

Mesophase/Isotropic Phase Interfacial Energy: Determination from Droplet Coalescence Kinetics

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Abstract. According to the theory of Frenkel, surface energy, viscosity, and droplet size control the rate at which two touching spherical droplets coalesce. From the Frenkel relationship and observations of mesophase droplet coalescence, we have evaluated the mesophase/isotropic phase interfacial energy for a mesophase-containing pitch. The interfacial energy is quite small (~ 0.02 dyne/cm).

Introduction

Recently White,¹ on the basis of polarized light micrographs of quenched mesophase pitch samples, proposed that the relative surface energy at the interface between the mesophase and the isotropic phase is quite low. Smith² suggested that the magnitude of the interfacial energy, σ , could be estimated from measurements of the time constant, τ , for coalescence of two identical mesophase spherules using the Frenkel relation,³

$$\tau = \frac{\eta R}{\sigma},$$

where η is the viscosity and R is the spherule radius.

In this paper we report the determination of the interfacial energy by this method and show that it is several orders of magnitude smaller than the surface energy of ordinary liquids.

Experiment

The τ and R data for mesophase spherule coalescence were obtained by polarized-light hot stage cinematography. A sample of Ashland A240 pitch in the initial stages of mesophase formation was prepared and spherule coalescence at the free surface (under nitrogen atmosphere) examined at 440°C. The coalescence time τ for different spherule sizes was determined from a frame-by-frame examination of the film. In Fig. 1 frames from the film show three stages in the coalescence process and illustrate the determination of τ . We define τ to be the time elapsed between initial contact of the spherules and the final disappearance of the "waist" visible in the figure (an acceptable definition in view of the approximate nature of Frenkel's derivation). τ was found to scale linearly with R as it should from the Frenkel relation.

We did not measure viscosity and therefore used literature data⁵ to estimate a range of η -values appropriate for a petroleum pitch sample at 440°C in the early stages of mesophase formation (low degree of polymerization). Where possible we used data for low shear rates which generally represent a reasonable approximation to the flow conditions during mesophase formation. Complications involved in assessing viscosity are discussed elsewhere.⁶ Suffice it to say that a value of 10 poise was found to be a reasonable order of magnitude estimate for the apparent early stage viscosity at 440°C.

Determination of Interfacial Energy

From the Frenkel relation and the τ , R , and η data we estimate the mesophase/isotropic phase interfacial energy to be ~ 0.02 dyne/cm for Ashland A240 at 440°C. This value is in good agreement with results for nematic/isotropic interfacial energies for ordinary liquid crystals (i.e. ones composed of rod-shaped molecules) [Table I]. Furthermore, since the interfacial energy is three orders of magnitude smaller than the ordinary surface energy of typical liquids (~ 20 -50 dynes/cm),¹ the original suggestion of White¹ is confirmed.

The good agreement of our estimate of the pitch mesophase/isotropic phase interfacial energy with the various σ_{NI} values for ordinary nematogens leads us to two main conclusions: 1) the validity of the Frenkel relation for determining σ -values is confirmed; 2) as is the case for many of their other characteristics, pitch mesogens are similar to ordinary thermotropic liquid crystals in their surface behavior.

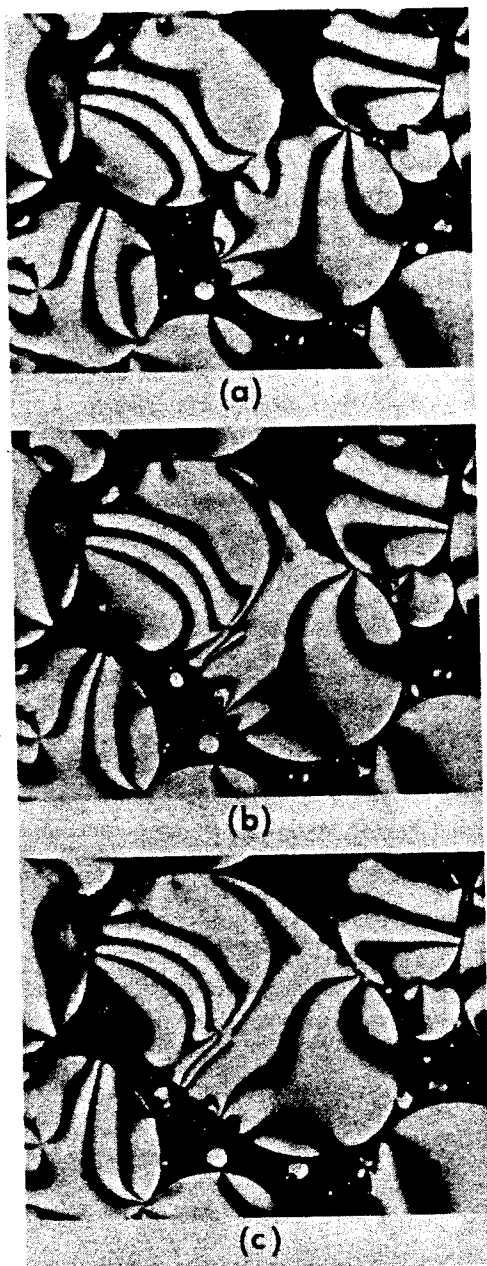


Figure 1. Coalescence of two mesophase droplets in isotropic pitch matrix at 440°C. (Initial radii 108 and 101 μm .) a) Initial droplet contact; b) partial coalescence to produce a "waist"; c) disappearance of the waist (definition of coalescence time).

References

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Table I. Mesophase/Isotropic Phase Interfacial Energy Results

Mesophase	$n(\text{poise})$	$R(\mu\text{m})$	$\tau(\text{s})$	$\sigma(\text{dyne/cm})$	Method	Reference
A240 pitch	-10	65	3.9	0.017	Frenkel	This work
Nematic PAP	-0.05	130	0.045	0.014	Frenkel	7
Nematic MBBA	---	---	---	0.023	Light Scattering	8
Nematic MBBA	---	---	---	0.016	Sessile Drop	9
Nematic MBBA	---	---	---	0.01 to 0.02	Theory	10
Nematic 5CB	---	---	---	0.011	Theory	11

PAP = p-azoxyphenetole; MBBA = 4-methoxybenzylidene-4'-n-butylaniline;
5CB = 4-cyano-4'-n-pentylbiphenyl.