Viscosity of the Homologous Series of 4-(*trans*-4-*n*-Alkylcyclohexyl)isothiocyanatobenzenes

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This paper presents the results of the viscosity measurements performed for the isotropic phase of the homologous series of mesogenic 4-(*trans*-4-*n*-alkylcyclohexyl)isothiocyanatobenzenes (C_nH_{2n+1}−CyHx−Ph−N=C=S, *n*CHBT) for $n = 0$ to $n = 12$.

Introduction

The momentum transport refers only to the fluids, and therefore, the phenomenon distinguishes from other transport phenomena like the diffusion or heat transfer, for instance. From the macroscopic point of view, the momentum transfer can be quantitatively described by the shear viscosity, which is defined as a proportionality coefficient between the shear stress and the shear rate (velocity gradient).

A practical importance of studies of the liquid viscosity is self-evident. Recently, a great demand for the experimental data is due to the impetuous development of the computer simulation methods used for the elucidation and better understanding of the transport phenomena at the molecular level.[1−3] The demand often concerns the viscosity data for series of compounds of the same structure and polarity but of different length of the molecules. We believe that the results presented in this paper will be useful in this field, but one should realize that at present the computer simulations are too crude for quantitative treatment of compounds as complex as 4-(*trans*-4-*n*-alkylcyclohexyl)isothiocyanatobenzenes.

Experimental Section

The compounds studied, 4-(*trans*-4-*n*-alkylcyclohexyl)-isothiocyanatobenzenes, $n = 0$ to 12, were synthesized and purified at the Institute of Chemistry, Military University of Technology, Warsaw. They are chemically stable mesogens, first synthesized in 1985.[4] The purity of the compounds, minimum 99.5%, was controlled by the chromatography. The melting points and the nematic to isotropic phase transition temperatures are given in Table 1. The viscosity measurements were performed in the isotropic phase of the compounds.

The viscosity was determined with a Haake viscometer Rotovisco RV 20 with the measuring system CV 100, the share rate being 275 s^{-1}. The measuring system consists of the rotary beaker filled with the liquid and the cylindrical sensor of Mooney-Ewart type (ME 15) placed in the center of the beaker. The liquid gap was 0.5 mm. The uncertainty of the viscosity determination was 0.5%. The temperature was stabilized within ±0.1 K.

Table 1. Melting Point (T_m) and Nematic to Isotropic Phase Transition Temperature ($T_{n,i}$) for the Homologous Series of 4-(*trans*-4-*n*-Alkylcyclohexyl)isothiocyanatobenzenes[a]

n	T_m/K	$T_{n,i}$/K	*n*	T_m/K	$T_{n,i}$/K
0	303.2		7	310.0	325.8
1	318.0		8	301.2	320.7
2	296.1	(269.2)[b]	9	311.7	326.3
3	311.7	314.6	10	315.2	323.7
4	307.6	(306.7)	11	321.1	328.0
5	340.6	(324.8)	12	323.2	325.9
6	285.7	316.0			

[a] *n* denotes the number of carbon atoms in the alkyl chain. [b] The parentheses denote the monotropic phase transition.

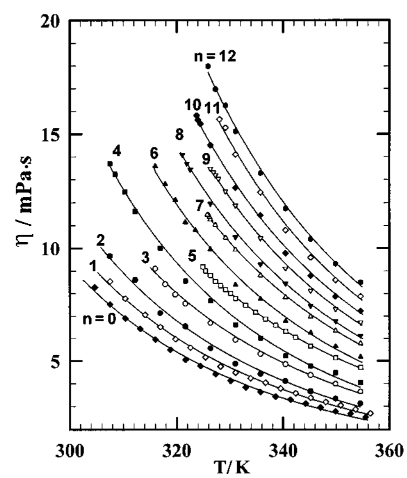

Figure 1. Temperature dependence of the shear viscosity 4-(*trans*-4-*n*-alkylcyclohexyl)isothiocyanatobenzenes ($n = 0$ to 12) in the isotropic phase. *n* denotes the number of the carbon atoms in the alkyl chain. The solid lines represent the best fitting of eq 1 to the experimental values.

Results and Discussion

The results of the viscosity measurements for the homologous series 4-(*trans*-4-*n*-alkylcyclohexyl)isothiocyanatobenzenes are presented in Figure 1 and Table 2.

A theoretical or even empirical description of the temperature dependence of viscosity is not an easy task, and several models and empirical formulas have been proposed.

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Table 2. Experimental Values of the Shear Viscosity η of the Homologous Series of 4-(*trans*-4-*n*-Alkylcyclohexyl)isothiocyanatobenzenes for the Temperatures above $T_{n,i}$[a]

T/K	η/mPa·s	T/K	η/mPa·s	T/K	η/mPa·s
		$n = 0$			
304.7	8.29	324.5	4.78	344.2	3.13
307.5	7.53	327.3	4.43	347.0	2.95
310.4	6.90	330.1	4.13	349.9	2.79
313.2	6.43	332.9	3.84	352.7	2.68
316.0	5.96	335.8	3.64	355.5	2.54
318.8	5.51	338.8	3.43		
321.6	5.06	341.4	3.30		
		$n = 1$			
307.5	8.54	325.4	5.17	342.3	3.59
310.4	7.78	328.2	4.76	345.2	3.38
314.2	7.06	331.1	4.48	348.0	3.20
316.9	6.51	333.9	4.24	350.8	3.05
319.8	5.97	336.7	4.04	353.6	2.87
322.6	5.59	339.5	3.79	356.5	2.70
		$n = 2$			
302.8	11.51	321.6	6.55	340.5	4.12
307.5	9.67	326.4	5.56	345.2	3.67
312.2	8.62	331.1	4.89	349.9	3.35
316.9	7.13	335.8	4.44	354.6	3.13
		$n = 3$			
316.0	9.11	326.4	6.69	345.2	4.38
317.9	8.42	331.1	5.95	349.9	3.99
319.8	7.96	335.8	5.32	354.6	3.65
321.6	7.56	340.5	4.86		
		$n = 4$			
307.5	13.71	321.6	8.56	345.2	4.77
308.5	13.24	326.4	7.68	349.9	4.48
310.4	12.47	331.1	6.61	354.6	4.05
312.2	11.62	335.8	6.02		
316.9	10.01	340.5	5.24		
		$n = 5$			
324.9	9.18	330.1	8.01	340.5	6.32
325.4	9.01	331.1	7.78	342.3	6.05
326.4	8.81	332.9	7.48	345.2	5.66
327.3	8.54	334.8	7.17	349.9	5.14
328.2	8.36	336.7	6.87	354.6	4.71
329.2	8.18	338.6	6.59		
		$n = 6$			
316.0	13.60	323.5	10.80	340.5	6.77
317.9	12.82	326.4	9.96	345.2	6.26
319.8	12.12	331.1	8.38	349.9	5.65
321.6	11.15	335.8	7.76	354.6	5.18
		$n = 7$			
325.8	11.48	327.3	11.03	340.5	7.83
326.0	11.46	329.2	10.47	345.2	6.98
326.2	11.39	331.1	9.94	349.9	6.34
326.4	11.27	335.8	8.80	354.6	5.78
		$n = 8$			
321.1	14.10	331.1	10.50	349.9	6.78
321.9	13.71	335.8	9.30	354.6	6.12
322.6	13.45	340.5	8.45		
326.4	11.96	345.2	7.45		
		$n = 9$			
326.4	13.49	329.2	12.50	345.2	8.12
326.9	13.33	331.1	11.88	349.9	7.31
327.3	13.21	335.8	10.45	354.6	6.72
327.9	13.04	340.5	9.12		
		$n = 10$			
323.7	15.82	331.1	12.66	349.9	7.87
324.0	15.63	335.8	11.45	354.6	7.22
324.5	15.45	340.5	9.79		
326.4	14.52	345.2	8.79		
		$n = 11$			
328.0	15.66	335.8	12.45	349.9	8.60
329.2	15.28	340.5	10.80	354.6	7.87
331.1	14.10	345.2	9.60		
		$n = 12$			
325.9	17.99	331.1	15.13	345.2	10.41
327.3	16.99	335.8	13.29	349.9	9.32
329.2	16.27	340.5	11.75	354.6	8.50

[a] n denotes the number of carbon atoms in the alkyl chain.

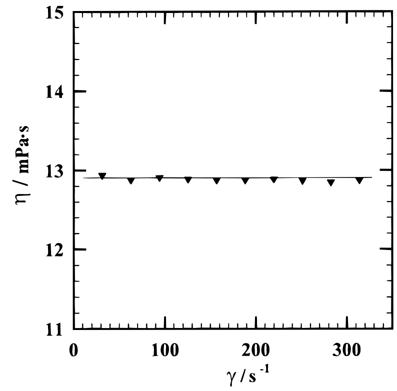

Figure 2. Newtonian behavior of the 4-(*trans*-4-*n*-hexylcyclohexyl)isothiocyanatobenzene in the isotropic phase at 318 K. γ denotes the shear rate (velocity gradient).

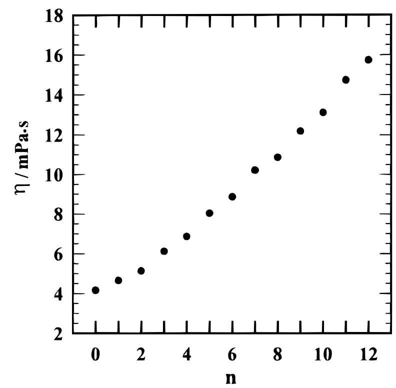

Figure 3. n dependence of the viscosity of the 4-(*trans*-4-*n*-alkylcyclohexyl)isothiocyanatobenzenes at constant temperature $T = 330$ K.

Table 3. Values of the Parameters A, D, and T_0 Resulting from the Best Fitting of Eq 1 to the Experimental Data and the Standard Deviations σ (Eq 2)

n	A	D	T_0	σ/mPa·s
0	−8.8235	2.7109	182.19	0.036
1	−9.1147	3.5560	169.23	0.040
2	−8.6362	2.4702	190.26	0.128
3	−8.3478	2.1726	197.78	0.061
4	−8.2954	2.1359	200.64	0.083
5	−9.6702	7.2704	132.00	0.030
6	−7.5744	1.3481	224.00	0.137
7	−8.4205	2.8323	189.87	0.027
8	−8.4577	3.0876	184.92	0.060
9	−8.0553	2.1958	206.00	0.075
10	−8.7607	3.9339	174.72	0.121
11	−7.1286	1.0707	241.26	0.116
12	−7.5126	1.6581	220.97	0.096

Unfortunately, one of the simplest and physically comprehensible, the Arrhenius formula, fits the experimental η(T) dependence for not too many liquids.

The solid lines in Figure 1 represent the best fitting of the Vogel−Tamman−Fulcher (VTF) equation[5]

$$\ln \eta(T) = A + \frac{DT_0}{T - T_0} \qquad (1)$$

to our viscosity data. A, D, and T_0 are fit parameters. Equation 1 was successfully used for the reproduction of the $\eta(T)$ dependence for some glass-forming liquids.[5] The physical meaning of the parameters A, D, and T_0 is discussed in ref 6. As can be seen in Figure 1, eq 1 quite well reproduces the $\eta(T)$ dependence also for the mesogenic compounds studied. The values of A, D, and T_0 parameters,

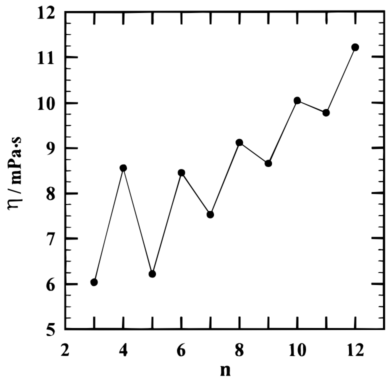

Figure 4. *n* dependence of the viscosity of the 4-(*trans*-4-*n*-alkylcyclohexyl)isothiocyanatobenzenes at constant reduced temperature $T^* = 1.05$.

resulting from the fitting, are presented in Table 3. The table also contains the values of the standard deviation calculated with the following equation:

$$\sigma = \left(\frac{\sum_i (\eta_{exp} - \eta_{calc})^2}{n_d - n_p} \right)^{1/2} \qquad (2)$$

where n_d and n_p denote the number of the experimental points and the number of the parameters, respectively.

It is worth noticing that the fitting of the Arrhenius equation to the presented experimental data gives a standard deviation about three times higher than that in Table 3.

Within the available range of the shear rate, the compounds show Newtonian behavior, which is demonstrated in Figure 2 for 4-(*trans*-4-*n*-hexylcyclohexyl)isothiocyanatobenzene, as an example.

The analysis of the temperature dependence of the viscosity within the homologous series of 4-(*trans*-4-*n*-alkylcyclohexyl)isothiocyanatobenzenes leads to the following conclusions: (i) At constant temperature the viscosity monotonically increases with the length of the molecules (Figure 3) and (ii) at constant reduced temperature $T^* = T/T_{n,i}$, where $T_{n,i}$ denotes the nematic to isotropic phase transition temperature (see Table 1), the viscosity shows the odd−even effect, well-known for other physical properties of mesogenic liquids.

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