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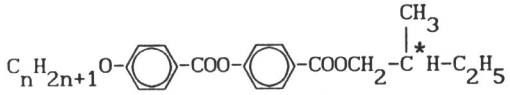
CHIRAL ESTERS AND THEIR MIXTURES WITH STABLE S_C^* PHASE AT AMBIENT TEMPERATURE

JÁNOS SZABON, LAJOS BATA, KATALIN FODOR-CSORBA, NÁNDOR ÉBER, ANIKÓ VAJDA
Central Research Institute for Physics of the Hungarian Academy of Sciences, H-1525 Budapest 114, P.O.B. 49. Hungary

Abstract Calculated and experimental phase diagrams of binary mixtures of the homologous series of (S)(+)-4-(2'-methylbutyl)-benzoate esters of the 4-n-alkoxybenzoic acids were compared. Eutectics occured if the length ratio of the components were smaller than **r**=0.9. If **r**≥0.9, co-crystallizations were detected. In mixtures of neighbouring homologues even the rule of additivity was valid for the melting curve (**r**=0.93-0.96, isomorphous systems). Eutectic mixtures of the **n=8** and **n=7** homologues (exhibited stable chiral smectic C phase around room temperature) were proved in spite of their length ratio of 0.96. Spontaneous polarization and helical pitch were measured both in the single compounds as well as in their mixture.

1. INTRODUCTION

The S(+)-4-(2'-methylbutyl)benzoate esters of the 4-n-alkoxybenzoic acids



were synthesized via the reaction of the 4-n-alkoxybenzoic acid chlorides and S(+)-4-(2'-methylbutyl) 4-hydroxybenzoate. The alkoxy chain varied from **n=7** to **n=16**, thus the lengths of the molecules were in the range of 3.025 nm to 4.150 nm. The purity of these compounds was checked by IR and NMR spectroscopy as well as by chromatographic and DSC methods.[1] Their phase transition temperatures and other properties were studied and compared with data in the literature.[2-5]

All the homologues studied have monotropic chiral smectic C^*, S_C^*, phases, i.e. their melting temperatures are above the temperatures of the S_C^* - S_A^* phase transition. By measuring the thermodynamic

properties of the single compounds one can calculate the isobaric binary phase diagram to predict the range of existence of the S_C^* phase in the mixture.[6-8]

The spontaneous polarization and the helical pitch of the single compounds as well as of a binary mixture were measured.

2. EXPERIMENTAL

The thermodynamic data of the single compounds and their binary mixtures were studied by means of a Perkin Elmer-DSC2 differential scanning calorimeter, equipped with a subambient accessory and a PC based data acquisition system. Sample weights were 1-3 mg. Heating and cooling rates were varied between 1.25-10°C/min.

To measure the temperatures of second order phase transitions depolarized light intensity measurements, DLI, were made using a hot-stage microscope with crossed polarizers, equipped with a selenium light detector connected to a two-channel potentiometric recorder. Heating and cooling rates were varied between 1.25-5°C/min.

Diagrams of state of the binary mixtures were established by the Kofler-contact method[6] using a polarizing microscope with a Peltier heating-cooling stage as well as by determining the transition temperatures of samples of different concentrations by DSC and DLI.

The eutectic temperatures of the mixtures could be calculated from the measured enthalpies and melting temperatures of the single compounds[7] by applying the relations of Le Chatelier, Schröder and van Laar.[8]

The estimation of the molecular length was based on an improved Corey-Pauling spacefilling model[9] using the all-trans stretched molecular conformers of the alkoxy chains.

Spontaneous polarization for substances **n=7,8,9** as well as the mixture of **n=8** with 36 mol% **n=7** was measured by a Diamant-bridge technique.

The helical pitch of the S_C^* phase was obtained by measuring the distance between the lines corresponding to the full pitch, using 10μm thick nearly homogeneous planar aligned cells under an Amplival pol-u polarizing microscope.

3. RESULTS

The thermodynamic data as well as the molecular lengths of the compounds are given in Table I. As all the S_C^* phases of the pure homologues are monotropic, enantiotropic mesophases could only be obtained by the eutectic depression of melting in mixtures.

TABLE I Molecular length, phase transition temperatures and enthalpies for the homologues of the S(+)-4-(2-methylbutyl)-benzoate esters of 4-n-alkoxybenzoic acids. () denotes monotropic phase transition.

n	L	Crystal - S_A^*		(S_C^* - S_A^*)		S_A^* - I	
	nm	^oC	$kJmol^{-1}$	^oC	$kJmol^{-1}$	^oC	$kJmol^{-1}$
7	3.025	42.2	-21.0	(23.5)	≤0	52.0	-4.03
8	3.150	34.0	-23.7	(31.0)	≤0	57.0	-4.30
9	3.275	57.0	-30.7	(36.0)	≤0	57.5	-4.65
10	3.400	51.1	-27.7	(39.0)	≤0	59.0	-5.11
11	3.525	56.7	-26.5	(38.0)	≤0	60.0	-5.24
12	3.650	58.1	-32.3	(40.5)	≤0	60.5	-5.60
16	4.150	47.8	-50.2	(34.5)	≤0	61.0	-6.90

3.1. Isobaric phase diagrams

The calculation of the phase diagrams[7] was based on the following assumptions:

- the two components are immiscible in solid phase, i.e. do not form mixed crystals,
- the liquid phase is an ideal mixed one, i.e. the activity coefficients of the components in the liquid phase equal one,
- the melting enthalpies are temperature-independent.[7,8]

The calculated eutectic temperatures with the corresponding concentrations are given in Table II. The **A-B** components are denoted by their alkoxy carbon number **n=7-12,16.**

TABLE II Calculated eutectic temperatures and concentrations (in mol% of B) for the **A-B** binary mixtures.

A / **B**	**n=7** (°C at x_B)	**n=8** (°C at x_B)	**n=9** (°C at x_B)	**n=10** (°C at x_B)	**n=11** (°C at x_B)	**n=12** (°C at x_B)
n= 7	- -	12.7 46.6%	25.5 67.9%	22.2 61.8%	24.1 65.4%	26.9 70.8%
n= 8	12.7 53.4%	- -	21.7 72.6%	19.0 66.2%	20.5 69.7%	22.9 75.5%
n= 9	25.5 32.1%	21.7 27.4%	- -	32.9 43.3%	35.7 48.3%	38.3 53.4%
n=10	22.2 38.2%	19.0 33.8%	32.9 56.7%	- -	31.8 54.6%	34.5 60.0%
n=11	24.1 34.6%	20.5 30.3%	35.7 51.7%	31.8 45.4%	- -	37.5 54.9%
n=12	26.9 29.2%	22.9 24.5%	38.3 46.6%	34.5 40.0%	37.5 45.1%	- -
n=16	27.5 28.1%	23.9 22.5%	36.5 50.3%	33.6 41.9%	35.8 48.1%	37.7 54.4%

Isobaric phase diagrams of the binary mixtures were measured. Eutectic systems were detected in most cases except mixtures of neighbouring homologues, which proved to be more or less isomorphous systems. As examples, diagrams of state are presented in Figure 1 for the **n=8** and **n=12** compounds as component **A**. The other component of the mixtures, **B**, were homologues with small differences in the number of the carbon atoms in their alkoxy chains. In other words, the ratios of their molecular lengths,

$$r = \begin{cases} L_A/L_B & \text{if } L_A<L_B \,, \\ L_B/L_A & \text{if } L_B<L_A \,, \end{cases}$$

were close to 1. Here L_A and L_B mean the molecular lengths of the **A** and **B** components of the mixture, respectively. Dotted lines mark S_C^*-S_A^* phase transitions in the supercooled state.

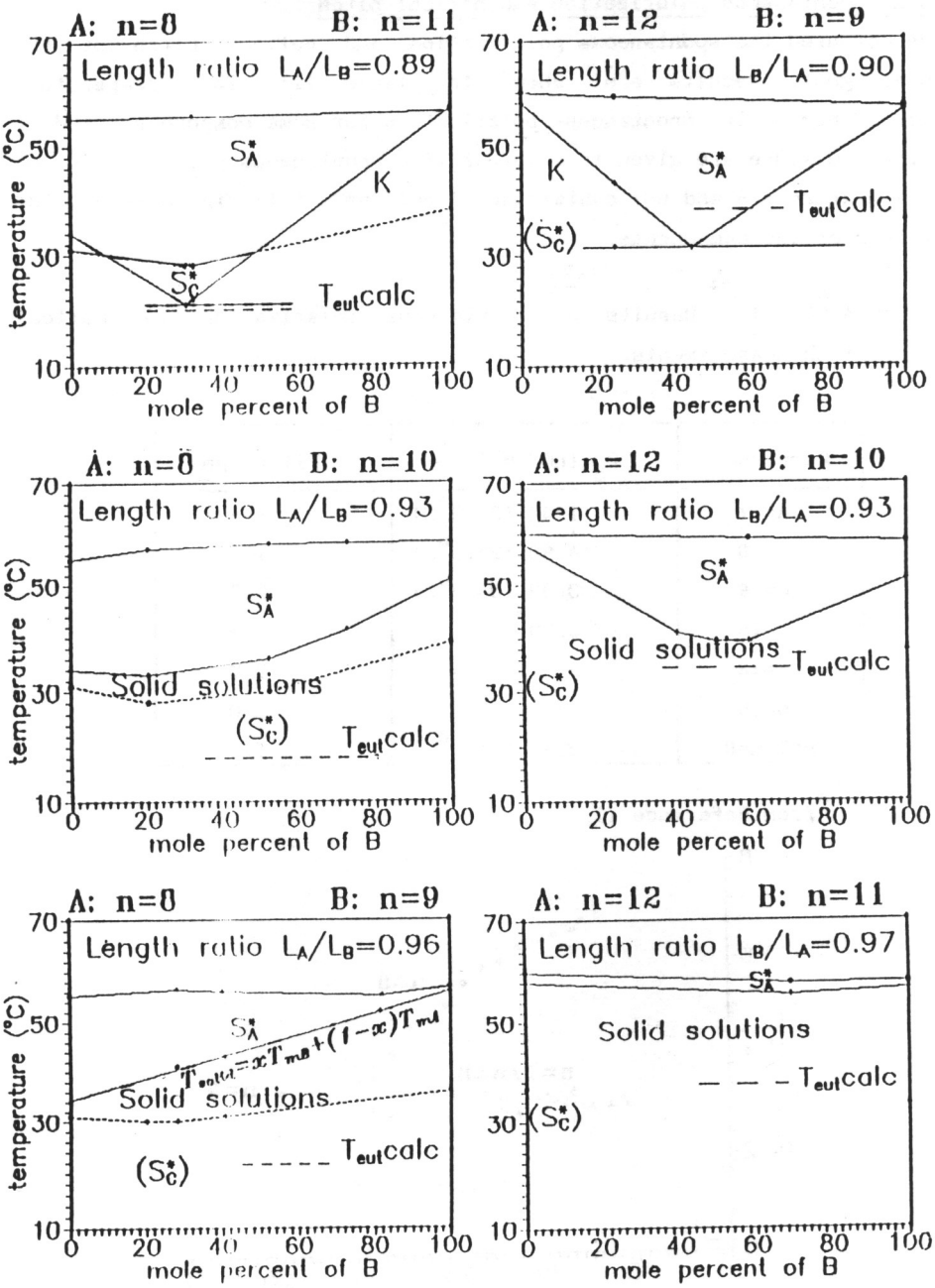


FIGURE 1 Isobaric binary phase diagrams, at different length ratio values. Dotted lines monotropic transitions, dashed lines calculated values.

3.2. Spontaneous polarization and helical pitch

We measured the spontaneous polarization and helical pitch of the homologues. Results are shown in Table III. The temperature dependence of the spontaneous polarization for some compounds and a binary mixture are given in Figure 2. The spontaneous polarization of the mixture **n=8** and **n=7** containing 36 mol% **n=7** fell in between the values of the components.

TABLE III Results of spontaneous polarization and helical pitch measurements.

Compounds	P_S (nC/cm^2)	Pitch (μm)
n= 7	1.42 (22.5°C)	---
n= 8	4.90 (26.5°C)	1.3
n= 9	3.33 (34.5°C)	2.7
n=10	5.00*	---
n=12	---	2.0
n=16	---	2.0
n=7/n=8	3.12 (21.0°C)	2.6

*from Reference 11.

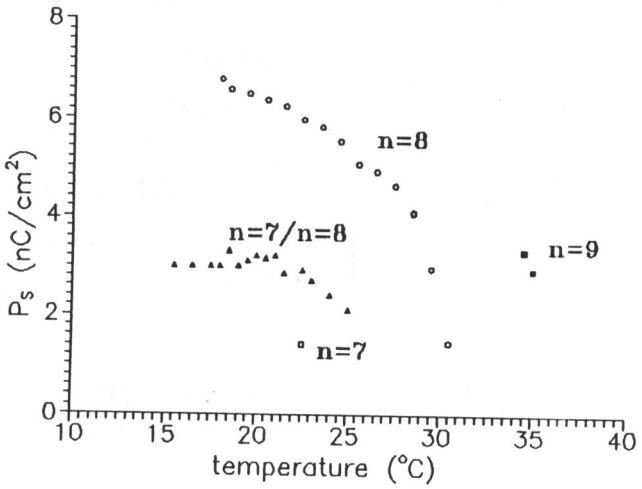


FIGURE 2 Temperature dependence of the spontaneous polarization for compounds **n=7**, **n=8**, **n=9** and a mixture **n=7/n=8**.

4. DISCUSSION

The calculated and the experimental isobaric phase diagrams can be compared. The differences, **D**, of the observed melting temperatures, T_{exp}, and the calculated eutectic ones, T_{calc},

$$D = T_{exp} - T_{calc}$$

taken at the calculated eutectic compositions, are demonstrated in Table IV as a function of the difference in the alkoxy carbon numbers of the components, denoted by **d**, as well as a function of the ratio of their molecular lengths **r**.

TABLE IV The differences **D** between the calculated and the experimental melting temperatures at the calculated eutectic composition for two series of binary mixtures of homologues **n=12**, and **n=8**, compared to earlier studies of nematogens[7] with the same differences, **d**, of the alkoxy carbon numbers.

d	r	A: n=12		A: n=8		Ref. 7
		B:	D (°C)	B:	D (°C)	D (°C)
8	0.76			n=16	-4	+1 -1
5	0.83	n= 7	-4			
4	0.86	n= 8	-6	n=12	-6	-2
4	0.88	n=16	-12			+8
3	0.90	n= 9	-6	n=11	+1	
2	0.93	n=10	+5	n=10	+14	+10 (0)
1	0.96			n= 9	+26	
1	0.96			n= 7	0	
1	0.97	n=11	+22			

In all systems presented in Table IV the calculated and the measured melting temperatures do not coincide ($D \neq 0$), except the anomalous case of **n=8/n=7**:

-if $r \leq 0.83$, i.e. $d \geq 5$, eutectics occured and **D** seems to decrease as the difference of the molecular lengths grows,

-at $0.86 \leq r \leq 0.88$, i.e. **d=4**, the *negative* differences were the greatest,
-if $r \geq 0.93$, i.e. $d \leq 2$, great *positive* differences could be observed.
In the system of **n=8/n=7**, **r**=0.96, **d**=1, there is no difference: **D** = 0.

Compared to the binary mixtures of other homologous systems[7,8] studied earlier similarities as well as differences can be observed.

In the majority of our binary systems eutectics occured if $r \leq 0.83$, $d \geq 5$, similarly to nematogens[7]. This is also in aggreement with the earlier results on n-paraffins[10] as eutectics were found in binary systems if the molecular lengths of the components were sufficiently different.

Contrary to nematogens[7], if $0.86 \leq r \leq 0.88$, i.e. with 4 carbons as difference in lengths, greater *negative* extrema were demonstrated (Table IV). The greater depression of melting points are probably due to the hindered packing arising from chirality.

As a result of co-crystallization, solid solutions (i.e. mixed solid crystals) occured in binary mixtures of neighbouring members of the homologous series of 4-n-alkoxy azoxybenzenes[7] (**d**=2, their length ratios were $r \geq 0.80$). Similarly, great *positive* differences were found in our chiral mixtures between measured and calculated melting temperatures due to co-crystallization. (However, the ratios of the molecular lengths of the components were $r \geq 0.93$, which were greater values than **r**=0.80 above.) As can be seen in Figure 1., for the system of **n=8/n=9**, the melting temperatures are additive according to the equation of

$$T^{x}_{solid} = T^{B}_{melting} + (1-x)T^{A}_{melting} \qquad \text{(x=mole fraction of B)}$$

indicating complete solid solubility.

The binary mixture of the **n=8/n=7** system is rather different from the others (Table IV). At the length ratio of **r**=0.96, **d**=1, at which in the other systems solid solutions occured, a pronounced eutectic behaviour catches the eye (see Figure 3). At the first instance this reminds us of the PAA-PAP system in which deep eutectic appeared in spite of the smallest value of **d** (**d**=2, dialkoxy compounds), due to the methoxy and ethoxy side groups[7] which differ frequently from the normal trend of clearing and melting point behaviour.

In the **n=8/n=7** system the side chains are rather longer. Their

diagram of state shows ideal melted as well as solid phases with no solid solution in spite of one methylene group as the only difference between the structure of the components. The additivity rule for the temperatures of the S_C^*- S_A^* phase transition, T_{CA},

$$T_{CA}^{x} = xT_{CA}^{B} + (1-x)T_{CA}^{A} \qquad \text{where } x=x_B ,$$

was strictly valid in this system.

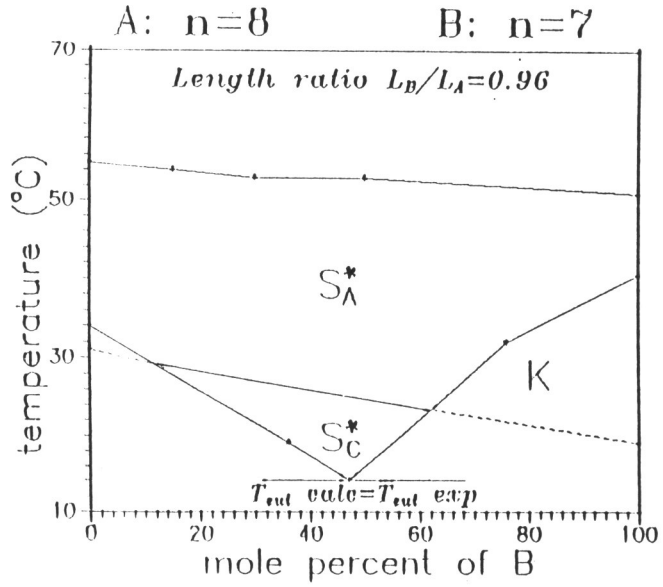


FIGURE 3 Diagram of state for the binary mixture of n=8/n=7.

SUMMARY

Eutectics were found in binary mixtures of homologues of the S(+)-4(2'-methylbutyl)benzoate esters of the 4-n-alkoxybenzoic acids up to the length ratio of r=0.9. Stable S_C^* phases were detected in most cases as the experimental solidus lines showed steep depressions in the diagrams of state while the S_C^*-S_A^* transition lines were more or less additive.

On the other hand mixed solid crystals could be detected in mixtures consisting neighbouring homologues ($r \geq 0.93$) which melted above the temperature of the calculated eutectic as well as the S_C^* phase. Even the rule of additivity was found to be valid concerning melting points in a few mixtures indicating isomorphous systems.

An anomalous behaviour was detected in case of the binary system **n=8/n=7**. The rule of additivity was valid only for the temperature curve of the S_C^*-S_A^* phase transition, and eutectics occured, with $T_{exp} - T_{calc} = 0$ in spite of the similarity of the components. The values of the spontaneous polarization fell in between those of the components.

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