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THERMODYNAMICS AND STATISTICAL MECHANICS OF LIQUID CRYSTALS AND--ETC(U)

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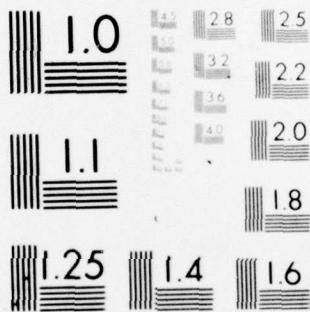
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM	
1. REPORT NUMBER ARO 5425.18-C	2. GOVT ACCESSION NO.	3. REPORT'S CATALOG NUMBER	
4. TITLE (and Subtitle) THERMODYNAMICS AND STATISTICAL MECHANICS OF LIQUID CRYSTALS AND THEIR SOLUTIONS		5. TYPE OF REPORT & PERIOD COVERED Final Report 1 Sep 66 - 31 Dec 76	
6. AUTHOR(s) Daniel E. Martire		7. CONTRACT OR GRANT NUMBER(s) DA-ARO-D-31-124-G817 DA-ARO-D-31-124-G1167 DA-ARO-D-31-124-73-G2	
8. PERFORMING ORGANIZATION NAME AND ADDRESS Georgetown University Washington, D. C. 20007		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE 10 1977	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 126p.		13. NUMBER OF PAGES 5	
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		15. SECURITY CLASS. (of this report) Unclassified	
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)			
18. SUPPLEMENTARY NOTES The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.			
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Thermodynamic properties Solutions Liquid crystals Solvents Phase transformations Mixtures Statistical mechanics Binary systems(materials)			
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This is a brief summary of the liquid crystal research supported by ARO at Georgetown University during the past ten years. Research has been directed toward a more detailed understanding, on a molecular level, of the thermo- dynamic properties of (a) phase transitions in liquid crystals and (b) binary mixtures of nonmesomorphic solutes and nematic (or cholesteric) solvents.			

FINAL REPORT

1. ARO PROJECT NUMBER: CRD-AA-IP-6425-C
2. PERIOD COVERED BY REPORT: 1 September 1966 - 31 December 1976*
3. TITLE OF PROJECT: Thermodynamics and Statistical Mechanics of Liquid Crystals and Their Solutions
4. GRANT NUMBER: DA-ARO-D-31-124-G817 (9/1/66 - 8/31/69)
DA-ARO-D-31-124-G1167 (9/1/69 - 8/31/72)
DA-ARO-D-31-124-73-G2 (9/1/72 - 12/31/76)*
5. NAME OF INSTITUTION: Georgetown University
6. AUTHOR OF REPORT: Daniel E. Martire, Professor
7. LIST OF MANUSCRIPTS PUBLISHED UNDER ARO SPONSORSHIP DURING THIS PERIOD, INCLUDING JOURNAL REFERENCES: Listed following Summary of Research
8. SCIENTIFIC PERSONNEL SUPPORTED (6 MONTHS OR MORE) BY THIS PROJECT AND DEGREES AWARDED DURING THIS REPORTING PERIOD:
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 - (i) Gwo-Chung Lin, Graduate Student (Ph.D., June 1975)
 - (j) Ghassan A. Oweimreen (Ph.D. expected June 1977)

* Performance period of the grant extended by 16 months (9/1/75 - 12/31/76) without additional funding.

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Daniel E. Martire
January 14, 1977

SUMMARY OF RESEARCH

The liquid crystal research supported by ARO at Georgetown University during these past ten years has been directed toward a more detailed understanding, on a molecular level, of the thermodynamic properties of (a) phase transitions in liquid crystals and (b) binary mixtures of nonmesomorphic solutes and nematic (or cholesteric) solvents.

The potential of gas-liquid chromatography (glc) for studying the thermodynamics of infinitely dilute solutions of nonmesomorphic solutes in liquid-crystalline solvents was demonstrated in an exploratory investigation (1). Subsequent experimental studies confirmed the validity of our glc approach by establishing the absence of surface effects (3,10) and the agreement between glc data and extrapolated static measurements (11). The glc method and a statistical-thermodynamic model were then successfully employed in obtaining and interpreting thermodynamic solution quantities for a wide range of solutes in nematic and cholesteric solvents (8,13,15,22). Our understanding of the unique solvent properties of liquid crystals has been advanced through these studies. Other novel applications of glc were developed: analytical separation of geometric isomers using a nematic liquid phase (4); determination of nematic order parameters by a solute probe method (9); and complementary thermodynamic studies to interpret the effect of organic solutes on the selective reflectance of visible light by cholesteric mixtures (12). Apparatus were designed and tested (11,20) for the thermodynamic study of mixtures of nonmesomorphic solutes at finite concentration in nematic solvents. Experiments were conducted to investigate the effect of solute size, shape and flexibility on nematic phase stability (14,20).

Several statistical-mechanical models were developed to provide the necessary framework for interpreting the thermodynamic properties of liquid-crystalline phase transitions in one and two component systems. A scaled-particle theory (5,6,7) of rigid rods (one component) demonstrated the primary role of repulsive forces (or packing effects) in the nematic-isotropic liquid transition. A lattice model (2) of rigid rods was used to investigate the secondary effect of attractive forces. The results of both models suggested the probable importance of end-chain flexibility in homologous series. Accordingly, a rotational-isomeric model (15) and a lattice model of particles consisting of rigid central cores and semiflexible pendant groups (17) were developed to investigate the effect of end-chain flexibility. The results of these models (and available thermodynamic data) strongly indicated that the nematic-isotropic transition can be adequately described in terms of molecular packing and flexibility effects, with attractive forces providing a uniform background and having only a minor effect on the transition properties. A simple tunnel model of rigid rods (one component) was developed and successfully applied to interpret the thermodynamic behavior of the smectic A - nematic phase transition (21). Finally, models involving two components - mixtures of rigid rods of different lengths (16) and mixtures of rigid rods and spheres (18,19,20) - were developed to aid in interpreting the experimental results (14,20) for solute-induced nematic-isotropic phase transitions.

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Note:

- a. D.E. Martire is one of the authors of each of the above manuscripts.
- b. Reprints of manuscripts number 21 and 22, which are largely based on G.C. Lin's doctoral dissertation (see following page for abstract), will be sent to ARO following publication of the papers.

Thermotropic Liquid Crystals: A Cell Model for the
Smectic A-Nematic Transition and A Thermodynamic
Investigation of Dilute Solutions in Nematic
and Isotropic MBBA
(Ph.D. Dissertation of Gwo-Chung Lin)

Abstract

In order to gain a better understanding of the fundamental nature of the smectic A-nematic transition in liquid crystals, a simple cell model is applied to a fluid of aligned, rigid, cylinders in Part I. Particle motion is separated into components parallel and perpendicular to the long axis of the molecules. The partition functions are formulated by considering the contribution from particles localized within their cells and the contribution from positional disorder in the nematic phase. The transition temperature is determined by equating the Helmholtz free energies of the two phases, in the limit of zero external pressure.

When realistic values for the dimensional and energetic parameters are used in the model calculations, reasonable values are obtained for the transition temperature, absolute density and configurational energy. It is found that: (a) the smectic A phase becomes more favored (i.e., the transition temperature increases) as the strength of segmental core-core interactions and/or the length of the central core increases, (b) the transition enthalpy, entropy and fractional volume change decrease with increasing terminal interactions (ϵ'), while the transition temperature is virtually insensitive to ϵ' . The most significant success of the model is its ability to produce the observed trends in the transition temperature and entropy in homologous series.

In Part II, gas-liquid chromatography is used to obtain infinite dilution activity coefficients and partial molar enthalpies and entropies of solution for 26 nonmesomorphic solutes in both the nematic and isotropic phases of N-(p-methoxy-benzylidene)-p-n-butylaniline (MBBA). The data are interpreted in the light of Chow and Martire's, and Humphries, James and Luckhurst's statistical thermodynamic solution models, and are compared with results obtained for other nematogenic compounds.

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42

