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Dedicated to the 125th birthday of Academician Yakov Kivovich Syrkin

Phase equilibria in 4-pentyloxybenzoic acid – long-chain *n*-alkane systems

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Objective. *The work's objective is to develop methods for the thermodynamic modeling of systems of liquid crystal – organic solvent.*
Methods. *Four binary systems of nematic 4-pentyloxybenzoic acid (5OBA) with n-alkanes (hexadecane, octadecane, icosane, and docosane) were investigated via thermal analysis methods (differential thermal analysis, polarization microscopy, visual polythermal analysis, and the polytherm solubility method). The accuracy in determining phase transitions temperatures is within 0.3 K. To describe the phase equilibria, models based on the Hildebrand and Hansen solubility parameters were used. Hansen solubility parameters were estimated using the Stefanis scheme. Hildebrand solubility parameters, molar volumes, and vaporization enthalpies were calculated using a group contribution scheme.*
Results. *Phase equilibria in the systems of 5OBA with n-alkanes were studied. Four T–x diagrams were obtained by thermal analysis methods, coordinates of invariant points (eutectics and metatectics) were determined in the systems. A linear dependence of the metatectic coordinate (x_1 is a fraction of 5OBA, mol. %) on the number of C atoms in the alkane (N) was established: $x_1 = -0.3131 \times N + 85.467$. Solubility polytherms of 5OBA with solvents of different polarity were obtained: n-alkanes (hexane, octane), cyclohexane, aromatic compounds (benzene, toluene, and o-xylene), chlorobenzene, ethyl acetate, acetone, 1,4-dioxane, alcohols (propan-2-ol, propan-1-ol, butan-1-ol), and acetonitrile. The dependence of 5OBA's solubility on the difference in the solubility parameters of the components and the distance Ra was established.*
Conclusions. *The model for regular solutions based on solubility parameters allows us to calculate the solubility polytherms of mesogens and to select solvents for the purification of mesogens by the mass crystallization method. The best solubility of 4-pentyloxybenzoic acid at 298 K appears in chlorobenzene.*

Keywords: *liquid crystals, nematic, phase diagrams, thermal analysis, 4-pentyloxybenzoic acid, n-alkanes, solubility, thermodynamic modeling, Hildebrand solubility parameter, Hansen solubility parameter.*

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К 125-летию со дня рождения академика Я.К. Сыркина

Фазовые равновесия в системах 4-пентилоксибензойной кислоты с длинноцепочечными *н*-алканами

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Целью *работы является разработка методов термодинамического моделирования систем жидкий кристалл – органический растворитель.*

Методами *термического анализа (дифференциальный термический анализ, поляризационная микроскопия, визуально-политермический анализ и метод политерм растворимости) исследованы 4 бинарные системы нематической 4-пентилоксибензойной кислоты (5OBA) с н-алканами (гексадекан, октадекан, эйкозан, докозан). Точность определения температур фазовых переходов – в пределах 0.3 K. Для моделирования политерм растворимости 5OBA использована модель регулярных растворов на основе параметров растворимости Гильдебранда и Хансена. Параметры растворимости Хансена мезогенов рассчитаны по групповой схеме Стефаниса. Параметры растворимости Гильдебранда, мольные объемы и энтальпии испарения рассчитаны по схеме групповых вкладов.*

Результаты. *Методами термического анализа исследованы фазовые равновесия в системах 5OBA с н-алканами. Получены 4 T–x-диаграммы, определены координаты нонвариантных точек (эвтектики и метатектики) в системах. Установлена линейная зависимость координаты метатектики (x_I – доля 5OBA, мол. %) от количества атомов C в алкане (N): $x_I = -0.3131 \times N + 85.467$. Получены политермы растворимости 5OBA с растворителями разной полярности: н-алканы (гексан, октан), циклогексан, ароматические (бензол, толуол, о-ксилол), хлорбензол, этилацетат, ацетон, 1,4-диоксан, спирты (пропан-2-ол, пропан-1-ол, бутан-1-ол), ацетонитрил. Установлена зависимость растворимости 5OBA от разницы в параметрах растворимости компонентов и приведенного радиуса.*

Заключение. *Модель регулярных растворов с использованием параметров растворимости позволяет рассчитать политермы растворимости мезогенов и подобрать растворители для очистки мезогенов методом массовой кристаллизации. Лучшая растворимость при 298 K 4-пентилоксибензойной кислоты – в хлорбензоле.*

Ключевые слова: *жидкие кристаллы, нематический, фазовые диаграммы, термический анализ, 4-н-пентилоксибензойная кислота, н-алканы, растворимость, термодинамическое моделирование, параметр растворимости Гильдебранда, параметр растворимости Хансена.*

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Introduction

This article is dedicated to the memory of Academician Yakov Kivovich Syrkin, an outstanding scientist and teacher. His research interests lied primarily in the fields of chemical kinetics and the nature of chemical bonds. On the other hand, his university course on physical chemistry was different from the standard course in this subject, mainly due to a revision of the chemical thermodynamics part [1, 2]. Research related to thermodynamic description of systems containing liquid crystals is relatively new for the Ya.K. Syrkin Department of Physical Chemistry at the M.V. Lomonosov Institute of Fine Chemical Technologies of the MIREA – Russian Technological University, however certain success has already been achieved here (see, for example, [3–5]).

Liquid crystals (LCs) are widely used in a variety of applications [6–8], especially in display technologies [8–12]. Modern liquid crystalline materials (LCMs) are multiple-component mixtures, because no individual mesogen has all the necessary

properties to be used as a material for display devices. Today, there are two major tasks for those who design new materials – purification of individual LCs and creation of LCMs with a wide range of mesophase existence. The final step of mesogen purification is usually performed by multiple recrystallizations from a solution; this is why research on LC – non-mesogen (solvent) systems is needed (see, for example, [5]).

Since experimental research on LC-containing systems is rather laborious, thermodynamic modeling is in demand.

The objective of this work is to develop methods for thermodynamic modeling of systems of liquid crystal-organic solvent.

One of the most interesting types of mesogen is 4-alkyloxybenzoic acids that allow generation of supramolecular ensembles with new properties. The number of publications on systems with a mesomorphic component that forms hydrogen bonds has soared since the mid-1990s (see, for example, [13–16]). Later, 4-alkyloxybenzoic acids (nOBA) have been used most often as model objects (see, for example, [17–23]). Certain patterns are observed in this homologous series. Acids with a short alkyl chain form only a nematic mesophase. Starting with the 4-heptyloxybenzoic acid (7OBA), the mesomorphic components also have a smectic phase. A specific feature of systems with alkyloxybenzoic acids is the formation of the mesomorphic component in melts and solutions of dimers. The connection between the structure of the nOBA crystalline phases, mesophase types, and length of the mesogen alkyl chain are summarized in articles [24–26].

Materials and Methods

Thermal analysis is described in detail in [5]. The temperatures for phase transitions of individual components and mixtures were determined using standard techniques of differential thermal analysis (DTA) and polarization microscopy [5]. DTA data were confirmed by visual polythermal analysis (thermostating and heating of 0.8–1.2 g samples were performed in a TR-150 thermoreactor, Russia). The accuracy of temperature measurements for phase transitions was within 0.3 °C. The solubility polytherms were obtained by solubility studies (thermostating of saturated solutions – in a TW-2.02 thermostat (Latvia), at low temperatures (down to –30 °C) – in a TLM type microfridge).

We selected the following substances as components for studying the phase diagrams: 4-pentyloxybenzoic acid (5OBA) that forms a nematic phase, and long-chain *n*-alkanes (*n*-hexadecane, *n*-octadecane, *n*-icosane, and *n*-docosane). The 5OBA of the p.a. grade, was twice recrystallized from ethyl acetate. The presence of admixtures in 5OBA was determined by cryometry [5] and did not exceed 1 mol %. As non-mesogens, we have selected *n*-alkanes (C_nH_{2n+2}, n = 16, 18, 20, 22) which may be interesting as additives to lower viscosity [27]. The components' properties are shown in Table 1. The purity of alkanes was controlled by chromatography ("Crystal 2000M" gas chromatograph with a flame ionization detector and an HP-ultra-2 quartz capillary column (phase: polymethyl siloxane with 5% phenyl siloxane), with a length of 50 m and inner diameter of 0.2 mm). The analysis was performed in the following mode: detector temperature 250 °C, vaporizer temperature 270 °C. Retention times for *n*-alkanes were determined from chromatograms of small amounts (4–8%) of these substances dissolved in heptane. Alkane concentrations were calculated based on 3–5 chromatograms, relative to the internal standard (*n*-tridecane). The retention times (min:s) for alkanes and the internal standard were as follows: *n*-heptane – 4:16; *n*-tridecane – 15:39; *n*-hexadecane – 19:51; *n*-octadecane – 22:01; *n*-icosane – 25:00; *n*-docosane – 26:25. The amounts of admixtures in *n*-hexadecane, *n*-octadecane, *n*-icosane, and *n*-docosane did not exceed 2 mol %.

For studies of 5OBA solubility polytherms, we used organic solvents of different polarity: *n*-alkanes

Table 1. Phase transition temperatures of components

Component	Formula	Reagent grade	$T_{ph.tr.}$, °C	
			Exp.	Lit. [29]
5OBA	$C_5H_{11}O\text{-}C_6H_4\text{-}COOH$	pure analysis	K 124.3 N 152.1 I	K 124.4 N 151.4 I*
n-Hexadecane	$n\text{-}C_{16}H_{34}$	pure analysis	18.2	18.3
n-Octadecane	$n\text{-}C_{18}H_{38}$	pure analysis	28.2	28.2
n-Icosane	$n\text{-}C_{20}H_{42}$	pure analysis	36.4	36.8
n-Docosane	$n\text{-}C_{22}H_{46}$	pure analysis	44.0	44.0

* K 124.4 N 151.4 I – 5OBA crystals melt at 124.4 ºC forming a nematic (N) phase that at 151.4 ºC forms an isotropic phase.

(hexane, >99%, octane, 98%), cyclohexane, >99%, aromatic compounds (benzene, >99%, toluene, >99%, and *o*-xylene, >99%), chlorobenzene, >99%, esters (ethyl acetate, >99%, and *n*-butyl acetate, >99%), alcohols (propan-2-ol, >99%, propan-1-ol, >99%, and butan-1-ol, >99%), acetone, 99.8%, 1,4-dioxane, >99%, and acetonitrile, >99%. Extra purification of the solvents was performed using standard techniques [28].

Results and Discussion

The minimal set of non-variant equilibria in the systems studied with *n*-alkanes is represented by eutectics and metatectics. The coordinates for the non-variant points are shown in Table 2.

Let us look at the phase diagram of the system 5OBA (I) – *n*-hexadecane (II) (Fig. 1). The eutectic is close to degeneracy:

$$K_I + K_{II} \overset{t_e}{\rightleftarrows} I$$

At the temperature of 118.9 °C (t_m), the interaction between the crystals of LC (I) and the isotropic solution leads to the formation of a boundary nematic solution through a metatectic reaction (with 5OBA content equal to 80.3 mol. %):

$$K_I + I \overset{t_m}{\rightleftarrows} N$$

The T–x diagrams for systems of 5OBA (I) with *n*-octadecaneand *n*-docosane (II) look similar (Figs. 2–4).

The metatectic coordinate moves towards lower 5OBA content upon growth in the alkane length (n is the number of C atoms in the alkane) (Fig. 5). A linear dependence of the metatectic coordinate (x_I is a fraction of 5OBA, mol.%) on the number of C atoms in the alkane was established: $x_I = -0.3131 \times n + 85.467$.

Table 2. Metatectic and eutectic coordinates for 5OBA (I) – alkane (II) systems

System of LC (I) – alkane (II)	Temperature, °C / alkane, mol. %	
	Metatectic	Eutectic
5OBA – *n*-hexadecane	118.9 / 19.7	13.1 / >99.5
5OBA – *n*-octadecane	118.0 / 19.9	25.3 / >99.5
5OBA – *n*-icosane	117.8 / 20.8	33.9 / >99.5
5OBA – *n*-docosane	118.7 / 21.5	40.2 / >99.5

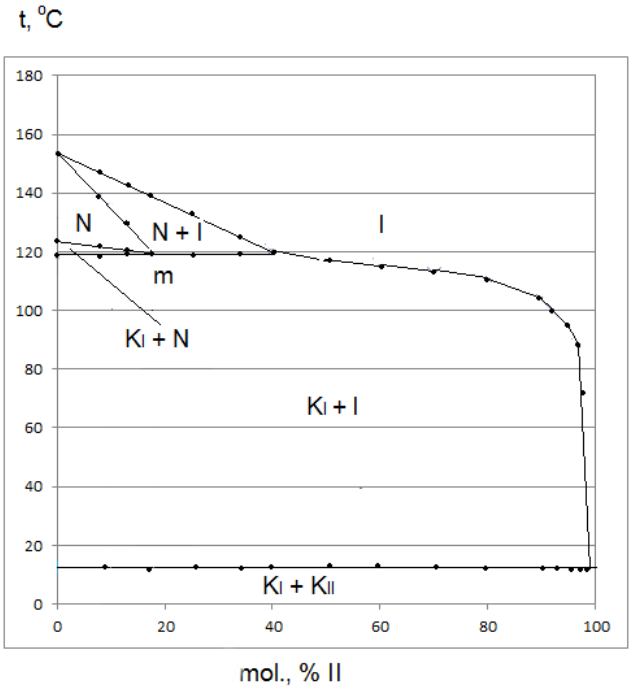

Fig. 1. 5OBA (I) – *n*-hexadecane (II)

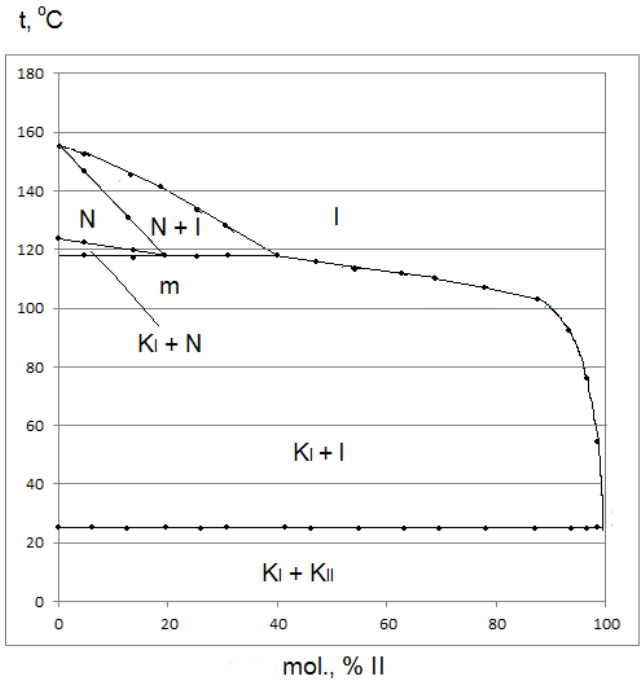

Fig. 2. 5OBA (I) – *n*-octadecane (II)

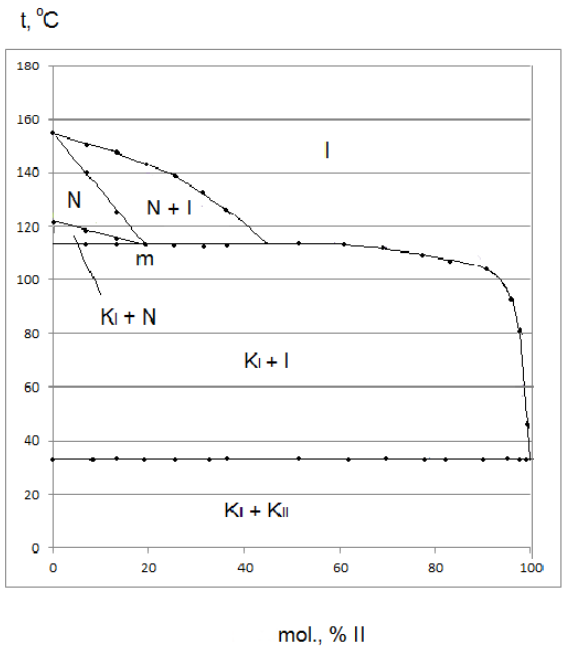

Fig. 3. 5OBA (I) – *n*-icosane (II)

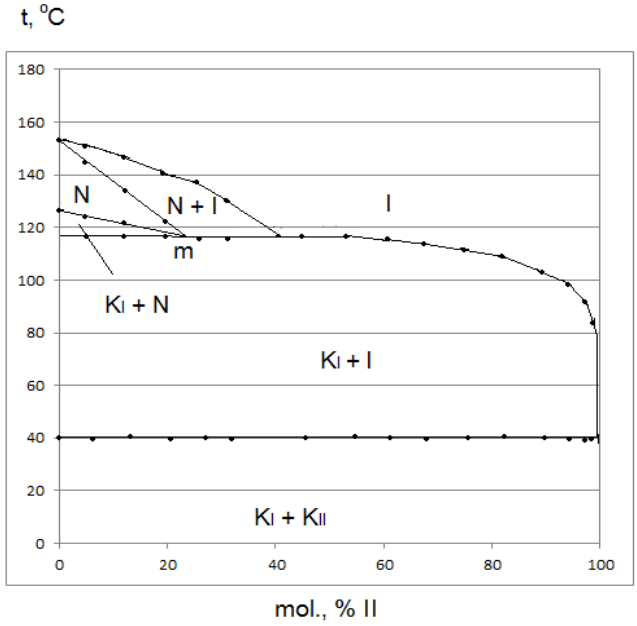

Fig. 4. 5OBA (I) – *n*-docosane (II)

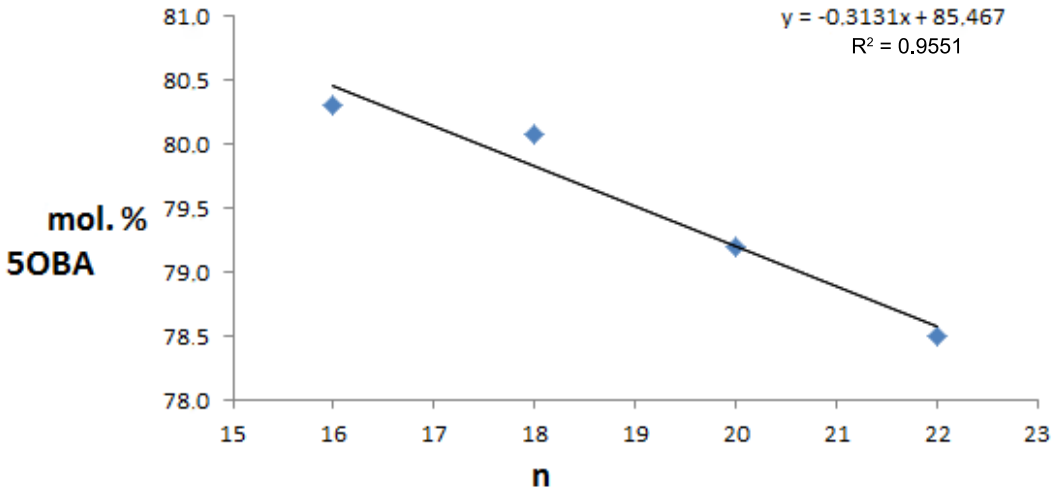

Fig. 5. Dependence of the metatectic coordinate for 5OBA – C_nH_{2n+2} systems on the number of atoms C in the alkane.

For the metatectic point, we calculated an excess Gibbs energy for 5OBA: $G^E_1 = RT_m\ln(\gamma_1)$, where R is the universal gas constant; T_m is the metatectic temperature; γ_1 is the activity coefficient of LC. This value decreases from +0.48 to 0.43 kJ/mol upon increasing the non-mesogen's chain length. Therefore, systems of 5OBA with *n*-alkanes exhibit positive deviation from the ideality, allowing us to use the model of regular solution with solubility parameters to describe such systems [5].

We have studied the solubility polytherms of 5OBA with various types of solvents. Fig. 6 shows solubility data for 5OBA in *n*-hexane, *n*-octane, cyclohexane, benzene, toluene, propan-1-ol, and ethyl acetate. It is evident that 4-pentyloxybenzoic acid dissolves the best in ethyl acetate and alcohol, and the worst in *n*-alkanes; aromatic compounds are somewhat in the middle range. The data on LC solubility (x_1 is a molar fraction) can be described well by a linear function of inverse temperature:

$$-\ln(x_1) = a - b / T$$

Coefficients a and b of the linear function are shown in Table 3.

To correlate the solubility of 5OBA at 298 K in different solvents, models based on Hildebrand and Hansen solubility parameters have been suggested that

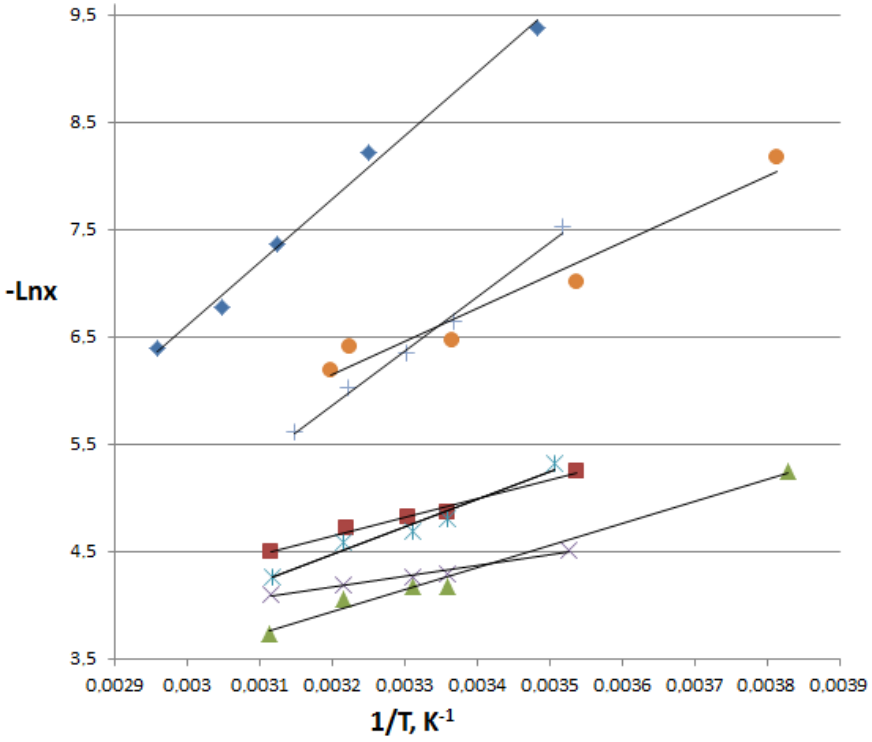

Fig. 6. Solubility polytherms of 5OBA: ◆ – *n*-hexane, ● – *n*-octane, + – cyclohexane, ■ – benzene, ✳ – toluene, × – propan-1-ol, ▲ – ethyl acetate.

Table 3. Parameters for 5OBA polytherm solubilities

№	Solvent	*b*	*a*	R^2
1	Hexane	5861.5	–10.963	0.9933
2	Octane	3067.9	–3.662	0.9512
3	Cyclohexane	5043.2	–10.268	0.9943
4	Benzene	1730.3	–0.894	0.9837
5	Toluene	2577.8	–3.781	0.9634
6	Ethyl acetate	2065.0	–2.673	0.9880
7	Propan-1-ol	993.4	0.990	0.9784

are widely used for systems with positive deviation from the ideality (see, for example, [30–32]):

$$\delta = \sqrt{\frac{\Delta H_{v,298} - RT}{V}}$$ – Hildebrand solubility parameter,

where $\Delta H_{v,298}$ is an evaporation enthalpy, V is a molar volume of the component.

$\delta_i = [\delta_{id}^2 + \delta_{ip}^2 + \delta_{ih}^2]^{0.5}$ – Hansen solubility parameter, where δ_{id} is a dispersion component, δ_{ip} is a polar component; δ_{ih} is a component that takes into account the possibility of hydrogen bond formation.

Hildebrand and Hansen solubility parameters for solvents were taken from the reference book [31], and calculations for 5OBA were performed using the scheme of Stefanis group components [32]: $\delta_d = 18.46$, $\delta_p = 6.91$, and $\delta_h = 5.93$ $MPa^{1/2}$.

Fig. 7 shows the dependency of 5OBA solubility ($\ln X_1$) at 298 K on the solvent solubility parameter (δ_2, $MPa^{1/2}$). It is evident that the expected peak value (maximal solubility) is the same as the calculated Hildebrand solubility parameter for 5OBA (22.3 $MPa^{1/2}$). When the difference in solubility parameters for the components is lower, 5OBA solubility is higher.

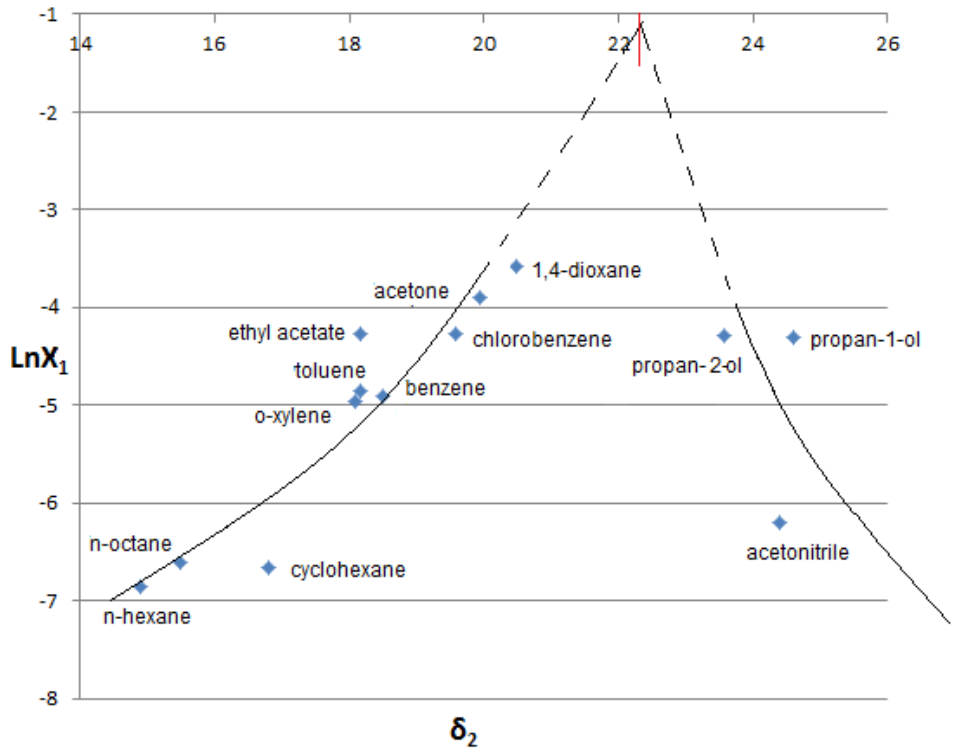

Fig. 7. Solubility plot of 5OBA (ln) vs. δ_2 at 298 K.

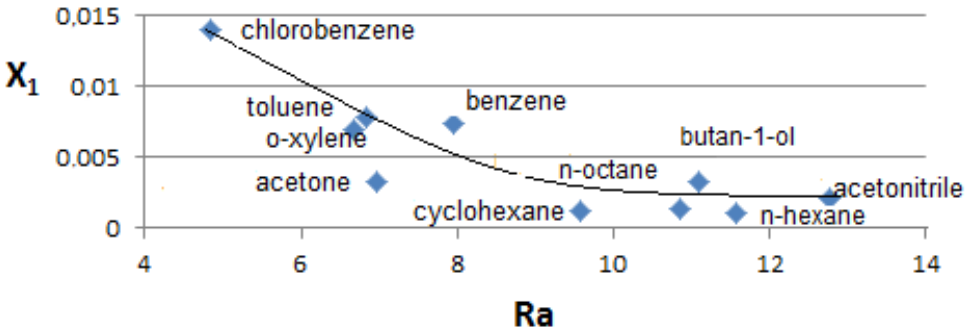

Fig. 8. Solubility plot 5OBA (X_1) vs. R_a at 298 K.

Figure 8 shows the dependency of 5OBA solubility (molar fraction X_1) at 298 K on an equivalent radius (R_a). The formula for calculation of the equivalent radius is as follows [31, 32]:

$$R_a^2 = 4.(\delta_{d(1)} - \delta_{d(2)})^2 + (\delta_{p(1)} - \delta_{p(2)})^2 + (\delta_{h(1)} - \delta_{h(2)})^2,$$

where $\delta_{d(1)}$ and $\delta_{d(2)}$ are parameters of dispersion interaction; $\delta_{p(1)}$ and $\delta_{p(2)}$ are parameters of polar interaction between the LC and the solvent; $\delta_{h(1)}$ and $\delta_{h(2)}$ are parameters of components which take into account hydrogen bond formation upon interaction between the LC and the solvent.

When choosing a solvent for purification of individual LCs, it is necessary to have data on solubility and mutual miscibility of the components [5]. The graph showing the dependency of LC solubility on equivalent radius (Fig. 8) demonstrates that, when the difference in solubility parameters increases, solubility decreases; and when the R_a decreases, LC solubility increases, respectively. This is line with the basic assumptions of the Hansen theory [31] and it allows us to estimate the LC solubility in various types of solvents *a priori*.

Conclusions

1) T–x diagrams for the systems of 4-pentyloxybenzoic acid with *n*-alkanes (C_{16}, C_{18}, C_{20}, C_{22}) contain at least two non-variant points: metatectic and eutectic. In the systems studied, the eutectic is close to degeneracy. The metatectic

coordinate depends on the number of carbon atoms in the alkane, in a linear manner.

2) We have demonstrated the possibility of estimating the solubility of the mesomorphic 4-pentyloxybenzoic acid in various types of solvents, using Hildebrand and Hansen solubility parameters. Calculations based on the solubility parameters allow us to select solvents for mesogen purification by mass recrystallization. The best solubility at 298 K for 4-pentyloxybenzoic acid appears in chlorobenzene.

The authors declare no conflicts of interest.

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