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CORRELATION BETWEEN GAS CHROMATOGRAPHIC AND INFRARED SPECTROSCOPIC BEHAVIOUR IN NEMATIC PHASES*

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SUMMARY

Gas chromatographic measurements on selected nematic liquid crystals as stationary phases show a slight change in the slope of the log V_g^0 *vs.* T^{-1} functions. IR measurements were performed in order to check this effect by an independent technique, by observing the temperature dependence of the position of the OH band of 2-octanol, which was dissolved in the nematic phase. This position of the OH band was used as an indicator of intermolecular interactions and was compared with the log V_g^0 data. Analogously to the GC measurements, the IR results also show discontinuities in the ν_{OH} *vs.* T^{-1} function and in the slope of this function. Possible reasons for this behaviour are discussed.

INTRODUCTION

In a previous paper[1] we described the application of mesomorphic phases, particularly nematic phases, of certain 4-*n*-pentylacetophenone O-(4-*n*-alkoxybenzoyl)oximes as stationary phases in gas chromatography (GC). We examined V_g^0 as a function of temperature, in order to obtain a basis for thermodynamic considerations. In the course of that work we considered it surprising that for the higher members of the homologous series (from the hexyloxyoxime ester) there was a slight change in the slope of the log V_g^0 *vs.*T^{-1} functions. For sake of clarity, we designate the higher temperature region of the nematic phase as nematic 2 for molecules possessing more than five carbon atoms in their alkoxy chain, and the lower region as nematic 1. By this procedure we did not intend to introduce anything like the idea of nematic polymorphy. The changes in the slope were found in the middle of the nematic region. The slope of the log V_g^0 *vs.* T^{-1} function is less steep at higher temperatures, which indicates a decrease in the differential molar enthalpy of solution ($-\Delta H_2$) in this region (neglecting the temperature dependence of the enthalpy of condensation, which is justified in such a small range of temperature, the differential molar enthalpy of solution becomes identical with the partial molar enthalpy of solu-

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* Dedicated to Professor Dr. Horst Sackmann on the occasion of the 60th anniversary of his birthday on February 3rd, 1981.

tion). We were surprised by this result, because to our knowledge the behaviour of any nematic phase used in GC is uniform over its whole range of existence and also in our case a phase change does not occur. Very careful calorimetric measurements[2] did not give any indication of a change of the phase in the range of temperature concerned.

In order to check and to complete these measurements[1], we again used[3] infrared (IR) spectroscopy as an independent method and investigated two problems. Firstly, we added about 2% of 2-octanol to the octyloxyoxime ester (C_8) and to the pentyloxyoxime ester (C_5). The positions of the OH bands of these particular solutions were recorded at 5°C intervals in the nematic range of C_5 and C_8. These positions were also believed[3] to be indicative of molecular interactions. Secondly, we recorded at the same temperatures the intensity behaviour of pure C_5 and C_8 in the range 900–1400 cm^{-1}.

EXPERIMENTAL

The experimental conditions used in the GC work[1] and the details of the IR measurements using mesomorphic phases[3] have been described previously. For the additional IR investigations we used sodium chloride cells of 0.6 mm thickness and carbon tetrachloride (Uvasol grade; E. Merck, Darmstadt, G.F.R.) as a solvent.

RESULTS AND DISCUSSION

Only qualitative results were obtained by measuring the intensities of the pure substances in the range 900–1400 cm^{-1}. From the spectrum of C_8 it can be concluded that the intensities of all bands in this range decrease uniformly from the melting point at 48.0°C up to about 75°C. Then, on increasing the temperature to 95°C (nematic–isotropic transition point = 96.0°C) the intensities of the bands remain nearly constant, with perhaps a very slight increase. Thus by this method we found qualitative agreement between the IR and GC behaviour.

The results obtained in determining the wavenumbers of the OH band as a function of T^{-1} are summarized in Fig. 1. Clearly there is a discontinuity in ν_{OH} and in the slope of this function when C_8 is used as a solvent. An analogous result was obtained by using the heptyloxyoxime ester as a solvent. Also, it is evident that there is no comparable change in the ν_{OH} *vs.* T^{-1} function with C_5 as a solvent, but ν_{OH} varies about the same with respect to T^{-1}. Similar results were obtained when the butyloxyoxime ester was used.

An interpretation of our results should take into account three main points. Firstly, we may consider the thermodynamic relationships based on the previous results[1]; secondly, the properties of the hydrogen bond should be discussed; and lastly, we should take into consideration the behaviour of particular nematic phases.

In order to obtain a basis for thermodynamic considerations, the average values of ΔH_2 and ΔS_2 of 22 organic compounds[1] were calculated, using the nematic states and the isotropic melts as stationary phases. The differences in these values are summarized in Table I.

Considering Table I, we should mention that there remain certain regularities in these differences. In particular, Table I can be used to compare the average thermodynamic data obtained using C_2–C_5 as stationary phases with the corresponding

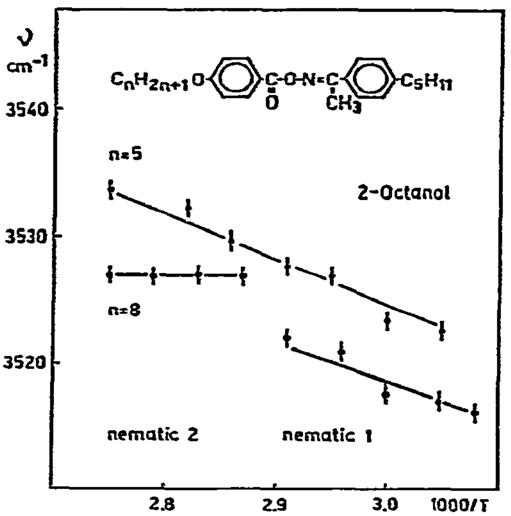

Fig. 1. Wavenumbers (ν, cm^{-1}) of the OH stretching band of 2-octanol in pentyloxyoxime and octyloxyoxime esters *versus* $10^3/T$ (°K^{-1}).

TABLE I

DIFFERENCES IN THERMODYNAMIC DATA (AVERAGE FOR 22 COMPOUNDS GIVEN IN REF. 1) WHICH RESULT ON COMPARING THE BEHAVIOUR OF THE ISOTROPIC AND THE NEMATIC PHASES OF THE OXIME ESTERS AS STATIONARY PHASES

n = carbon number in the alkoxy chain.

Parameter	*n*							
	2	*3*	*4*	*5*	*6*	*7*	*8*	*9*
	Nematic/isotropic				*Nematic 2/isotropic*			
$\Delta\Delta H_2$ (kJ mol^{-1})	7.1	4.2	8.0	3.8	11.8	3.4	3.4	7.6
					Nematic 1/isotropic			
					0.0	0.0	0.0	2.5
	Nematic/isotropic				*Nematic 2/isotropic*			
$\Delta\Delta S_2$ (J mol^{-1} °K^{-1})	15.5	0.0	8.8	6.7	18.9	− 1.3	0.0	9.7
					Nematic 1/isotropic			
					−19.3	−18.9	−18.9	−10.5

data for C_6–C_9 as stationary phases. Evidently the differences obtained for C_2–C_5 are in better agreement with the results for the higher temperature range of the C_6–C_9 oxime esters than for the lower range. Therefore we conclude that the higher temperature nematic state of the C_6–C_9 oxime esters is similar to the nematic state of C_2–C_5 oxime esters. There are considerable differences between the data for the nematic 1 state of the C_6–C_9 compounds and the other findings. In particular we should emphasize the decrease in entropy that occurs in this range, which clearly indicates an increase in the order of the arrangement of the substrate molecules, probably predominantly as a consequence of the higher molecular order existing in particular nematic regions, as is discussed below. Fig. 2, showing a $-\Delta H_2$ *vs.* $-\Delta S_2$ relationship, provides evidence of this behaviour.

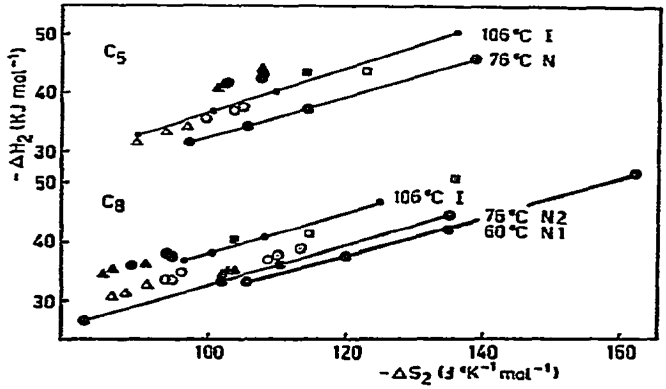

Fig. 2. Partial molar enthalpy of solution (ΔH_2) *versus* partial molar entropy of solution (ΔS_2) in pentyloxyoxime and octyloxyoxime esters. I indicates the isotropic and N the nematic state. The substrates are as follows: —●— and —•—, C_8–C_{12} *n*-alkanes; △ and ▲, xylenes; ○ and ●, chlorotoluenes; □ and ■, *n*-hexanol, in the nematic or isotropic state, respectively; △, ⊙ and ⊡, xylenes, chlorotoluenes and *n*-hexanol, respectively, in the nematic state at 60°C.

The second point to be considered concerns the dependence of the OH frequencies of hydrogen bonds on temperature, particularly those of 1:1 associates. We previously published some results concerning this problem[4], and we shall base our considerations on those results. However, first it should be mentioned that the variation in the OH frequency with temperature for 1:1 associates causes some problems in the use of the Badger-Bauer rule[5], because the linear plot of ln K *vs.* T^{-1}, which implies a constant enthalpy of association over the whole temperature range, does not agree with a varying ΔH.

In principle, two effects should be responsible for the variation in ν_{OH} as a function of temperature. Both may be deduced from the properties of the potential curves of the hydrogen bonds, namely the anharmonicity and the steepness. Considering that the wavenumber relating to the hydrogen bond interaction is about 100 cm^{-1}, and in this instance $h\nu < kT$, then a considerable or even predominant part of the associated complexes will exist in an excited state of vibration. With increasing anharmonicity and increasing excitation there is a change in the equilibrium position of the proton, and consequently a change in the length of the hydrogen bond and also a change in ν_{OH}. This effect will be less in the case of a stronger hydrogen bond, because then kT does not exceed $h\nu$ to the same extent, thus causing a smaller number of excited associates. Similarly, there will be a smaller variation in ν_{OH} in the case of a less anharmonic potential of the hydrogen bond.

These considerations are sufficient to explain the changes in ν_{OH}, but cannot explain the change in the slope of ν_{OH} or even a discontinuity in ν_{OH} with varying temperature. As a possible reason for these effects, we can postulate the existence of at least two basic centres in the acceptor molecules, in the present instance the oxygen and the nitrogen atoms. Owing to steric effects, which are dependent on the length of the alkoxy chains and also on the temperature, the accessibility of the different acceptor positions is changed, thus leading to different possibilities of forming hydrogen bonds.

We tried to check this idea experimentally by dissolving 2-octanol (0.028 mole/l) in carbon tetrachloride as a solvent. This solution shows only one sharp OH band due to the monomeric alcohol. Then a three-fold molar amount of heptyloxyoxime ester was added. In addition to the free OH band two associate bands now appeared (3490 and 3510 cm^{-1}), which varied to slightly different extents on changing the temperature. Surprisingly, but not associated with our main problem, these variations do not obey the Badger–Bauer rule, which requires a higher increase in the lower wavenumber band on decreasing the temperature, but in this instance the intensity of the band near 3510 cm^{-1} is more sensitive to the variation in temperature. Independent of this fact, we can infer in the nematic state also the existence of two (or more) basic centres per molecule, but because of the stronger interactions in this state the different OH bands of the alcohol may not be well resolved.

It should be mentioned that the hydrogen bonds represent only one aspect of all possible interactions, and therefore the occurrence of similar behaviour by two substances in forming hydrogen bonds is not sufficient to allow the conclusion that there are identical interactions and identical thermodynamic behaviour in the phases under investigation.

The third point to be discussed, namely the properties of particular nematic phases, may perhaps be based upon the theory of cybotactic groups, which has been deduced from some X-ray patterns and was discussed in detail by De Vries[6] and others. Whereas in the nematic state the molecules usually show a parallel arrangement of their longitudinal axis only, in the cybotactic groups there is a second parameter of order. As was pointed out by De Vries, the parallel-orientated molecules of the nematic state may form groups similar to a planar rhombus with angles of 45° and 135°. The formation of such groups may start at a temperature in the middle of the nematic region.

In this instance we may consider the possibility that only the members with a larger number of carbon atoms in the alkyl chain possess cybotactic groups at lower temperatures. Such groups showing a higher degree of order may be responsible for the effects measured here. It is desirable to check the behaviour of the nematic phases under discussion by X-ray measurements.

CONCLUSIONS

The IR results are in clear agreement with those of the GC investigations. The changes in the slope of the log V_g^0 *vs.* T^{-1} functions in particular instances of nematic phases are also accompanied by a change in the slope of the OH band position of an alcohol as a function of T^{-1}.

ACKNOWLEDGEMENT

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