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Isotope Effects in Liquid Crystal Systems

I: Phase Relationships in the Dodecylamine-H_2O, Dodecylamine-D_2O Systems

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The phase diagrams and heats of fusion and transition have been determined for the dodecyl amine ($-NH_2$)/H_2O and dodecyl amine ($-ND_2$)/D_2O systems using direct optical observation and differential scanning calorimetry.

INTRODUCTION

It is well established that isotope effects on condensed phase properties such as vapor pressure, temperatures of phase transitions, free energy, enthalpy, and volume changes on solution, etc., form useful probes of reasonable sensitivity in studies in intermolecular forces. This general field has been reviewed by Jancso and Van Hook,[1] and those same authors have more recently discussed the properties of solutions of isotopic isomers one in the other, and in each other.[2] Most quantitative discussions of condensed phase isotope effects apply detailed structural models in the context of Bigeleisen's[3] 1961 formulation, employing a harmonic cell model for the liquid phase.[4] The general success of this and related approaches connecting condensed phase isotope effects and intermolecular forces led us to the conclusion that it would be of interest to examine condensed phase isotope effects in liquid crystal systems. The properties of liquid crystals including transition temperatures, phase diagrams, and optical and related properties,

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are sensitive functions of the inter and intra molecular forces in such systems.[5] Therefore an investigation of the isotope dependences of liquid crystal properties is pertinent to the eventual development of the condensed phase properties in terms of the inter and intramolecular forces. We have begun the experimental part of the program with a study of phase relationships in the dodecyl amine (—NH_2/—ND_2)/water (H_2O/D_2O) system which displays a number of different amphiphilic liquid crystal phases.

Solutions of amphiphilic compounds (molecules containing a hydrophilic group at the end of an ~8–20 carbon atom chain) in water have attracted a good deal of attention. Amphiphiles containing one amine group as the only hydrophile are especially interesting because these compounds dissolve relatively more water than other amphiphiles and form liquid crystal phases.[6] The polar group is relatively small and the observation that some crystallinity is retained when water penetrates the solid and forms layers between polar groups may be connected with the molecular dimensions.[7] Phase behavior in the systems *n*-octyl, *n*-dodecyl, and *n*-octadecyl amine/water has been investigated by Ralston, Hoerr and Hoffman.[8] Larsson and Al-Mamun[9] have reported on tetradecyl amine/water and Collision and Lawrence[10] on the octadecyl amine/water system, but only above 10°. Puzzling minor differences are exhibited in the phase diagrams reported from these different laboratories.

Van Hook and others,[1,11] Krishnan and Friedman[12] and Selecki, Tymanski and Chmielewski[13] have reviewed H_2O/D_2O solvent isotope effects on thermodynamic properties but little or no work has focused on solvent isotope effects *per se* in amphiphilic liquid crystal systems. Ellis, Lawrence, McDonald and Peel[14] made an NMR investigation of the monooctanoin/D_2O system but the D_2O was introduced as a convenient NMR solvent and not for the purpose of an investigation of the solvent isotope effects. Clifford and Pethica[15] have similarly made relaxation studies in the H_2O/D_2O-sodium alkyl sulfate systems using an NMR technique. Krasz and O'Reilley[16] have investigated the H/D isotope effect on the helix-coil transition in the γ-benzyl-1-glutamate/1,2 dichlorethane system.

EXPERIMENTAL

Materials: Aldrich 98% dodecyl amine was recrystallized twice from acetonitrile[17] and then fractionally distilled two times in a rotating band column at 135°, 15 torr. The melting point of the purified amine was 28.3° in good agreement with the most recent data.[17,18] The IR spectrum of the purified sample was identical with that tabulated by Sadtler.[19] The deuterated amine was prepared by mixing molten protioamine with an excess of D_2O

for several hours. The process was repeated three times and the ratio of total D_2O to amine was 70 : 1. Deuterium analysis of the product amine was made by IR using a set of six standard samples of varying H/D ratio, and showed 98% deuteration. The melting point of the deuterated amine was 29.1°. One or two component mixtures were made up gravimetrically and were protected from air throughout the measurements.

Phase diagrams: Three different experimental techniques were used in the determination of the various transition temperatures for this system. In the first a heating/cooling apparatus similar to that reported by Skau[20] and others[21] was employed. A copper cylinder (70 mm d × 150 mm h) hollowed out to hold a sample tube (20 mm d) and wrapped with an electrical heating coil is placed in good thermal contact with a Peltier cooler. The entire system is well wrapped with insulation. The speed of heating or cooling can be conveniently controlled by adjusting the different voltages and was normally about 0.3° per minute. The sealed sample tube contains a thermistor probe for temperature measurement. The copper bar is appropriately pierced with a sighting hole and the sample observed through a telescope. Transition temperatures for solid–liquid or liquid–liquid crystal transitions were picked off from temperature-time plots and confirmed optically. Observations were made on both heating and cooling, but cooling curves did not usually give reproducible results for the more sluggish solid–solid transitions as has been previously noted.[8] The thermistor serving as the thermometer forms one leg of a DC bridge and the imbalance was read potentiometrically. The thermistor bridge was calibrated by platinum resistance thermometry.

In the second technique we simply placed 5 to 10 gram samples in glass tubes in a thermostat provided with windows and a stirrer. The temperature was controlled to approximately $\pm 0.02°$ and was slowly raised as the samples were gently stirred. The phase transitions were observed visually. This technique nicely supplements the one first described but was found to be much too tedious to employ in mapping out the entire phase diagram. Third, and finally, differential scanning calorimetry was found to be a convenient way to detect phase transitions especially for samples above 0.8 mole fraction water. Heats of transition in this system are small and therefore unconventionally large (60–80 mg) samples were required. The temperature of first deviation from the DSC baseline was taken as the transition temperature.

Heats of fusion and transition: The heats of fusion of the pure amines as well as the heats of some of the transitions observed for the solutions were determined by differential scanning calorimetry (Perkin–Elmer DSC-1B).[21,22] The amine is quite volatile and we employed sealed pans constructed following a modification of the method of Freeberg and Allman.[23] Lauric acid (m.p. 43.22°, $\Delta H_f = 183.1$ j/g), benzoic acid (m.p.

122.4°, $\Delta H_f = 141.9$ j/g), and indium (m.p. 156.3°, $\Delta H_f = 28.4$ j/g) were used as standards and the areas of the DSC curves determined by planimetry.

RESULTS

Phase diagrams for the two systems, $CH_3(CH_2)_{11}NH_2/H_2O$ and $CH_3(CH_2)_{11}ND_2/D_2O$ are presented in Figure 1. The diagrams for both systems are essentially of the same shape but the transition temperatures in

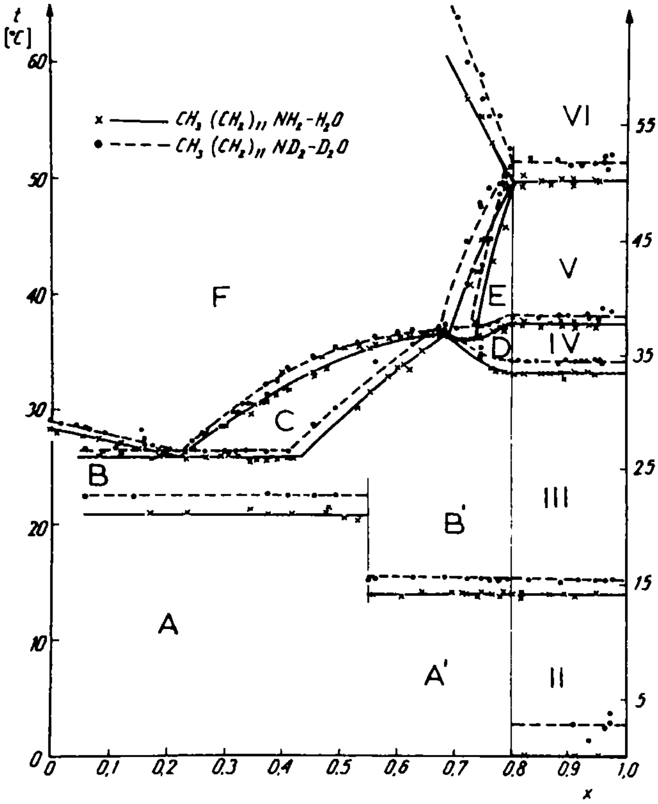


FIGURE 1 Phase diagrams for the systems dodecylamine-H_2/H_2O and dodecyl amine-d_2/D_2O. (x = mole fraction water).

In the region 0 to 55 % water, on increasing the temperature the system passes from a mixture of solids (A) through a solid–solid transition to a second solid mixture (B) then to a two phase solid–liquid region and finally into an isotropic liquid solution, F. Above 80 % water it passes from a crystalline tetrahydrate/ice mixture, I, to crystalline tetrahydrate/solution mixture, II, then melts, III, passes through three different liquid crystal phases, III, IV, V (first described by Ralston[8]), before entering the region at the upper right, VI, consisting of two isotropic liquid layers. The solubility limits of phases II, III, IV, V lie very close to $X = 1$ and are not shown in the figure.

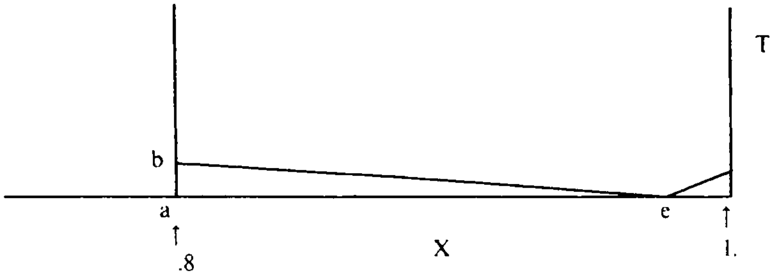
the deuterated solutions are more or less uniformly displaced from protio by about 1 or 2 degrees toward higher temperature. The diagrams are similar, but not identical, to that reported by Ralston.[8] The principal differences occur in the low temperature solid phase region. Previous workers[9,10] in this general area have also reported discrepancies with Ralston. Over the concentration range between 0 and approximately 55 mole % water we observe a solid–solid transition (A → B, Figure 1) at 22.5° for the deuterated (D), and 20.8° for the non-deuterated (H) system. The high temperature heterogeneous mixture displays a eutectic B, C, C′, F near 0.23 fraction water at 26.5° (D) or 26.0° (H). Above ~0.55 water a solid solid transition (A′ → B′) is seen at 15.3° (D) or 14.0° (H) respectively. In the region just below 80% the solution passes through two mesomorphic forms (D and E, Figure 1) finally melting to an isotropic solution (F) which at higher temperatures yet separates into two liquid layers (area VI) with the upper rich in amine, the lower in water. Above a water fraction of 0.8 we have found five distinct transitions. The first (I → II) assigned to the melting of ice to a mixture of hydrate plus water is observed at 2.3° (D) or 0.0° (H). This particular transition was observed only by DSC and the precision on the temperature is considerably less than that obtained over the rest of the diagram. The chance of systematic error due to dilution of the D sample by ambient water also increases due to the necessarily small sample size. As the temperature in this region (0.8 to 1 mole fraction water) is increased one passes successively through three different mixtures of isotropic and mesomorphic liquid crystal solutions originally reported by Ralston.[8] The temperatures of transitions are for the D solutions II → III (Figure 1) 15.3°, III → IV 34.5°, IV → V 38.1°, and V → VI 51.7°, while for the H solutions they are 14.0; 33.5; 37.6 and 50.1 degrees respectively. These temperatures are well established having been observed by combinations of all three of the techniques described above. At very high water concentrations (above 0.9995 fraction[8]) an isotropic solution exists above the ice melting point. This homogeneous region is not shown in Figure 1 as it lies too close to the right hand ordinate to be distinguished from it on the scale of the figure.

Heats of fusion and transition: Heat data was obtained by differential scanning calorimetry. This technique is relatively imprecise even under the best of circumstances. In the present case the relatively small heats of transition in the 0.8 to 1.0 mole fraction water region (where most of our experiments were made) exacerbates the problem. Some of the experimental scatter may also be due to sluggish transitions and/or metastability in the liquid crystal transitions. As a consequence statistical errors on the derived heats of transition are large, typically between 10 and 25%. On the other hand the pure amine thermograms are uncomplicated by multiple or concentration dependent transitions and yield data of relatively good precision. We have obtained heats of fusion of 51.68 ± 0.78 kj/mole (—NH_2) and 51.25 ± 0.70 kj/mole (—ND_2). The approximately 1.5% error bars represent one standard deviation and there is no measurable isotope effect at this level of precision.

In the region $0.8 < X_{\text{water}} < 1.0$ five distinct transitions as specified above and in Figure 1 are observed. In each case the enthalpies of transition can be represented across this concentration range as

$$h_{i,j} = m_{i,j} X_{\text{water}} + b_{i,j} \tag{1}$$

X is the mole fraction. This behavior is consistent with the conclusion reached by Ralston that the transitions in this region of the phase diagram consist of simple diagrams of the type



The diagram is greatly exaggerated and the eutectic, *e*, is found far over near pure water at $X > 0.9995$.[8] Also the temperature difference, *b*–*a*, is small, so that on the scale of Figure 1, or of the DSC experiment, the curves *be* and *ae* effectively coincide. As a consequence the heat of transition in this region is expected to vary linearly between that characteristic of the mixture at 0.8 fraction water, to that at the eutectic, very near pure water. The slope, $m_{i,j}$ in Eq. (1), is therefore connected with the energetics of the tetrahydrate-eutectic disproportionation reaction. To show this consider a sample with water content, $0.8 < X < 1$. From the tie line lever rule the ratio of tetrahydrate to eutectic is given by $(X - 0.8)/(X_e - X)$. Therefore

$$h_{\text{tot}} = (X - 0.8)h_e + (1 - X)h_t, \tag{2}$$

where the eutectic composition has been approximated as unity with a heat of transition, h_e. Further h_t is the heat of transition of the sample of 0.8 composition, and h_{tot} is the predicted heat of transition at composition X assuming a linear combination. The equation can be rewritten (24)

$$(h_e - h_t)X + (h_t - 0.8h_e) = h_{\text{tot}} \tag{3}$$

which is of the experimentally observed form (equation 1).

The DSC heat data obtained in the region $0.8 < X_{\text{water}} < 1.0$ are presented in Table I, together with least square parameters for fits to equations of type

TABLE I

DSC measurements of heats of transition: joules/gram of solution

A: Dodecyl amine (-NH_2)/H_2O solutions

	Transition				
Mole % water	I-II	II-III	III-IV	IV-V	V-VI
82.3_9	—	42.7	—	—	—
85.2_6	—	52.0	20.8	12.6	4.1
85.2_6	—	40.5	20.5	10.0	2.8
88.6_7	—	46.3	17.7	8.7	1.7
91.0_2	80.0	47.0	—	5.7	1.8
92.5_9	45.4	41.8	16.8	6.4	1.5
95.0_0	—	42.7	—	—	—
96.1_9	—	30.5	16.0	6.2	1.5

B: Dodecyl amine (-ND_2)/D_2O solutions

Mole % water	I-II	II-III	III-IV	IV-V	V-VI
80.15	27.6	43.2	—	—	—
84.6_0	31.1	47.1	—	—	—
89.0_4	41.8	35.2	—	—	—
90.88	46.3	39.5	12.2	5.1	2.5
93.3_5	72.4	34.3	14.2	5.4	1.3
94.8_4	72.5	29.1	12.3	4.3	0.9
96.1_9	68.5	25.5	15.5	5.1	1.5
96.8_5	84.5	21.9	9.7	4.3	1.0
96.8_5	88.7	23.1	11.9	3.6	0.8

C: Fits to Eq. (1) and Eq. (3)

	Eq. (1) (joules/gram)			Eq. (3) (joules/gram)	
Transition	m	b	R	h_e	h_t
I-II	328 ± 82	-242 ± 75	0.8	430	102
II-III	-147 ± 33	169 ± 30	0.75	120	267
III-IV	-75.2 ± 18	85.2 ± 17	-0.79	40	115
IV-V	-58.0 ± 9.1	60.0 ± 8.4	-0.9	8	66
V-VI	-20.3 ± 3.5	20.5 ± 3.3	-0.9	1	21

(1). The parameters derived from substitution into equation 3 are also given but it is to be recognized that the large relative errors of the least square fits put very large errors on the values derived for h_t and h_e for the different transitions and make them of qualitative significance only. The plots of heats of transition versus concentration are shown for two transitions in Figure 2. No isotope effects on the heats of transition can be detected within the experimental precision and data for both H and D systems have been plotted and least squared together.

The value of $m_{\mathrm{I,II}}$ (Eq. 1), within experimental error equal to the heat of fusion of ice, confirms the assignment of this transition as (tetrahydrate

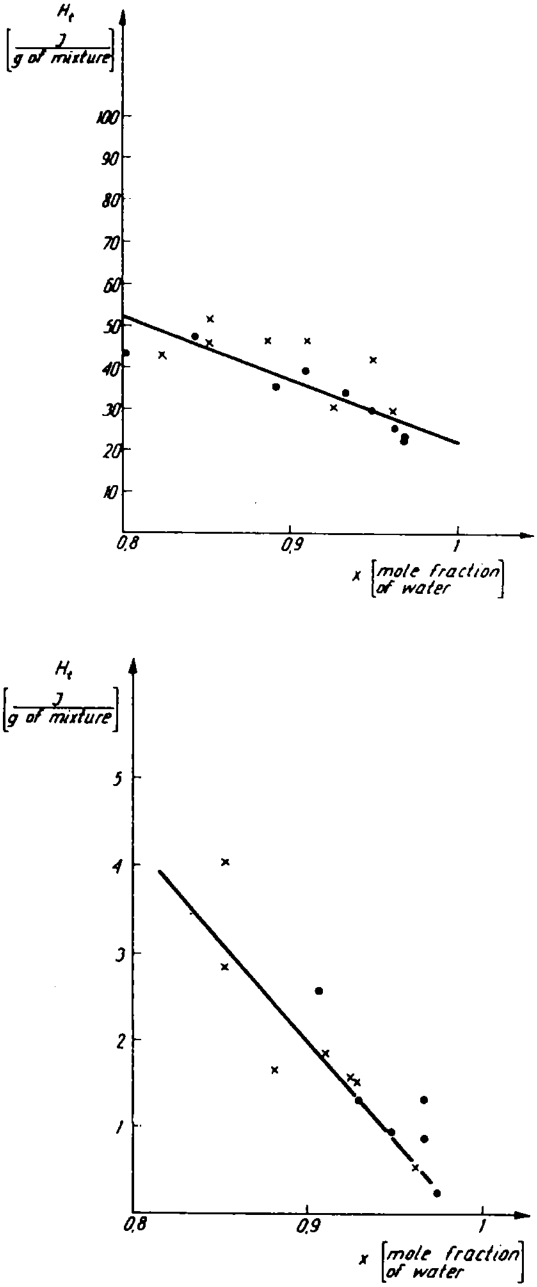


FIGURE 2 Dependence of measured heats of transition on water content for two transitions. • Deuterated solution x protiated solution. A. Transition II → III. B. Transition V → VI.

+ ice → tetrahydrate + water). The heats of transition, h_e and h_t (Eq. 3 and Table I), between the higher temperature phases show a smooth and marked decrease across the series II–III, III–IV, IV–V, V–VI.

CONCLUSIONS

In the comparison of the $C_{12}H_{25}NH_2/H_2O$ and $C_{12}H_{25}ND_2/D_2O$ systems the transition temperatures of the deuterated sample lie consistently higher then the protiated one. No unusually large effects are observed in the liquid crystalline regions. Isotope effects on the heats of transitions are too small to be observed by the relatively imprecise DSC technique. In the 0.8 to 1.0 mole fraction water region enthalpy differences between the various mesomorphic and liquid phases decrease smoothly as the temperature is raised.

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References

1. G. Jancso and W. A. Van Hook, *Chem. Rev.*, **74**, 689 (1974).
2. G. Jancso and W. A. Van Hook, *Physica A*, **91**, 619 (1978); *J. Mol. Struct.* **48**, 107 (1978); *Can. J. Chem.*, **55**, 3371 (1977); *J. Chem. Phys.*, **68**, 3177, 3191 (1978); *Acta. Chem. Sci. Hung.* (in press).
3. J. Bigeleisen, *J. Chem. Phys.*, **34**, 1485 (1961).
4. M. J. Stern, W. A. Van Hook, and M. Wolfsberg, *J. Chem. Phys.*, **39**, 3179 (1963).
5. See for example: P. A. Winsor, *Chem. Rev.*, **68**, 1 (1968).
6. A. Lawrence, *Mol. Cryst. Liq. Cryst.*, **7**, 1 (1969).
7. G. H. Brown (Ed.), *Advances in Liquid Crystals*, Academic Press, N.Y., 1976, Vol. 2.
8. A. W. Ralston, C. W. Höerr, and E. J. Hoffman, *J. Am. Chem. Soc.*, **64**, 1516 (1942).
9. K. Larsson and M. A. Al-Mamun, *Chem. Phys. Lipids*, **12**, 176 (1974).
10. R. Collison and A. Lawrence, *Trans. Faraday Soc.*, **55**, 662 (1959).
11. Q. C. Craft and W. A. Van Hook, *J. Solution Chem.*, **4**, 901 (1975); **4**, 923 (1975); J. Pupezin, G. Jakli, G. Jancso, and W. A. Van Hook, *J. Phys. Chem.*, **76**, 743 (1972).
12. H. L. Friedman and C. V. Krishnan, in *The Physics and Physical Chemistry of Water*, Vol. III (F. Franks, Ed.), Plenum, N.Y., 1973, Chap. 13.
13. A. Selecki, B. Tyminski, and A. G. Chmielewski, *Isotopenpraxis*, **6**, 138 (1970).
14. B. Ellis, A. Lawrence, M. McDonald, and W. Peel, Proc. Symp. Ordered Fluids and Liq. Crys., *Am. Chem. Soc.*, **1969**, 277.
15. J. Clifford, *Trans. Faraday Soc.*, **61**, 1276 (1965); J. Clifford and B. Pethica, *Trans. Faraday Soc.*, **60**, 1483 (1964).
16. F. E. Karasz and J. M. O'Reilly, Proc. Symp. Ordered Fluids and Liq. Crystals, *Adv. Chem. Ser.*, **63**, 180 (1965).
17. A. W. Ralson *et al.*, *J. Org. Chem.*, **9**, 102 (1944).
18. Beilstein, B, IV, H4, 201, p. 407.
19. Sadtler Co., Standard Infrared Spectra, 28226K (1973).

20. E. L. Skau, *Proc. Am. Acad. Arts Sci.*, **67**, 551 (1933).
21. A. Weissberger, *Techniques in Chemistry*, Vol. 1, Part V, Wiley, New York, 1971.
22. W. W. Wendlant, *Thermal Methods of Analysis*, Wiley, New York (1974).
23. F. E. Freeberg and T. G. Alleman, *Anal. Chem.*, **38**, 1806 (1966).
24. According to Ref. 8 region I is a two phase mixture of tetrahydrate and ice so for transition I → II the notation summarized in Eq. (3) does not strictly apply.