrix whose viscosity is comparable to that of the LC.)

The coalescence process did not begin immediately after two droplets came into contact. A delay time (as much as two orders of magnitude greater than the coalescence time itself) intervened between droplet contact and the start of coalescence. The delay time is plotted as a function of droplet size in Figure 3; the extrapolated delay time for $R = 0$ is non-zero. The delay is probably related to the draining of a thin liquid film existing between droplets when they first appear to come into contact. This draining phenomenon has been studied in other systems.[35,36] The delay may also be associated with director reorientation processes at the droplet interfaces or other factors influencing the rupturing of the interface. The delay time did not introduce any significant error into our determinations of σ since, at the end of the delay period, it was possible to determine the start of the coalescence process to within one frame of our video recording instrument.

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TABLE II

Coalescence data for 5CB droplets in uncured N65

TEMPERATURE (°C)	DROPLET RADII (μm)		COALESCENCE TIME (ms)
−8.3	7.98	8.51	600
−5.3	7.35	6.44	433
1.9	8.84	12.65	383
1.5	4.52	5.20	218
1.5	7.23	7.05	267
2.9	6.87	7.22	267
2.1	5.81	5.40	267
9.3	5.99	5.67	167
14.1	8.14	8.44	217
15.0	2.46	2.88	67
15.0	2.26	2.60	67

5CB droplets in uncured N65

Droplet sizes and coalescence times for the 5CB/N65 system are given in Table II. In order to produce 5CB droplets in N65 it was necessary to use a rather large concentration (0.91 volume percent) of liquid crystal. It was possible to observe coalescence events from about −10°C to +15°C, but, as discussed above, isotropic droplets were unobtainable. Thus this system, like ROTN-404/N65, was not very satisfactory. For such a large liquid crystal concentration the droplet density was rather high, making measurements from VCR tapes somewhat difficult. Furthermore, hydrodynamic effects for such high LC concentrations undoubtedly contributed to experimental error.

A more serious source of error was again the large difference in droplet and matrix viscosities. Viscosities were derived from Equations (2) and (4). Recalling that the viscosity of N65 is several orders of magnitude larger than that of the LC, we anticipated that interpretive errors could appear as a result (see discussion above). Substitution of the derived viscosities in the Frenkel equation yielded the σ versus T plot shown in Figure 4. Once again the derived interfacial free energies are low: on the order of 10^{-2} dyne/cm. From calculations based on alternative viscosity models, we have concluded that, for viscosity differences as large as those for both ROTN-404/N65 and 5CB/N65 systems, the associated error in σ could approach an order of magnitude.

The viscosity considerations and other difficulties with these systems led us to search for a low viscosity matrix in which both nematic and isotropic droplets could be formed. That matrix was PDMS for which the viscosity is the same order of magnitude as that of 5CB over the entire temperature range of interest.

5CB droplets in PDMS

We found that, by using a concentration of 16.7 volume percent 5CB in PDMS, it was possible to obtain dispersed droplets over the nematic and isotropic ranges and at temperatures approaching T_{sol} (~73°C). Due probably to the presence of a small amount of dissolved PDMS in the 5CB (and perhaps due also to droplet size

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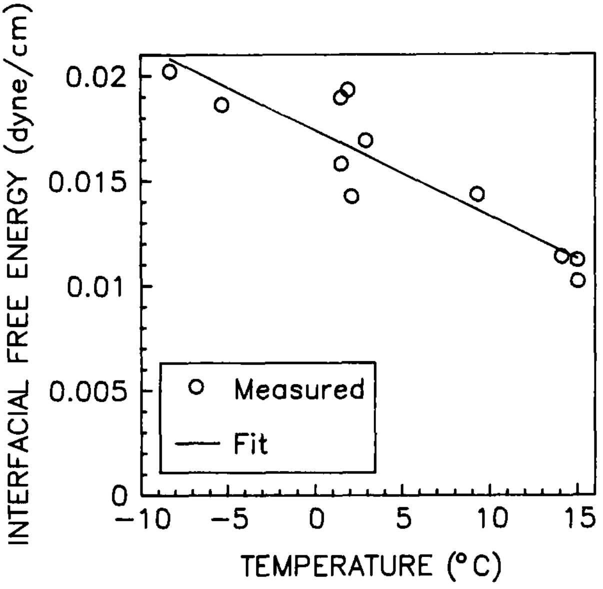

FIGURE 4 Temperature dependence of interfacial free energy for nematic 5CB droplets in uncured N-65 matrix as calculated from coalescence time using Frenkel expression (Equation 3). As discussed in text, determination of appropriate viscosity was most questionable aspect of the analysis.

effects), the crystal-nematic temperature of the dispersed droplets (with diameters ranging from 20 to 50 μm) was depressed to about −25°C, some 25°C below T_{KN} of large regions of 5CB in the same sample and about 50°C below that of pure bulk 5CB. (Furthermore, nematic droplets could be supercooled to almost −40°C before crystallization occurred.) As previously mentioned, the nematic-isotropic temperature of the droplets was depressed to 34.6°C, only 0.7°C below that of pure bulk 5CB, suggesting that the amount of PDMS dissolved in the LC was small.

Although nematic droplets could be obtained at temperatures as low as −25°C, coalescence events were unobservable below −10°C due to the increasingly high viscosity of the system. It was possible to determine coalescence times up to 70°C, only a few degrees below T_{sol} (~73°C). Spin Physics camera images of a typical coalescence event are shown in Figure 5. Coalescence times for various temperatures and droplet sizes are listed in Table III. Viscosities were evaluated using the appropriate coefficients as described in previous sections. Interfacial free energies were then derived using Equation 3).

In Figure 6 is plotted the temperature dependence of σ for the 5CB/PDMS system. The values of interfacial free energy derived for 5CB/PDMS are considerably more reliable than those for the other two systems studied. We calculate that the error associated with viscosity should be about +0/−0.04 dyne/cm at low temperature and ±0.05 dyne/cm at high temperatures.

In the figure several features are immediately apparent. First, the magnitude of σ is on the order of 10^{-1} dyne/cm. Second, the scatter is too large to permit a discontinuity in σ to be observed at the T_{NI} (34.6°C) although least squares fit lines

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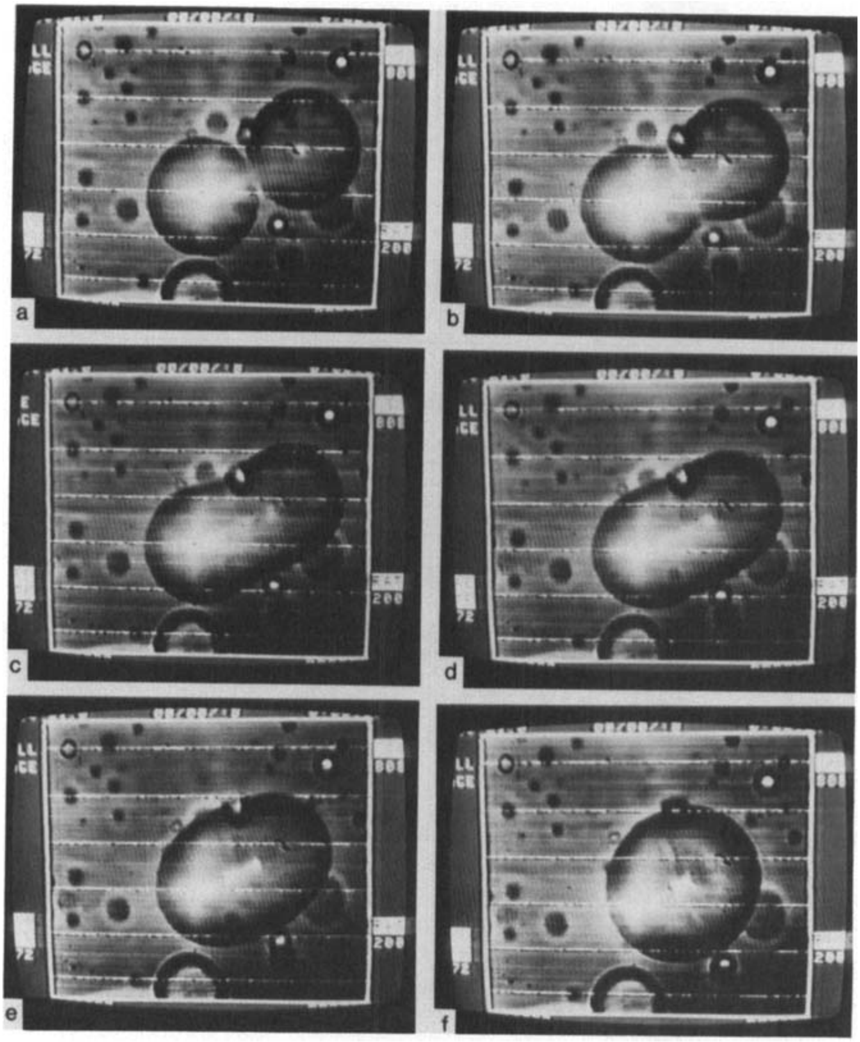

FIGURE 5 Spin Physics camera images of six stages of a coalescence event for nematic 5CB droplets in PDMS matrix at 32°C. The two droplets have nearly identical initial radii (25.1 and 25.4 μm respectively). The elapsed times for the six photographs are: a) 0 ms; b) 0.5 ms; c) 1 ms; d) 1.5 ms; e) 2 ms; and f) 7.5 ms.

below and above T_{NI} do permit a value to be derived. Third, there appears to be a small decrease in the negative slope of the curves on going from the nematic to the isotropic phase. Fourth, σ decreases toward zero as the critical solution temperature is approached. The best linear fits to the interfacial free energy are given by:

$$\sigma_N = 0.2575 - 0.00333T \quad (T < 34.6°C) \tag{9}$$

and

$$\sigma_I = 0.2234 - 0.00223T \quad (T > 34.6°C). \tag{10}$$

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TABLE III

Coalescence data for 5CB droplets in PDMS

TEMPERATURE (°C)	DROPLET RADII (μm)		COALESCENCE TIME (ms)
−10	36.7	33.5	33.5
−10	17.9	17.9	13.0
−5	8.6	8.1	4.5
−5	9.8	10.2	6.5
−5	10.2	12.5	7.0
5	10.1	9.0	4.5
5	11.0	7.7	4.0
5	16.4	22.3	6.0
15	40.8	34.6	12.0
15	19.6	18.7	6.0
15	34.0	29.1	10.5
15	19.6	17.3	6.0
25	14.6	15.8	4.0
25	9.3	9.2	3.0
25	8.3	7.8	3.0
25	16.8	14.1	3.0
30	31.1	26.8	9.0
30	29.0	32.0	8.0
30	13.1	14.3	3.5
30	22.7	26.2	6.0
32	25.4	25.1	7.5
32	13.4	17.8	3.5
32	15.9	16.7	4.0
32	22.4	20.0	5.5
33	23.8	16.7	5.0
33	22.9	15.6	5.0
33	20.3	27.8	5.5
33	13.7	14.6	3.0
34	12.6	18.1	3.5
34	17.1	16.5	3.5
36	25.1	34.0	6.5
36	24.5	25.0	5.0
36	19.3	23.6	5.0
37	16.5	12.6	3.0
37	19.7	20.8	4.0
37	17.3	23.2	4.5
40	16.7	11.7	3.0
40	17.5	23.3	4.5
45	26.5	29.0	5.5
45	22.0	14.7	3.5
45	18.8	18.2	4.0
50	12.9	18.4	2.5
50	19.4	26.6	5.5
50	23.9	29.8	4.0
50	15.0	17.5	3.0
60	16.3	20.6	3.0
60	11.4	17.9	2.0
60	18.7	10.2	2.0
70	14.9	16.7	3.0
70	23.2	22.3	3.5
70	16.2	11.9	2.5

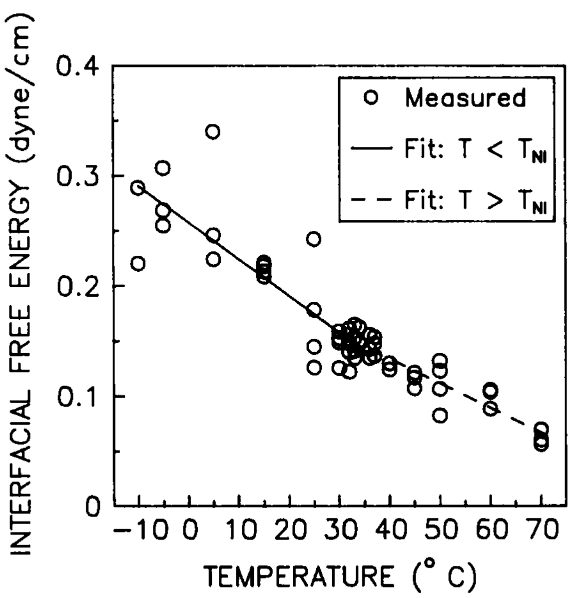

FIGURE 6 Temperature dependence of interfacial free energy for nematic 5CB droplets in PDMS matrix as determined from coalescence time using Frenkel expression. Two of the three features of Figure 1 are seen: steeper negative slope for the nematic phase and decrease of σ toward zero as the critical solution temperature is approached.

At T_{NI} the difference of the two fits is $\Delta\sigma_{NI} = -0.0039$. This difference is small compared to experimental scatter, and therefore no significance is attached to it. The value of T_{sol} obtained by setting σ_I in Equation (10) equal to zero is approximately 100°C, somewhat higher than the experimental value of ~73°C.

Droplet configuration

Drzaic[37] has investigated director alignment in nematic droplets dispersed in polymer matrices and has observed the director orientation to change from axial to bipolar as the LC elastic constant ratio k_{33}/k_{11} increased. He has suggested[38] that the magnitude of the σ we measure could depend on the director configuration, which could be different for the two polymers we used. He predicted that the 5CB/PDMS system should exhibit a radial configuration and that the 5CB/N65 system should have a bipolar arrangement. We have examined the director configurations in both samples using polarized light microscopy. We found that, in N65, droplets of 5CB (20 to 70 μm in diameter) did indeed exhibit a radial configuration whereas, in PDMS, 5CB droplets exhibited behavior consistent with a bipolar configuration. These results tend to confirm Drzaic's predictions.

The magnitude of any effect of director configuration on σ is expected to be on the order of σ_{NI}, the nematic-isotropic free energy which is roughly 10^{-2} dyne/cm. Thus director configuration effects on σ-values derived for 5CB/PDMS are roughly the same size as experimental uncertainties associated with the viscosity. In the case of 5CB/N65 (or ROTN-404/N65), the director orientation effect is comparable

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to the derived values of σ discussed above. However, we recall that viscosity uncertainties could shift the derived interfacial energies by as much as an order of magnitude, so that the effect of liquid crystal alignment is again relatively unimportant in these cases. It was precisely because of the viscosity problem that we turned our attention to the 5CB/PDMS system in the first place.

DISCUSSION

We have, using the Frenkel coalescence equation, derived values for the surface free energy of nematogen/polymer-matrix interfaces and shown that their magnitudes fall in the 10^{-2} to 10^{-1} dyne/cm range. Furthermore, we have demonstrated that in a σ vs. T plot, the slope becomes slightly less negative upon passing through the nematic-isotropic transition temperature, behavior similar to that seen for nematogen-air interfaces by Schwartz, *et al.* Finally, we have found that the magnitude of the nematogen/matrix interfacial free energy approaches zero as the critical solution temperature is approached, behavior which we anticipated in analogy with the Eotvos equation for ordinary surface free energy near the critical point. Therefore we anticipate that the magnitudes of the interfacial free energies in a polymer-dispersed liquid crystal film could be somewhat greater than 10^{-1} dyne/cm since the liquid crystal solubility in a cured polymer matrix may be less than that for the uncured matrices studied in the present work.

As mentioned previously, the σ-values derived from this work (at least for the 5CB/PDMS case) can be regarded as lower limits for a PDLC. Since no measurements of σ for a LC/solid interface exist and calculated values are very uncertain (but are on the order of 10 dyne/cm)[2], an upper limit is hard to estimate. However, recent work at Kent State University[39] indicates that as degree of polymer cross-linking increases (and the polymer matrix becomes more rigid), the anchoring energy, W, decreases somewhat. This reduction in W is felt to due to a smaller degree of entanglement between matrix molecules and LC molecules as the interface becomes more well-defined. If there is a correlation between σ and W, one might reasonably argue that σ for a PDLC is comparable to that for a LC droplet imbedded in a fluid polymer matrix.

In addition to the presentation of specific results for a specific nematogen/isotropic liquid system, the present work may have further significance in demonstrating the potential usefulness of the droplet coalescence technique for determining interfacial free energies of other liquid/liquid systems. However, it should be kept in mind that best results will be obtained when the two liquids have comparable viscosities and densities.

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