Thermodynamic properties of solution by gas chromatography using a liquid crystal as solvent: cholesteryl myristate

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Thermodynamic properties of several organic compounds at infinite dilution in the three phases exhibited by cholesteryl myristate were determined from gas chromatographic data. Activity coefficients for the solutes are reported for the smectic A (74°C), cholesteric (80°C) and isotropic (86°C) phases of the liquid crystal. Excess solution thermodynamic properties are calculated and the results discussed in relation to solute-solvent interactions and orientations of the liquid crystal.

1. Introduction

The use of liquid crystals as stationary phases in gas-liquid chromatography (G.L.C.) is widely known [1, 2]. Analytical separation of stereoisomers, active and inactive geometric isomers, has been successfully carried out using a liquid crystal as the stationary phase [3–8]. The possibility of using G.L.C. to investigate thermodynamic properties of solutions can provide information on solute–liquid crystal interactions, on which the separation is based. One of the first studies concerning thermodynamic characteristics and the solvent properties of liquid crystals was carried out by Martire and coworkers [9]. They used cholesteryl myristate (CM) in its three mesophases as a solvent and four linear hydrocarbons and the three xylene isomers as solutes.

As an extension of the work carried out with CM, thermodynamic data at infinite dilution are reported here for 22 solutes in the smectic A, cholesteric and isotropic phases of CM. The solutes include a variety of compounds such as branched alkanes, aromatics, cycloalkanes and halogen derivatives.

2. Experimental section

2.1. Apparatus

The gas chromatograph employed was a Hewlett-Packard, model 5750 B equipped with a thermal conductivity detector. Injection port and detector temperatures were kept 10°C above the oven temperature. Column temperatures were measured with an immersion thermometer (± 0.1°C), and column pressure drop was determined with a mercury manometer. Helium was used as the carrier gas, its flow was regulated using a needle valve and measured with a soap film flowmeter. A Hewlett-Packard, model 7127 A, recorder was used to monitor the elution of solutes.

2.2. *Solvent*

The liquid crystal selected for this study was cholesteryl myristate and was supplied by Eastman-Kodak (Rochester, N.Y., U.S.A.). It was recrystallized three times from ethanol before being used. Transition temperatures were determined by G.L.C. and are in good agreement with literature values:

$$\text{CM}\quad \text{Solid} \xrightarrow{\;70\cdot2°C\;} \text{Smectic A} \xrightarrow{\;77\cdot6°C\;} \text{Cholesteric} \xrightarrow{\;82\cdot4°C\;} \text{Isotropic}$$
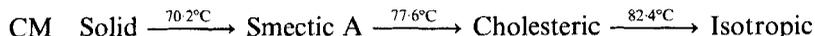
The solid support (60/80 mesh acid-washed Chromosorb W) was coated with the liquid crystal using a rotating evaporator with chloroform as solvent. The weight per cent of liquid phase on the solid support was obtained gravimetrically by ashing duplicate samples at 600°C. An average loading of 13·8 wt % CM was obtained. The coated support was packed in a glass column (170 cm × 0·2 cm i.d.) which had been previously rinsed with acetone and dried by passing a stream of nitrogen through it. The column was conditioned overnight in the gas chromatograph at 95°C.

2.3. *Solutes*

The solutes were obtained from Aldrich and were distilled in a packed distillation column before being used in the gas chromatograph. Samples of 0·1 μl were injected into the column with a Hamilton syringe. Retention times were obtained by averaging at least three experimental values and were measured with a precision of 0·1 s.

3. Results

3.1. *Activity coefficients*

Solute activity coefficients at infinite dilution, γ_f^∞, corrected for vapour phase non-ideality, were obtained from the relation

$$\ln \gamma_f^\infty \;=\; \ln \frac{1\cdot704 \times 10^7}{M_s V_g^0 p^0} - \frac{p^0 B_{22}}{RT}, \tag{1}$$

where M_s is the molecular weight of stationary phase, V_g^0 is the specific retention volume of the solute at the column temperature, p^0 is the vapour pressure of the pure solute, B_{22} is the second virial coefficient of the solute, R is the gas constant and T the temperature. Vapour pressures of the pure solutes were evaluated from the Antoine equation, using the constants given in the Dreisbach [10] tabulation. The second virial coefficient of the solute was obtained from the Beattie–Bridgeman correlation:

$$B_{22} \;=\; V_c \,[0\cdot461 - 1\cdot158\,(T_c/T) - 0\cdot503\,(T_c - T)^3], \tag{2}$$

where V_c is the critical volume and T_c is the critical temperature.

Values for the solute activity coefficients in the three liquid mesophases of CM are listed in the table and plots of $\ln \gamma_f^\infty$ versus $1/T$ are shown in the figure. The activity coefficients show a clear discontinuity and change of slope at the transition to a new mesophase. For the anisotropic phases it usually happens that $\gamma_f^\infty > 1$ while $\gamma_f^\infty < 1$ for the isotropic phase. The activity coefficients follow the trend smectic A > cholesteric > isotropic. The highest values of γ_f^∞ in the three mesophases correspond to 1,1,1-trichloroethane, 1,2,3-trichloropropane and *t*-butylbenzene. In the smetic A phase only chloroform shows a value of $\gamma_f^\infty < 1$, while in the cholesteric phase, chloroform, trichloroethylene and chlorobenzene show values of $\gamma_f^\infty < 1$. Some conclusions can be drawn regarding solute-solvent interactions by considering

Thermodynamic properties of solutes in the smectic A, cholesteric and isotropic phases of CM.

Solute	γ_f^∞			$\Delta \bar{H}_e^\infty$/kJ mol^{-1}			$\Delta \bar{S}_e^\infty$/J mol^{-1} K^{-1}			$\Delta \bar{H}^{\text{soln}}$/kJ mol^{-1}			$\Delta \bar{S}^{\text{soln}}$/J mol^{-1} K^{-1}		
	74°C	80°C	86°C	S_A	Ch	I	S_A	Ch	I	S_A 74°C	Ch 80°C	I 86°C	S_A 74°C	Ch 80°C	I 86°C
(1) Chloroform	0·993	0·787	0·655	18·12	21·68	6·03	52·27	63·53	20·55	−11·72	−7·99	−23·48	−33·73	−20·55	−61·73
(2) 1,1,1-Trichloroethane	2·031	1·590	1·269	16·99	26·95	9·75	43·06	72·44	25·19	−14·40	−4·27	−21·30	−47·42	−15·99	−61·31
(3) 1,2-Dichloroethane	1·619	1·260	1·040	16·49	23·56	9·71	43·52	64·87	26·70	−16·78	−9·50	−23·23	−52·40	−28·83	−64·95
(4) Trichloroethylene	1·087	0·852	0·729	16·49	21·18	4·85	46·83	61·31	16·15	−16·36	−11·51	−27·66	−47·83	−31·30	−74·45
(5) 1,2-Dichloropropane	1·713	1·298	1·075	19·54	27·62	9·17	51·85	76·08	24·94	−14·86	−6·57	−24·82	−47·33	−20·76	−69·68
(6) 1,1,2-Trichloroethane	1·413	1·049	0·887	19·21	24·44	6·57	52·43	68·84	19·29	−17·66	−12·14	−29·80	−53·74	−34·82	−81·86
(7) Tetrachloroethylene	1·284	1·014	0·845	15·86	24·65	8·20	43·65	69·72	24·27	−21·68	−12·64	−28·88	−64·57	−35·95	−79·10
(8) 1,1,2,2-Tetrachloroethane	1·594	1·139	0·973	28·58	30·80	4·48	78·47	86·21	12·68	−13·18	−10·42	−36·41	−41·81	−30·63	−101·24
(9) 1,2,3-Trichloropropane	2·023	1·425	1·165	23·23	33·31	9·71	61·10	91·40	25·78	−21·01	−10·63	−33·77	−66·37	−33·02	−95·38
(10) Methylcyclopentane	1·559	1·286	1·069	7·45	16·45	7·70	17·83	44·49	20·88	−22·93	−13·81	−22·39	−69·81	−41·22	−62·90
(11) Cyclohexane	1·478	1·198	1·003	10·09	21·26	7·37	25·82	58·72	20·51	−21·43	−10·09	−23·81	−64·95	−30·05	−66·29
(12) Cyclohexene	1·296	1·045	0·884	10·92	18·25	6·86	29·34	51·31	20·17	−21·01	−13·52	−24·69	−62·65	−38·67	−67·80
(13) Methylcyclohexane	1·606	1·288	1·074	13·27	19·88	7·16	34·23	54·20	19·33	−20·34	−13·56	−26·07	−62·57	−40·47	−73·20
(14) Benzene	1·242	0·998	0·834	12·72	23·31	7·91	34·90	66·08	23·52	−19·42	−8·66	−23·90	−57·79	−24·48	−65·03
(15) Toluene	1·287	1·017	0·863	15·94	21·59	6·95	43·82	61·06	20·63	−20·09	−14·19	−28·63	−60·01	−40·34	−78·51
(16) Ethylbenzene	1·510	1·166	0·973	17·20	25·19	7·87	46·12	70·14	22·18	−22·68	−14·35	−31·43	−68·76	−41·89	−87·34
(17) Chlorobenzene	1·248	0·964	0·825	20·55	24·61	6·19	57·33	70·02	18·83	−18·33	−13·98	−32·18	−54·61	−39·30	−88·01
(18) Bromobenzene	1·337	1·019	0·869	22·01	26·49	7·24	60·98	74·95	21·30	−20·55	−15·65	−35·82	−61·65	−44·44	−95·13
(19) Anisole	1·720	1·319	1·131	25·19	26·95	7·91	68·09	73·99	21·01	−19·25	−17·37	−35·95	−60·01	−51·43	−101·15
(20) Tert-butylbenzene	1·965	1·453	1·169	22·56	31·76	10·25	59·30	86·84	25·78	−22·43	−12·93	−34·19	−70·35	−39·80	−97·97
(21) 1,2,3-Trimethylbenzene	1·451	1·094	0·916	22·77	27·87	8·54	62·57	78·26	24·52	−24·19	−18·41	−37·08	−71·61	−52·86	−102·57
(22) 1,3,5-Trimethylbenzene	1·476	1·107	0·923	22·10	28·33	7·24	60·43	79·35	20·88	−22·93	−16·28	−37·12	−69·35	−46·96	−102·70
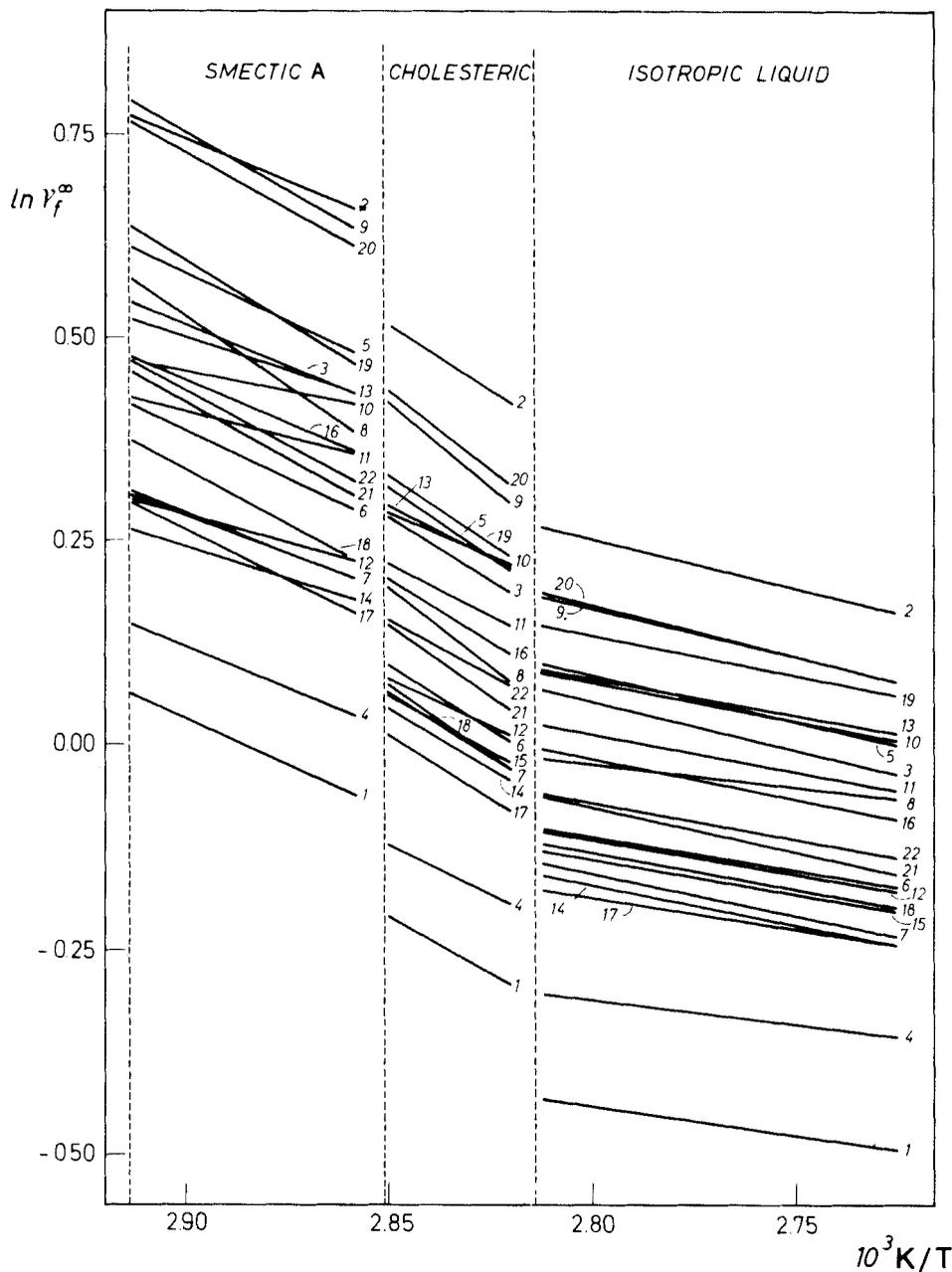
Activity coefficients of several solutes as a function of temperature in the three phases of CM
(dashed lines indicate the transition temperatures).

the orientational feasibility of some molecules. Tetrachloroethylene is a flat molecule because of its double bond, while 1,1,2,2-tetrachloroethane is more flexible because it can rotate internally. Thus, tetrachloroethylene can dissolve better in the ordered mesophases than 1,1,2,2-tetrachloroethane and this results in a lower γ_f^∞ for tetrachloroethylene. The high value of γ_f^∞ for *t*-butylbenzene can be due to its bulky *t*-butyl group which does not favour interaction with the liquid phase.

Liquid crystals are particularly selective for the separation of compounds on the basis of their molecular shape, and hence the discussion on activity coefficients for close boiling point solutes is similar to their retention behaviour. Solutes with high length-to-breadth molecular values and planar molecules show the largest retention times (lower γ_f^∞ values). This affinity for the liquid phase is the result of the parallel alignment of liquid crystal molecules in the anisotropic phases.

3.2. *Thermodynamic functions*

Partial molar excess enthalpy $\Delta \bar{H}_e^\infty$ and entropy $\Delta \bar{S}_e^\infty$ at infinite dilution were determined from the slope and intercept of a linear least-squares fit of $\ln \gamma_f^\infty$ versus $1/T$, as

$$\Delta \bar{G}_e^\infty = RT \ln \gamma_f^\infty$$
$$= \Delta \bar{H}_e^\infty - T \Delta \bar{S}_e^\infty. \tag{3}$$

The contributions to the activity coefficient are often referred to as the thermal activity coefficient (γ_T^∞) and athermal activity coefficient (γ_A^∞), i.e.

$$\ln \gamma_T^\infty = \Delta \bar{H}_e^\infty / RT \tag{4}$$

and

$$\ln \gamma_A^\infty = -\Delta \bar{S}_e^\infty / R. \tag{5}$$

The thermal contribution is also known as the residual part and it gives a measure of the energetic interactions between the solvent and solute molecules. As the liquid crystal and the solutes differ greatly in their molecular weight and volume, it has been suggested that the free-volume contribution due to the size difference between the solvent and solute should be deducted from the interaction parameter, κ, in the Flory–Huggins theory. Hence, the activity coefficient should be expressed as [11]

$$\ln \gamma_f^\infty = \left(\ln \frac{v_2}{v_1} + 1 - \frac{M_2 v_2}{M_1 v_1} \right) + \kappa$$
$$= \ln \gamma_{FH}^\infty + \kappa. \tag{6}$$

The interaction parameter is given by the sum of enthalpic and entropic contributions

$$\kappa = \kappa_H + \kappa_S$$
$$= \Delta \bar{H}_e^\infty / RT - \Delta \bar{S}_R^\infty / R. \tag{7}$$

Data of the thermodynamic functions $\Delta \bar{H}_e^\infty$ and $\Delta \bar{S}_e^\infty$ are listed in the table for the three phases. Calculations have also been made to evaluate the following parameters: γ_T^∞, γ_A^∞, γ_{F-H}^∞ and $\Delta \bar{S}_R^\infty$, although they are not shown here.

The natural logarithm values of the enthalpic contribution of the interaction parameter, κ_H ranges from 2·58 to 9·90 in the smectic A phase, from 5·60 to 11·3 in the cholesteric phase and from 1·63 to 3·43 in the isotropic phase. The large values of κ_H are compensated by very low κ_S and as a result for most compounds $\gamma_f^\infty > 1$, indicating a poorer solvatation of the solutes with the liquid crystal in the smectic A and cholesteric phases. This interaction becomes weaker in the isotropic phase as shown by a number of $\gamma_f^\infty < 1$ values. If the ratio $\gamma_T^\infty / \gamma_A^\infty$ is taken as a measure of the selectivity of the liquid phase [12] the cholesteric phase would have the highest selectivity and the isotropic phase the lowest.

The interaction parameter κ can be related to the solubility parameter by

$$\ln \gamma_T^\infty = \kappa$$

$$= (v_2/RT)(\delta_1 - \delta_2)^2. \tag{8}$$

Solubility parameters of the three phases of cholesteryl myristate, as determined from equation (8), fall into the following ranges: smectic A (74°C) ($\delta_1 = 31\cdot1$–$42\cdot3\,J^{1/2}\,cm^{3/2}$), cholesteric (80°C) ($\delta_1 = 32\cdot9$–$44\cdot0$) and isotropic (86°C) ($\delta_1 = 33\cdot1$–$39\cdot1$). The solubility parameter δ_1 is similar for series of solutes, except for the highly substituted chlorinated hydrocarbons. The narrowest range for δ_1 is observed in the isotropic mesophase, where the application of the solubility parameter concept is less questionable.

The solute partial molar enthalpies ($\Delta\bar{H}^{soln}$) and entropies ($\Delta\bar{S}^{soln}$) of solution, with the reference state of the solute at infinite dilution in an ideal mixture were determined from

$$\Delta\bar{H}^{soln} = \Delta\bar{H}_c^\infty - \Delta\bar{H}^{vap}, \tag{9}$$

$$\Delta\bar{S}^{soln} = \Delta\bar{S}_c^\infty - (\Delta\bar{H}^{vap}/T). \tag{10}$$

Solute molar heats of vaporization were determined from the Clausius–Clapeyron equation. The data for $\Delta\bar{H}^{soln}$ and $\Delta\bar{S}^{soln}$ are listed in the table. $\Delta\bar{H}^{soln}$ and $\Delta\bar{S}^{soln}$ are both negative for all solutes in the three phases. The highest values for $\Delta\bar{H}^{soln}$ and $\Delta\bar{S}^{soln}$ correspond to the isotropic phase. Correlations plots between $\Delta\bar{H}^{soln}$ and $\Delta\bar{S}^{soln}$ have been found for homologous series of solutes in conventional liquid phases. This enthalpy–entropy correlation is also observed for the three phases studied here. This plot is clearly illustrated for the smectic A phase. If a least-squares fit of all points is made, most of the cycloalkanes lie on the resulting straight line while the aliphatic compounds lie above and the aromatic compounds below this straight line. However, there is no general agreement as to the interpretation of these compensation plots in terms of specific solute-solvent interactions [13].

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