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Phase Diagram and Thermodynamic Properties of Disodium Cromoglycate-Water Lyomesophases

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Differential scanning calorimeter measurements have defined the phase diagram and enthalpic values of the disodium cromoglycate-water lyomesophase transitions. Addition of ethylene glycol and glycerol (up to 43.5 weight %) modifies these phases, extending significantly the temperature range of recently reported smectic-like Phase III.

INTRODUCTION

A lyotropic liquid crystalline system consisting of a solution of disodium cromoglycate (DSCG) in water was reported in 1973 by Hartshorne and Woodard.[1] Two phases were observed—a nematic phase (N phase) and a smectic phase (M phase). More recent work has shown that the N phase can be made cholesteric by adding a wide variety of water soluble chiral molecules,[2,3] and that another smectic phase (III) exists at lower temperatures than the N or M phases, prior to the transition to a solid phase.[4] In this work, the phase diagram and thermodynamic constants are determined via differential scanning calorimetry for these three phases in water, as well as the influence of adding glycerol or ethylene glycol on these parameters.

EXPERIMENTAL

DSCG was kindly furnished by Fisons Ltd. as a crystalline solid. It contains some tightly bound water, estimated at from 5 to 6 molecules in the relative humidity range 30–70%. Optically active additives were obtained from Aldrich or Sigma Chemical Companies and used without further purification. Differential scanning calorimetric (DSC) studies were performed on a Perkin-Elmer DSC-2C-TADS system using sealed aluminum pans containing the samples. DSCG, water, and/or optically active additives were mixed in rubber septum-capped vials which were annealed in an oven at 50°C for ~1–2 hours prior to placing in the DSC pans.

RESULTS AND DISCUSSION

The typical procedure in determining the temperature, enthalpy and entropy of a liquid crystalline phase transition via DSC is to heat and/or cool the sample at various scan rates, typically 2 to 40°/minute. Since the instrument measures heat per unit time, sensitivity is maximum at rapid scan whereas resolution is maximum at slow scan. On heating from the solid phase, the major enthalpic event in DSCG/H_2O is the conversion of solid to mesophase, which we will represent by T_m and ΔH_m. This enthalpy change accounts for ~95% of the total solid to isotropic phase enthalpy change. Experimentally, therefore, one can traverse the T_m regime at a slow or fast scan rate, isothermally hold the sample just above T_m, and then observe the other transitions at a rapid scan rate. The transitions involved are: Crystal (C) to Smectic III (III), III to Nematic (N), N to N + middle-smectic (M), III to N + M, III to M, N to N + Isotropic (I), M to M + I, N + I to I or M + I to I. A phase diagram describing all these transitions determined at a scan rate of 20°/minute is presented in Figure 1 for DSCG/H_2O. The transition C → III shows only a slight temperature dependence, the major change being an increase of about 2° between 10–15% DSCG in T_m. ΔH_m shows a decrease with increasing wt % DSCG (Figure 2); small discontinuities in ΔH_m are seen at ~15% DSCG. Figure 3 gives data on the enthalpy change ΔH_{III} for the transition III to N, N + M or M, and for $\Delta H_{\mathrm{N-N+I-I}}$. Again there is some evidence for a discontinuity in ΔH_{III} at 15–16% DSCG.

The evaluation of Phase III properties is made considerably easier upon the addition of either ethylene glycol (EG) or glycerol (G) to DSCG/H_2O. T_m is lowered and T_{III} is increased in both of these systems. Table I and II present these data as a function of EG and G concentration in 13% DSCG/H_2O. The decrease in T_m, which is dominated by the water in the phase, is undoubtedly associated with the reduced freezing points of the EG–H_2O and G–H_2O systems. The increase in T_{III}

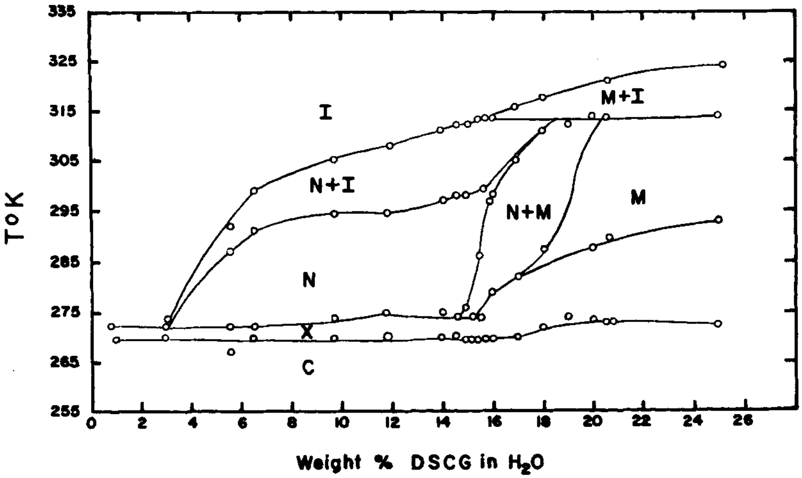

FIGURE 1 Phase diagram of DSCG/H₂O as determined via DSC at a scan rate of 20°/minute.

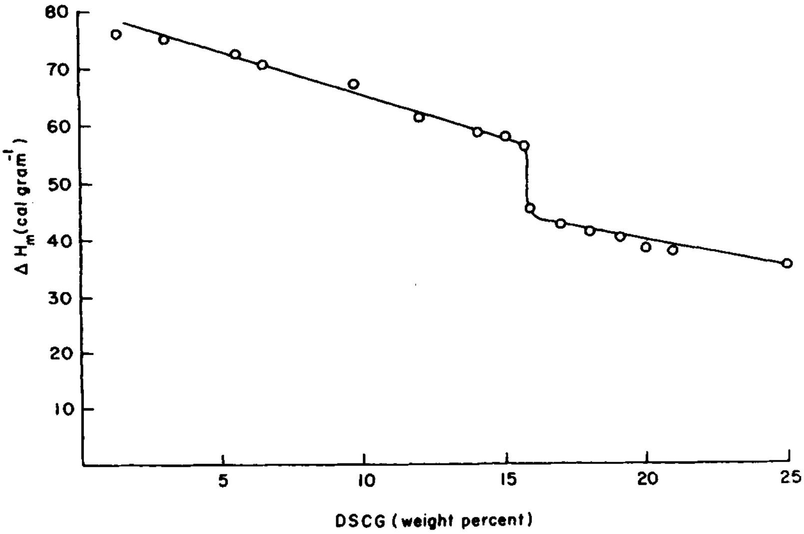

FIGURE 2 ΔH_m vs concentration in weight percent of DSCG in H_2O.

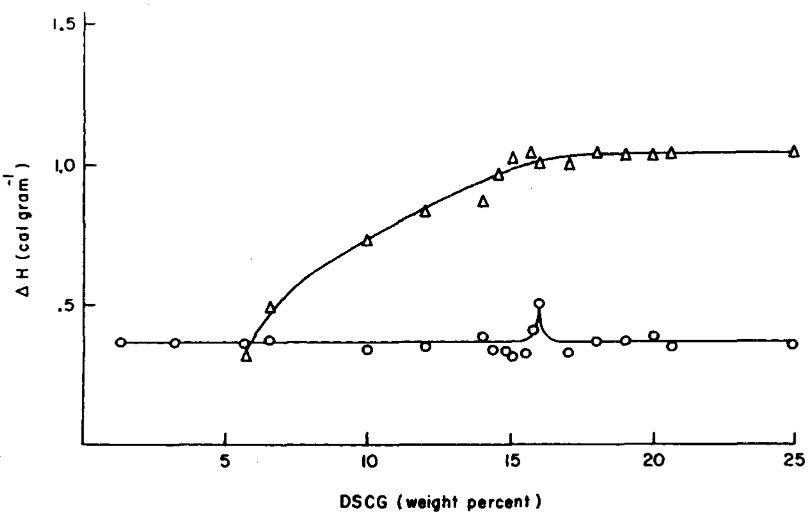

FIGURE 3 ΔH_{III} (O) and $\Delta H_{N \to N+I \to I}$ (Δ) for DSCG/H_2O system.

TABLE I

Transition temperatures and thermodynamic properties of DSCG (13 wt %)/H_2O/EG (8.7–43.5 wt %)[a]

EG(wt %)	Transition[b]	T°(K)	ΔH(cal g^{-1})	ΔS(cal Kg^{-1} $^{\circ}K^{-1}$)	$\Delta S/\Delta S_T$(%)
8.7	1	259.7	39.01	150.21	96.4
8.7	2	271.5	0.86	3.17	2.0
8.7	3	305.7	0.71	2.32	1.5
17.4	1	252.2	28.95	114.79	95.6
17.4	2	273.5	0.89	3.25	2.7
17.4	3	303.3	0.62	2.04	1.7
26.1	1	245.4	17.49	71.27	93.5
26.1	2	274.8	0.83	3.02	4.0
26.1	3	296.5	0.58	1.96	2.6
34.8	1	237.0	8.12	34.26	87.9
34.8	2	276.9	0.82	2.96	7.6
34.8	3	293.7	0.51	1.74	4.5
43.5	1	—[c]	—	—	—
43.5	2	276.5	0.83	3.00	—
43.5	3	289.4	0.29	1.00	—

[a] All data taken at a scan rate of 10°/minute.

[b] 1 = C → III; 2 = III → N; 3 = N → N + I → I total enthalpy change.

[c] T_m for 43.5% EG is too close to the instrumental lower temperature limit (~220 K) to allow a valid measurement.

TABLE II

Transition temperatures and thermodynamic properties of DSCG (13 wt %)/H_2O/Glycerol (8.7–43.5 wt %)[a]

Glycerol (wt %)	Transition[b]	T(°K)	ΔH(cal g^{-1})	ΔS(cal Kg^{-1} $°K^{-1}$)	$\Delta S/\Delta S_T$(%)
8.7	1	266.1	40.64	152.72	95.1
8.7	2	281.6	1.03	3.66	2.3
8.7	3	311.1	1.31	4.21	2.6
17.4	1	260.9	33.56	128.63	94.9
17.4	2	282.4	1.04	3.68	2.7
17.4	3	309.3	1.02	3.30	2.4
26.1	1	254.7	22.28	87.48	93.1
26.1	2	284.1	0.99	3.48	3.7
26.1	3	305.1	0.91	2.98	3.2
34.8	1	246.4	14.21	57.67	89.9
34.8	2	285.4	0.99	3.46	5.4
34.8	3	304.1	0.91	2.99	4.7
43.5	1	230.5	8.59	37.27	87.6
43.5	2	285.3	0.90	3.15	7.4
43.5	3	302.0	0.64	2.11	5.0

[a] All data taken at a scan rate of 20°/minute.

[b] $1 = C \rightarrow III$; $2 = III \rightarrow N$; $3 = N \rightarrow N + I \rightarrow I$ total enthalpy change.

parallels that observed with DSCG/H_2O, i.e. the lower the water concentration in the mesophase, the higher is T_{III}.

Optically, Phase III textures are hard to identify—in fact, only after the phase was reported via NMR measurements[4] were we able to search for and identify the phase via both DSC and optical observations. The discontinuities observed in ΔH_m (Figure 2) and in ΔH_{III} (Figure 3) as a function of wt % DSCG may imply that there are *two* Phase III's. The NMR results, however, did not distinguish any difference in Phase III order over the entire phase diagram, and so this possibility remains to be explored.

CONCLUSIONS

The phase diagram of DSCG/H_2O has been determined via DSC, specifying phase transition temperatures and enthalpic values for the multiple transitions. Addition of EG and G extend the temperature range of Phase III. A possibility exists that there are two "Phase III's", but this has not been confirmed.

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