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Liquid Crystals

Publication details, including instructions for authors and subscription information:

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To cite this Article Burmistrov, V. A. , Alexandriysky, V. V. and Koifman, O. I.(1992) 'Orientational effects of hydrogen bonding in liquid-crystalline solutions containing Schiff bases', *Liquid Crystals*, 12: 3, 403 – 415

To link to this Article: DOI: 10.1080/02678299208031057

URL: <http://dx.doi.org/10.1080/02678299208031057>

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Orientalional effects of hydrogen bonding in liquid-crystalline solutions containing Schiff bases

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(Received 18 March 1991; accepted 14 February 1992)

Intermolecular hydrogen bonding in binary mixtures containing nematogenic Schiff bases as solvents and proton-donating non-mesomorphic solutes has been considered. Reasons for the anomalous concentration dependences of solute order parameters are discussed. A solution structure model of acetic acid in nematic solvents is proposed; constants of complex-dimer equilibrium and coefficients of the orientational correlation of the non-mesogenic solute are calculated on the basis of this model. Hydrogen bonded complex structure using ^{13}C NMR has been studied and stability constants in isotropic solutions in chloroform have been calculated. The influence of the solvent orientational ordering on the complex stability is discussed. Data on the solvation isotopic effects in the solutions investigated, which confirm the adequacy of the model are given.

1. Introduction

Liquid-crystalline solutions of non-mesomorphic solutes are widely used in the spectroscopic investigation of the solute structure [1] as well as under the conditions of gas chromatographic analysis on liquid-crystalline stationary phases [2]. Electrooptic mixtures with dichroic dyes and stabilizers acting as non-mesogenic substances [3] are another field of application. This provides a reason for specific interest in such systems, and in particular in the investigations on the mechanism of the influence of the solute on various properties of both the solvent and the solution as a whole. It should be noted that a very rich experimental material has been obtained in this field. First, we refer to Martire and his co-workers investigations [4, 5] devoted to the analysis of the thermodynamic parameters of non-mesogens dissolved in both nematic and isotropic phases at infinite dilution as well as the influence of the properties of the components on these parameters. The solution thermodynamic parameters have been predicted within the framework of the generalized Maier-Saupe theory [6] as well as of lattice models [7].

The orientational ordering of the components is of high interest, because these determine the anisotropy of the physical properties of liquid crystals and determines their potential applications. Such investigations have been conducted for a large number of compounds incorporated into liquid crystal solvents [1]. However, as a rule, these substances were able to interact in a non-specific character with the liquid crystal. The introduction of specific interactions leads to a noticeable disturbance of the system [8] and can be a reason for obtaining incorrect data, in particular, on the geometry of the solute molecules. As a rule, this occurs for proton donating solutes which are able to form hydrogen bonds with liquid crystals having electron donating character [9].

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Diehl *et al.* [10,11] made a great contribution to studies of the orientational ordering of such proton-donors as methanol and phenol. To interpret the results cannot be explained from the viewpoint of a simple mutually parallel orientational correlation between the solute and the solvent, they proposed two orientational states of the solute that differ from each other [11]. However, the nature of orientational states in question and the influence of intermolecular hydrogen bonds on the properties of the binary system components still remains vague. Thus, the aim of the present paper is to investigate the influence of hydrogen bonds between the solvent and the proton donating solute on the orientational ordering and thermodynamic characteristics of the components.

2. Experimental

The solvents investigated are one of the most thoroughly studied class of liquid crystals namely the Schiff bases:

N	Compound	T_{CN}/K	T_{NI}/K
I	$\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{C}_6\text{H}_4-\text{C}_4\text{H}_9$	295	318.0
II	$\text{C}_2\text{H}_5\text{O}-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{C}_6\text{H}_4-\text{C}_4\text{H}_9$	310	352.0
III	$\text{C}_6\text{H}_{13}\text{O}-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{C}_6\text{H}_4-\text{CH}_3$	330	346.5
IV	$\text{C}_2\text{H}_5\text{O}-\text{C}_6\text{H}_4-\text{CH}=\text{N}-\text{C}_6\text{H}_4-\text{OCOC}_6\text{H}_{13}$	340	389.0

Ethanol, acetic acid and their deuteriated analogues ($\text{CH}_3\text{CD}_2\text{OH}$, $\text{CH}_3\text{CH}_2\text{OD}$, CH_3COOD) served as non-mesogenic proton donors. The nematic solvents were purified by recrystallization from ethanol, alcohols and acids [12]. ^1H and ^{13}C NMR spectra were recorded on a Tesla BS567 (100 MHz) spectrometer. The orientational order parameters were calculated from the dipolar coupling constants according to [1, 13]:

$$D_{ij} = -\frac{h\gamma_i\gamma_j S_{ij}}{4\pi^2 r^3}$$

Partial molar enthalpies of solution for the non-mesogens in the solvent were calculated [14] on the basis of the chromatographic data on retention of solutes at infinite dilution.

3. Results and discussion

3.1. Orientational ordering in binary mixtures

Since the orientational ordering of components is an informative fundamental characteristic of anisotropic systems, in the present paper we have measured the order parameters of the interproton vector of the methyl group of non-mesogens (S_2^{HH}) and the long molecular axis of the liquid-crystalline solvent (S_1) using ^1H NMR. It is noteworthy that S_1 of individual solvents is in good agreement with the literature data [15, 16].

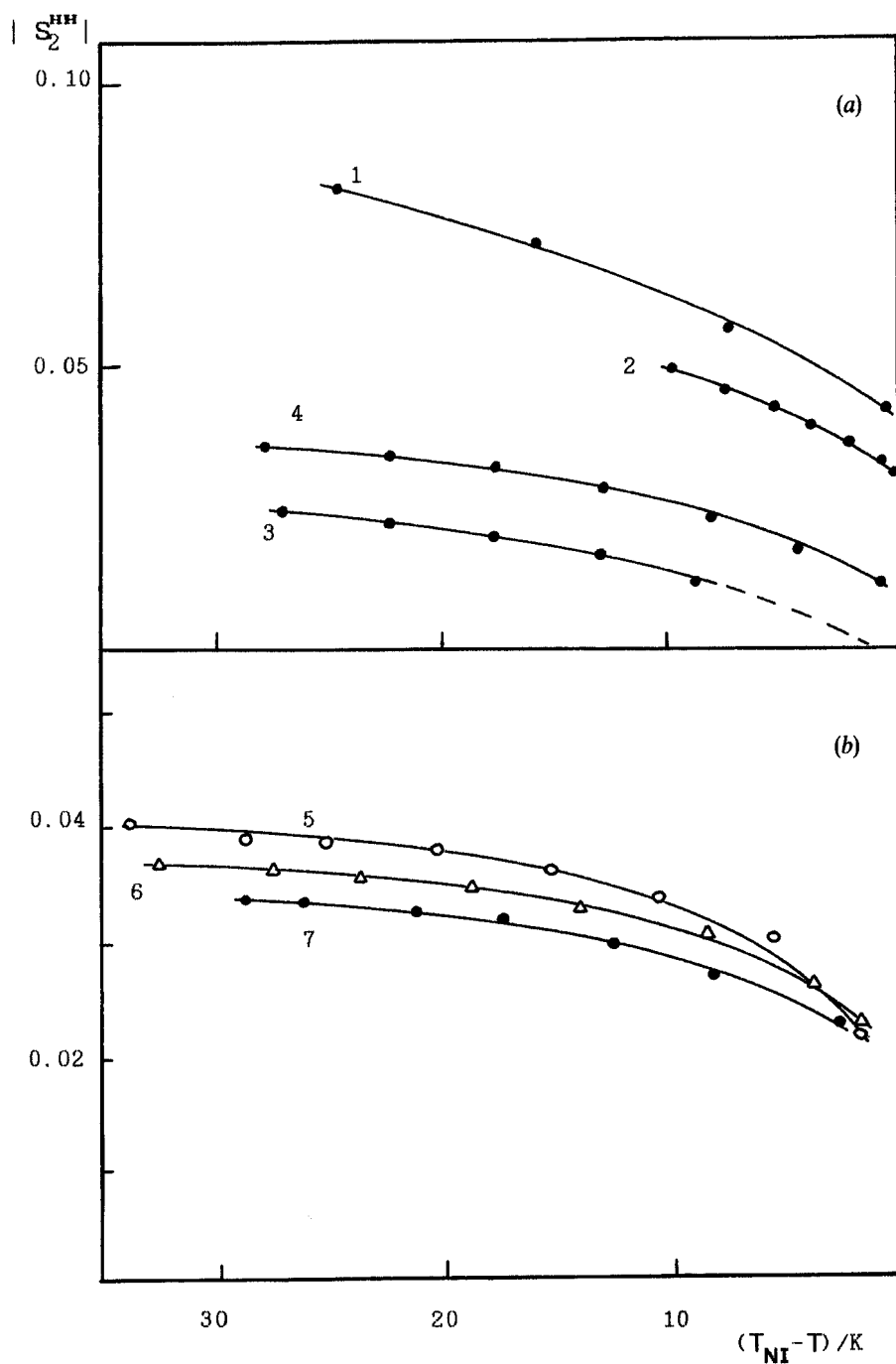
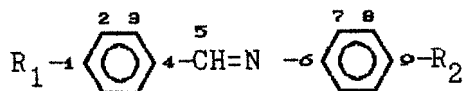


Figure 1. Temperature dependence of the orientational order parameter of acetic acid (a) and ethanol (CH_3CD_2OH) (b) dissolved in (II). (Mole fraction of solutes: 1, 0.011; 2, 0.023; 3, 0.088; 4, 0.117; 5, 0.05; 6, 0.100; 7, 0.146).

It is known [17] that the temperature dependence of S_2^{HH} is the simplest and most reliable test in a hydrogen bonding system for the realization of the orientational state differing significantly from that mutually parallel with the solvent. So, if specific interactions are absent these dependences can be approximated by the same curve for any concentration when using the shifted temperature ($T_{\text{NI}} - T$) (where T_{NI} is the beginning of the nematic–isotropic phase transition for the mixture), since in this case, the effect of any amount of the solute is described by the phase diagram [18]. There is no common approximation in our case (see figure 1), and so this indicates the existence of strong specific interactions. Special investigations are evidently necessary to draw unambiguous conclusions on the nature of these interactions. The problem becomes more complicated by the presence of several electron donating fragments in the molecules of most nematics. Thus obtaining information on the structure of hydrogen bonded complexes should be the first step.

3.2. Structure of hydrogen bonded complexes, i.e. Schiff base–proton donor

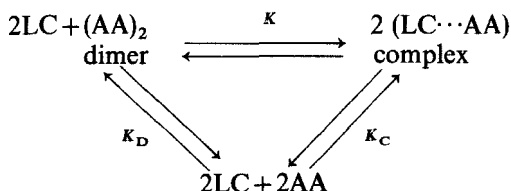
The structure of the complexes with a hydrogen bond has been studied by ^{13}C NMR of the isotropic solutions of mesogens II, IV in chloroform with the addition of various amounts of acetic acid. The analysis of the concentration dependences of the carbon chemical shifts (see figure 2) shows that the resonances of the C_1 – C_3 , C_5 , C_7 – C_9



carbons move downfield. Upfield shift changes of carbon nuclei directly connected with the $\text{CH}=\text{N}$ group (C_4 , C_6) are observed. Such changes of the chemical shifts as well as the character of the dependences in the region of proton donor low concentrations (see figure 2) point unambiguously to the formation of a hydrogen bond with participation of the nitrogen electron pair. Here, the character of the changes in the ^{13}C chemical shifts corresponds to the theoretical calculations of the electronic structure of benzilidene aniline on protonation and complex formation [19]. It should be noted that the character of the concentration dependences of the rest of the Schiff bases is the same as the liquid crystals shown in figure 2.

The oxygen atom of the $\text{C}=\text{O}$ of terminal group (IV) can be one of the possible participants in hydrogen bond formation. The analysis of the changes of the carbon $\text{C}=\text{O}$ resonance (see figure 2(b)) testifies to the formation of a substantially weaker hydrogen bond in this case in comparison with the $\text{CH}=\text{N} \cdots \text{HO}-\text{R}$ hydrogen bond.

The concentration dependences of $\Delta\delta_{\text{C}}$ (see figure 2(a)) were used to calculate the equilibrium, K , and stability constants, K_{C} , of complexes with the hydrogen bond as follows. The nucleus of the azomethine group (C_5) with the chemical shift which is the most sensitive to complex formation, has been chosen as the indicator. Taking into account a rapid exchange between various states of acetic acid in solution, simulation of the concentration dependences of the averaged chemical shift was performed according to the following scheme:



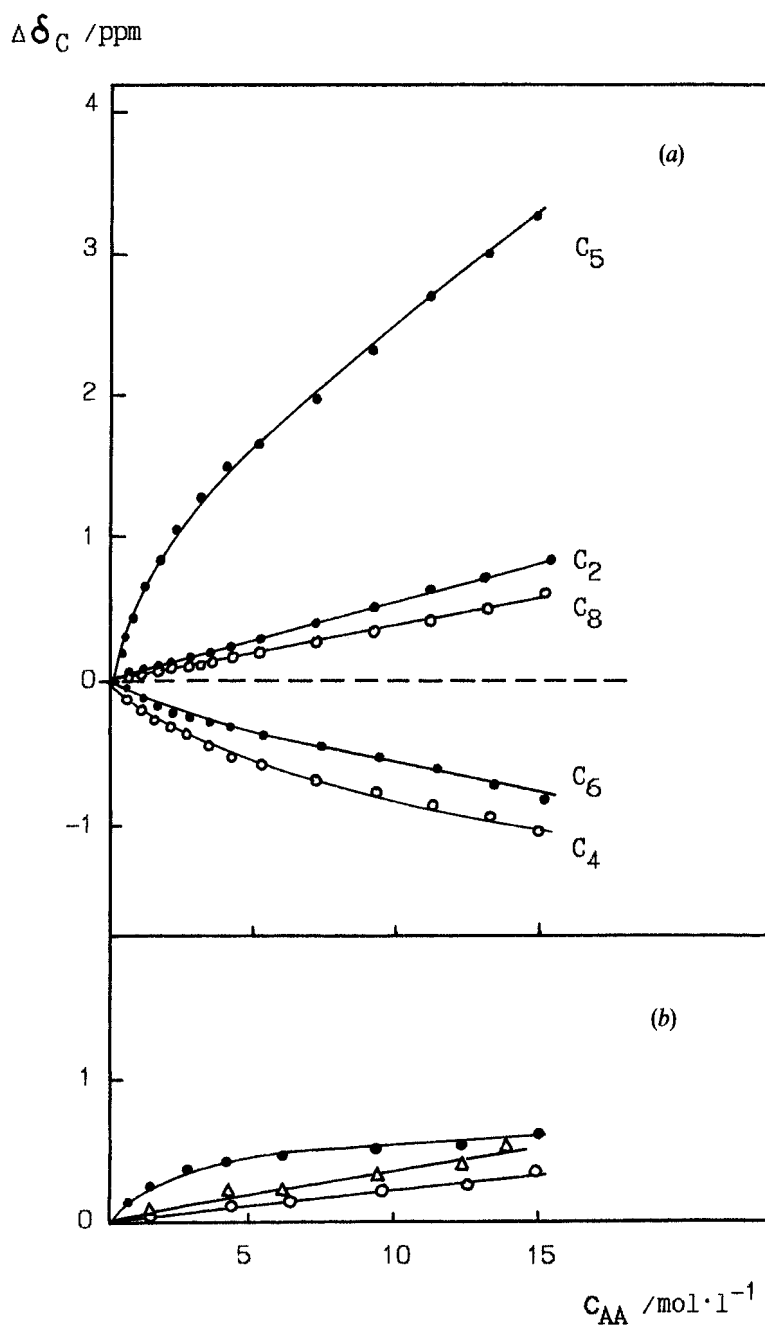


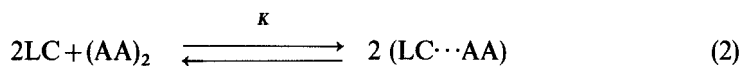
Figure 2. Dependence of the changes in the chemical shifts of (a) aromatic carbon nuclei of (II) and (b) aliphatic nuclei of (II) ($-\Delta-$, CH_2O) and (IV) ($-\circ-$, CH_2O , $-\bullet-$, $\text{C}=\text{O}$) on the acetic acid concentration in the CDCl_3 solutions at 318 K.

where AA is the molecule of acetic acid, and K_D is the stability constant of the dimer. The universal solvation contribution that is manifested in a linear dependence $\Delta\delta_C = f(C)$ at high concentrations of acetic acid (see figure 2(a)) was excluded from the total chemical shift change. The magnitudes of K_D for acetic acid in chloroform are taken from elsewhere [20]. The calculations allowed us to obtain K and K_C values for II, IV that are shown in table 1; they were used to calculate the enthalpies for formation of the hydrogen bonded complex ($\overline{\Delta H}$).

3.3. Simulation of the magnitude of the orientational order parameter

The various orientational states of acetic acid are not manifested clearly in the ^1H NMR spectra under rapid exchange. The total direct dipolar constants are determined by the averaged orientational order of the solute. Several orientational states being present, variation of the solute concentration should change the relationship between the dimer and the complex (see equation (1)) resulting in an anomalous concentration dependence of S_2^{HH} . This is confirmed by the data in figure 3.

Taking into account the equilibrium scheme 1 in the liquid-crystalline solution, we can suppose that a noticeable contribution to S_2^{HH} can be made by two orientational states of the non-mesomorphic solute, namely the hydrogen bonded complex and the cyclic dimer. In this case we can suppose that at low concentrations of AA its S_2^{HH} should be positive and at high concentration negative because of the different orientation of the methyl group interproton vector in the dimer and hydrogen bonded complex (see the structures in figure 3). The free acetic acid monomer can be excluded for two reasons (a) the small lifetime on rapid exchange between the dimer and the hydrogen bonded complex and (b) the small S_2^{HH} on rapid reorientation. Thus, the concentration dependences of S_2^{HH} (see figure 3) were simulated by the following equilibrium model:



using iteration procedures to minimize the deviations of the calculated curves from experiment. It is seen that the K value is not a stability constant being connected with the latter by

$$K = K_C^2 / K_D, \quad (3)$$

where K_C and K_D are stability constants of the complex and the dimer, respectively.

Table 1. Equilibrium constants K and K_C and formation enthalpies of hydrogen bonded complexes (acetic acid–Schiff base) in CDCl_3 solutions.

T/K	II		IV	
	$K/\text{l mol}^{-1}$	$K_C/\text{l mol}^{-1}$	$K/\text{l mol}^{-1}$	$K_C/\text{l mol}^{-1}$
298	2.5	43	1.9	37
303	2.7	40	2.1	35
308	2.8	36	2.3	33
313	3.0	34	2.4	29
318	3.2	31	2.6	28
	$\Delta H = -13.1 \text{ kJ mol}^{-1}$		$\Delta H = -12.1 \text{ kJ mol}^{-1}$	

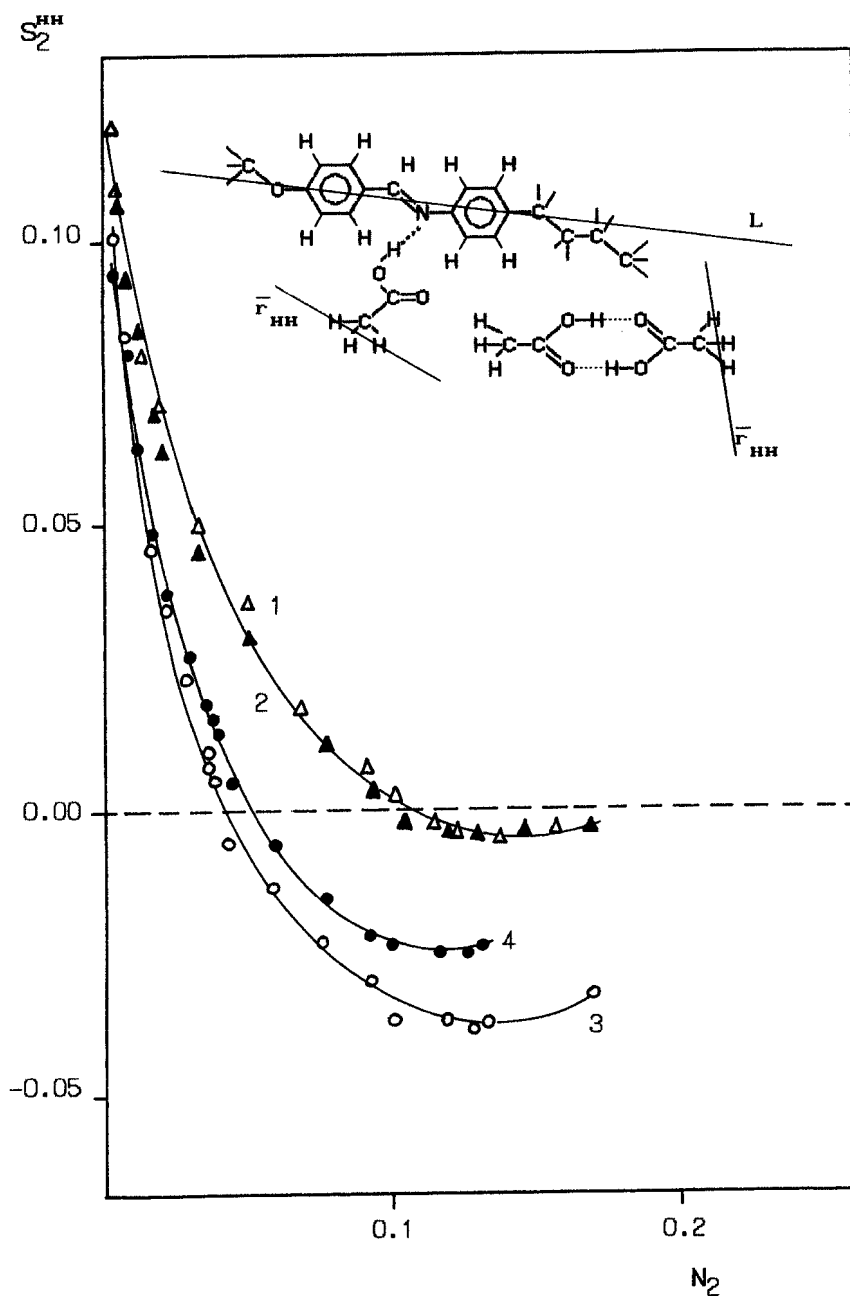


Figure 3. Molecular structure of the hydrogen bonded complex Schiff base-acetic acid and the dependence of the orientational order parameter of acetic acid on its mole fraction N_2 in solutions of (I) 1,2 and (III) 3,4. Temperature/K: 1 ($-\Delta-$), 287; 2 ($-\blacktriangle-$), 295; 3 ($-\circ-$), 323; 4 ($-\bullet-$), 329.

The equation for the calculation of the orientational order parameter of the solute on the basis of the equilibrium model in equation (2) takes the form

$$S_2^{\text{CALC}} = a^C S_1 N_2^C + a^D S_1 N_2^D, \quad (4)$$

where a^C , a^D are the orientational correlation coefficients of a non-mesomorphic solute in the complex and dimer, respectively, and N_2^C , N_2^D are the mole fractions of complex and dimer, respectively. The molar fractions of both orientational states are simply determined by K and by the total concentration of the non-mesogenic solute.

The computer simulation results are summarized in table 2. Before analysis of the obtained results, we should pay attention to the significance of the a^C and a^D coefficients. In fact they characterize the orientational correlation between the solute and anisotropic environment. Considering the orientational ordering of the methyl group interproton vector of acetic acid (\vec{r}_{HH}) the sign ‘-’ denotes predominantly mutually parallel, and ‘+’ mutually perpendicular arrangement of the long axes (L) of the solute and the liquid crystal [1, 13] (see figure 3).

The analysis of the K values shows a noticeable shift of the equilibrium in equation (2) towards the cyclic dimer of acetic acid. The latter high stability is evidently conditioned by a strong steric restriction both from the solvent environment and the Schiff base molecule itself on complex formation.

The contribution of the hydrogen bonded complex to the total S_2^{HH} becomes noticeable only at low concentrations of acetic acid (see figure 3). This is not surprising on taking into account the first order of complex formation on the solute, and the

Table 2. Calculated characteristics of solutions of acetic acid in nematic Schiff bases.

T/K	$K/\text{l mol}^{-1}$	$-a^D$	a^C
I			
283	0.027 ± 0.002	0.150 ± 0.002	0.180 ± 0.002
287	0.025 ± 0.002	0.137 ± 0.001	0.173 ± 0.002
291	0.025 ± 0.002	0.135 ± 0.001	0.169 ± 0.002
295	0.025 ± 0.002	0.131 ± 0.001	0.163 ± 0.002
298	0.024 ± 0.002	0.127 ± 0.001	0.159 ± 0.002
II			
303	0.029 ± 0.002	0.333 ± 0.003	0.185 ± 0.002
308	0.027 ± 0.002	0.306 ± 0.003	0.177 ± 0.002
313	0.029 ± 0.002	0.303 ± 0.003	0.170 ± 0.002
318	0.025 ± 0.002	0.264 ± 0.003	0.165 ± 0.002
323	0.024 ± 0.002	0.240 ± 0.003	0.161 ± 0.002
III			
326	0.057 ± 0.004	0.373 ± 0.004	0.139 ± 0.001
329	0.054 ± 0.004	0.334 ± 0.003	0.138 ± 0.001
332	0.056 ± 0.004	0.316 ± 0.003	0.137 ± 0.001
335	0.054 ± 0.004	0.293 ± 0.003	0.135 ± 0.001
338	0.058 ± 0.004	0.270 ± 0.003	0.128 ± 0.001
IV			
343	0.042 ± 0.003	0.268 ± 0.003	0.137 ± 0.001
348	0.043 ± 0.003	0.258 ± 0.003	0.127 ± 0.001
353	0.044 ± 0.003	0.240 ± 0.002	0.123 ± 0.001
358	0.043 ± 0.003	0.223 ± 0.002	0.121 ± 0.001
363	0.046 ± 0.003	0.209 ± 0.002	0.113 ± 0.001

Table 3. Orientational order parameters of individual nematic solvents.

Liquid crystal	S_1 at $T_{NI} - T = 15$ K	S_1 at $T_{NI} - T = 5$ K
I	0.60	0.50
II	0.68	0.56
III	0.74	0.62
IV	0.61	0.50

T_{NI} is the nematic–isotropic transition temperature.

second order effect in the case of dimerization. At the same time, stabilization of the dimeric associate is also connected with the effective arrangement of the latter in the nematic structure because of its rod-like shape. A direct comparison between K values (see table 2) in various solvents seems to be difficult due to the complex character of K (see equation (2)).

Negative a^D values (see table 2) denote parallel arrangement of the dimer long axis relative to the solvent. The values of a^D are determined mainly by the steric restriction of the liquid-crystalline environment. Stability of the orientational correlation liquid crystal–dimer (a^D) clearly decreases over the III > II > IV > I series (see table 2) together with S_1 (see table 3). The decrease of a^D with increasing temperature is found to be due to the increase of thermal motion together with a decrease of S_1 .

The coefficients of the orientational correlation of acetic acid in the complex (a^C) do not obey such unambiguous regularities. We believe, this is a result of the fact that solute order parameter in the complex is determined not only by S_1 but also by the orientation and stability of the intermolecular hydrogen bond.

Taking into account these results (see table 1), we can suppose that the stability of the hydrogen bond should depend both on the electron density on the nitrogen atom and on the steric accessibility of the electron pair. Since all of the mesogens investigated have the same structure of a rigid core we can suppose that the average angle between the hydrogen bond and the long axis of the mesogenic molecules should remain practically the same. The decrease in a^C over the I, II > III > IV series which is accompanied by an increase in mesophase transition temperature, can be a result of the decrease in stability and rigidity of the hydrogen bond. Both a^D and a^C decrease with increasing temperature of the solution (see table 2).

It is interesting to compare the results obtained when investigating complex formation in isotropic (chloroform) and anisotropic (nematic phase) solutions. There is approximately a two order decrease in the equilibrium constants of the hydrogen bond complex–dimer (K) when going from isotropic (see table 1) to anisotropic (see table 2) solvent; this suggests a relative destabilization of the hydrogen-bonded complex. This confirms our previous suppositions about the spatial restriction of the hydrogen bond by the liquid-crystalline environment. In addition we can say that the orientational manifestations of the hydrogen bond $-\text{COOH} \cdots \text{O}=\text{C}-$ in mesomorphic solutions, proton donor–mesogen (IV), are completely negligible, taking into account lower stability of such complexes (compared to hydrogen bonds on the $\text{CH}=\text{N}$ group) especially in the concentration region of stability of liquid crystal solutions (up to 0.25 m.f. of acetic acid), and also due to the low orientational ordering of the aliphatic chains [21].

These results show the strong influence of solute association on orientational ordering. Association processes can be excluded when investigating similar systems at infinite dilution of the proton-donating non-mesogen, this is possible in gas chromatographic experiments [2, 14].

3.5. Thermodynamics of Schiff base-proton donor mixtures

The ability to determine the thermodynamic characteristics of non-mesogens such as γ_2^∞ , $\overline{\Delta H}_2$ and $\overline{\Delta S}_2$ [14] is a doubtless advantage of the gas chromatographic method. Table 4 shows our data on the solution of acetic acid and ethanol in liquid crystals II-IV. Here we shall discuss only the values of solute partial molar enthalpy for two reasons. First, $\overline{\Delta H}_2$ can be considered a reliable criterion of the strength of solute-solvent intermolecular interactions [4, 5] at infinite dilution. Secondly, $\overline{\Delta H}_2$ is obtained from the gas chromatographic experiment (from the temperature dependence of the specific retention volume) with a minimum error [14] (in our case the relative error does not exceed 3.5 per cent).

First we note that solvent ordering strongly influences the thermodynamic values, as well as the order parameter. So, if in the isotropic phases of II-IV the values of $|\overline{\Delta H}_2|$ are practically the same (and this is understandable, since the chemical structures of solvents are very close) but in the nematic phase the enthalpy of solution in the highly ordered solvent III is much lower. These differences increase with increasing acidity of the solute (see table 4).

It is interesting to compare the behaviour of two electron donors (II and IV) in isotropic solution (chloroform, see table 1) and the nematic phase (see table 4). The intermolecular interaction enthalpy in the isotropic solution is determined by the electron donating properties of the Schiff base (introduction of the electron accepting substituent (OCOR (IV)) into the aniline ring weakens the hydrogen bond (see table 1). In liquid-crystalline solutions, the differences in the electronic properties are not of decisive importance, and the stability of the hydrogen bond is now also determined by the steric restrictions of the ordered solvent. So, $|\overline{\Delta H}_2|^{IV}$ becomes higher than $|\overline{\Delta H}_2|^{II}$, since $S_1^{IV} < S_1^{II}$.

3.6. Isotopic effects in orientational and thermodynamic characteristics of binary mixtures

This interpretation of the experimental data needs an independent confirmation. This results from the strong structuring of the mixtures under investigation and complex character of their self-association processes. Experimental confirmation of the

Table 4. Partial molar enthalpies and entropies† of non-mesomorphic solutes in Schiff bases.

Liquid crystal	CH ₃ COOH		C ₂ H ₅ OH	
	$-\overline{\Delta H}_2/\text{kJ mol}^{-1}$	$-\overline{\Delta S}_2/\text{JK}^{-1} \text{mol}^{-1}$	$-\overline{\Delta H}_2/\text{kJ mol}^{-1}$	$-\overline{\Delta S}_2/\text{JK}^{-1} \text{mol}^{-1}$
II, nematic	29.2	108	26.5	109
II, isotropic	39.6	128	—	—
III, nematic	15.4	66	21.8	94
III, isotropic	36.2	121	25.7	105
IV, nematic	29.1	100	—	—
IV, isotropic	—	—	—	—

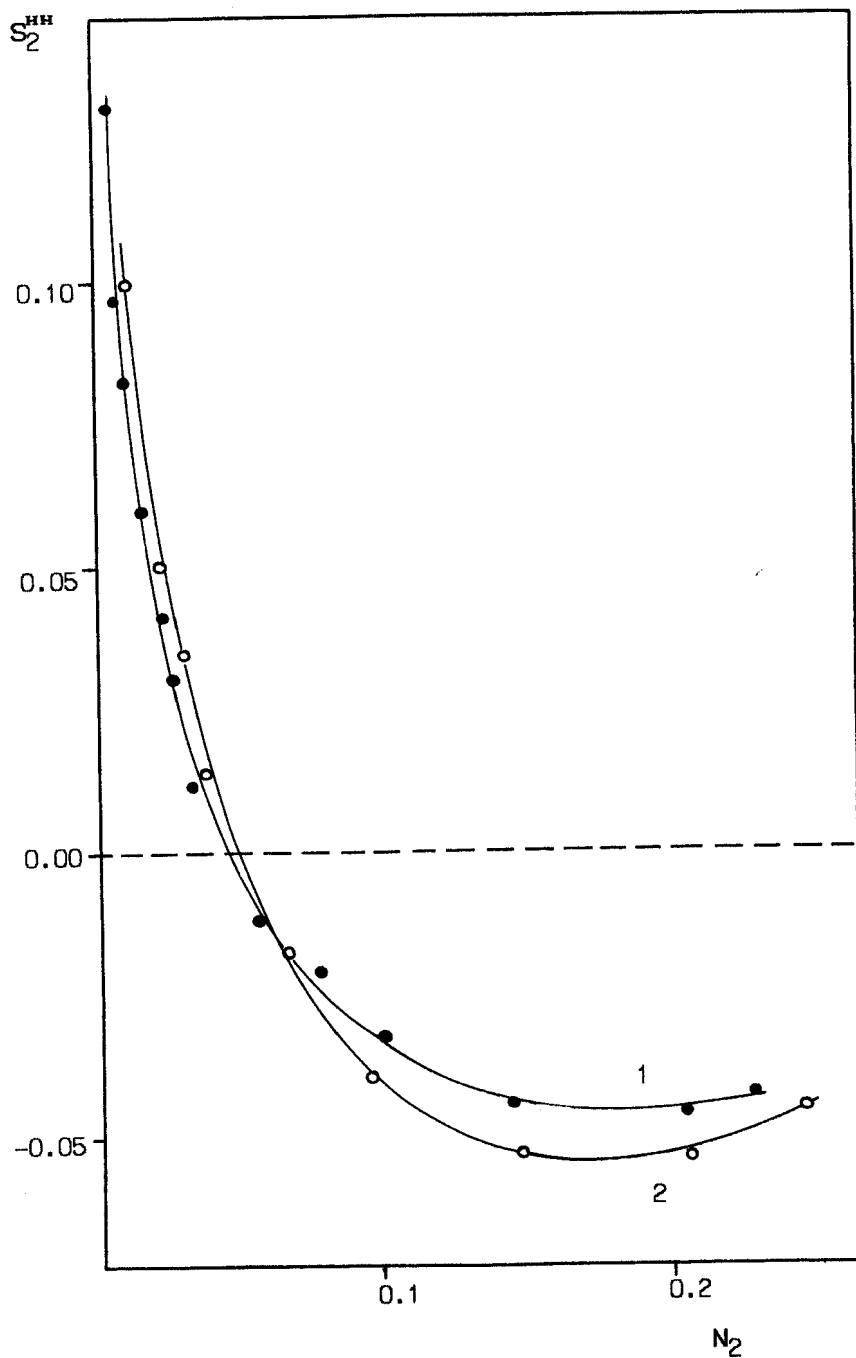


Figure 4. Dependence of the order parameter of acetic acid (1) and its monodeuterated analogue (2) dissolved in (II) at 308 K on the solute mole fraction N_2 .

Table 5. Isotopic effect in the thermodynamics of acetic acid and ethanol solution in (II).

Solute	$-\overline{\Delta H}_2/\text{kJ mol}^{-1}$	$-\overline{\Delta S}_2/\text{J K}^{-1} \text{mol}$
CH ₃ COOH	29.2	108
CH ₃ COOD	31.1	114
C ₂ H ₅ OH	26.5	109
C ₂ H ₅ OD	28.5	115

conclusions also causes difficulties related to the fact that even minor variations in temperature, mixture composition as well as structural modification of the solvent and solute change not only the stability of complexes but also the orientational ordering of the components in the various orientational states. We can understand that it is very difficult to separate the orientational contributions of these processes.

In our opinion the confirmation of the adequacy of the model proposed can be made by the study of the variations caused by minimum changes in the solute molecular structure. Isotopic substitution in the proton donating non-mesomorphic solute can serve as such a modification. It should not lead to noticeable changes in the molecular geometry, their dipole moments and dispersive intermolecular interactions with the solvent. We can expect only a strengthening of deuterium bonds [22]. In this connection we have studied the isotopic effects on the orientational and thermodynamic parameters of acetic acid (CH₃COOH and CH₃COOD) and ethanol (C₂H₅OH and C₂H₅OD) in nematogen (II) (see table 5 and figure 4).

As has been shown by the concentration dependence of the order parameter of the methyl group the interproton vector CH₃COOH and CH₃COOD (see figure 4), the isotopic effect is observed both at low and high solute concentrations. Such behaviour can only be caused by strengthening of both the complex and the acetic dimer. Here, since the increase in the solute order parameter under the conditions of predominant complex formation (low concentration) is caused by the strengthening of the deuterium bond, then there is a shift in the equilibrium from equation (2) towards the dimer in the region of high concentrations. Strengthening the cyclic dimer on isotopic substitution relative to the complex with the solvent is evidently conditioned by the double-centred character of the H(D)-bond in the dimer. This supposition is confirmed by the data obtained from gas liquid chromatography (see table 5). Indeed, at infinite dilution and in the absence of solute self-association the isotopic substitution both in acetic acid and ethanol molecules leads to the strengthening of the intermolecular interaction with the Schiff base (see table 5).

4. Conclusions

This paper has described investigations on various manifestations of intermolecular hydrogen bonds in binary liquid-crystalline mixtures containing proton donating non-mesomorphic solutes. It has been shown that the Schiff bases form hydrogen bonds with proton donating molecules with participation of the nitrogen atom of CH=N group both in isotropic and nematic solutions. The constants of the complex-dimer equilibrium and the coefficients of the orientational correlation in both states have been calculated by simulation of the concentration dependence of the order parameter for acetic acid in nematic solutions. The influence of orientational ordering and molecular structure of the solvent on the order parameters of the non-mesomorphic solute in associate and complex has been shown. The predominant

influence of the nematic solvent orientational ordering on the solution thermodynamics has been established when investigating the solution of proton donating solutes in liquid crystals by the method of gas liquid chromatography, while in isotropic solvents the main role is played by the electron donating properties of the Schiff base. The adequacy of the model used for the interpretation of the order parameter and thermodynamic parameters of the components is confirmed by the peculiarities of the solvation isotropic effects in nematic solutions of acids and alcohols.

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