

Viscosity of the Series of 1,*n*-Alkanediols

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The paper presents the shear viscosity data for the series of 1,*n*-alkanediols, HO(CH₂)_{*n*}OH, for *n* = 2–10.

Introduction

In recent papers^{1,2} we presented the results of the shear viscosity measurements performed for two homologous series of mesogenic compounds: 4-(*trans*-4'-*n*-alkylcyclohexyl)isothiocyanobenzenes (C_{*n*}H_{2*n*+1}CyHxPhN=C=S, *n* = 0–12) and *n*-alkyl-cyanobiphenyls (C_{*n*}H_{2*n*+1}PhPhC≡N, *n* = 2–12) in the isotropic phase. Within both series of rodlike molecules, at constant temperature, the viscosity increases, in a good approximation linearly, with the *n* number of CH₂ groups in the hydrocarbon tail of the molecules. The difference in molecular polarity of the both studied homologous series (3.5 D and 5 D), which leads, for example, to essentially different dielectric behavior,³ in the case of the viscosity has only a marginal importance.

This paper presents the shear viscosity data for 1,*n*-alkanediols, HO(CH₂)_{*n*}OH, compounds important both from technical and basic research points of view. The studied diols are strongly self-associated via the hydrogen bonds O—H···O formed by O—H groups situated at the ends of the hydrocarbon chains. The increase of the OH—OH distance in the diol molecule stands for a decrease of the number of O—H···O hydrogen bonds per unit volume.

Experimental Section

The 1,*n*-alkanediols were used as obtained; the purities of the compounds are given in Table 1.

The shear viscosity was measured with a Haake viscometer Rotovisco RV20 with the measuring system CV 100. In the available range of the shear rates (30 s⁻¹ to 300 s⁻¹) the studied compounds show Newtonian behavior (Figure 1). The accuracy of the viscosity determination was about ±1%.

Results and Discussion

The results of the viscosity measurements for 1,*n*-alkanediols are presented in Figure 2 and Table 2. The solid lines in the figure correspond to the best fitting of the Vogel–Tamman–Fulcher (VTF) equation:^{4,5}

$$\eta(T) = \eta_{\infty} \exp\left(\frac{DT_0}{T - T_0}\right) \quad (1)$$

to the experimental data. The values of the fit parameters η_{∞} , D , and T_0 are given in Table 3. The table contains also the standard deviation calculated with the equation

$$\sigma = \sqrt{\frac{\sum_i (\eta_{\text{exp}} - \eta_{\text{calc}})^2}{n_d - n_p}} \quad (2)$$

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Table 1. Purities of 1,*n*-Alkanediols Studied

<i>n</i>	name	source	purity
2	1,2-ethanediol	Merck	>99%
3	1,3-propanediol	Fluka	>97%
4	1,4-butanediol	Fluka	99%
5	1,5-pentanediol	Merck	>98%
6	1,6-hexanediol	Aldrich	99%
7	1,7-heptanediol	Aldrich	95%
8	1,8-octanediol	Fluka	>98%
9	1,9-nonanediol	Aldrich	98%
10	1,10-decanediol	Fluka	95%

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

Although the fitting parameters D , T_0 , and η_{∞} in eq 1 have no clear physical meaning, their dependence on the (*n*) number of CH₂ groups in 1,*n*-alkanediol molecules

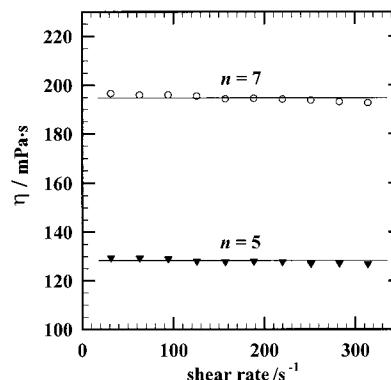


Figure 1. Examples of Newtonian behavior of 1,*n*-alkanediols (*n* = 5 and 7) at 293 K.

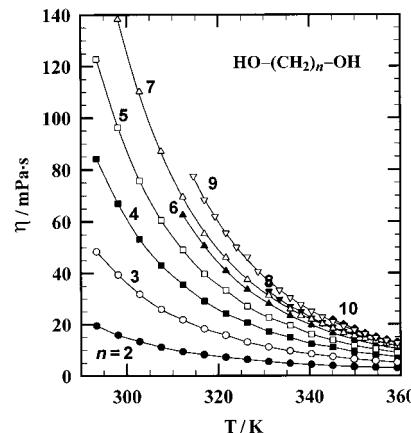


Figure 2. Temperature dependence of the shear viscosity of 1,*n*-alkanediols. The solid lines represent the best fitting of eq 1 to the experimental values of the viscosity.

Table 2. Experimental Values of the Shear Viscosity η of the Series 1,*n*-Alkanediols

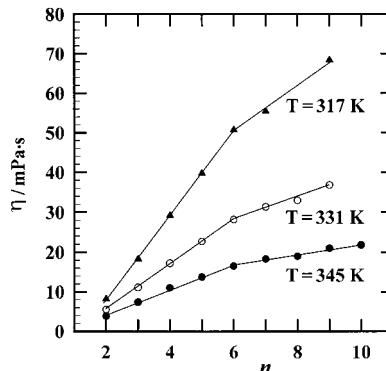
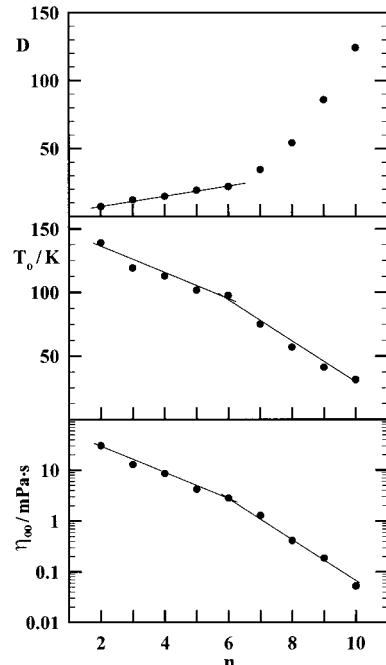
T/K	$\eta/\text{mPa}\cdot\text{s}$	T/K	$\eta/\text{mPa}\cdot\text{s}$	T/K	$\eta/\text{mPa}\cdot\text{s}$
<i>n</i> = 2					
293.4	19.52	316.9	8.21	340.5	4.32
298.1	15.82	321.6	7.17	345.2	3.86
302.8	13.34	326.3	6.30	349.9	3.46
307.5	11.10	331.0	5.50	354.6	3.20
312.2	9.365	335.8	4.77	359.3	2.96
<i>n</i> = 3					
293.4	48.45	316.9	18.24	340.5	8.38
298.1	39.41	321.6	15.78	345.2	7.38
302.8	31.80	326.3	13.06	349.9	6.42
307.5	25.84	331.0	11.15	354.6	5.76
312.2	21.81	335.8	9.59	359.3	5.15
<i>n</i> = 4					
293.4	84.26	316.9	29.14	340.5	12.36
298.1	67.03	321.6	24.19	345.2	11.03
302.8	53.21	326.3	20.70	349.9	9.21
307.5	43.14	331.0	17.23	354.6	8.22
312.2	35.61	335.8	14.86	359.3	7.26
<i>n</i> = 5					
293.4	122.80	316.9	39.73	340.5	16.09
298.1	96.32	321.6	33.31	345.2	13.75
302.8	75.79	326.3	27.04	349.9	11.68
307.5	60.53	331.0	22.66	354.6	10.20
312.2	49.11	335.8	19.56	359.3	8.89
<i>n</i> = 6					
312.2	62.62	331.0	28.14	349.9	14.05
316.9	50.66	335.8	23.35	354.6	11.98
321.6	41.04	340.5	19.70	359.3	10.41
326.3	33.63	345.2	16.51		
<i>n</i> = 7					
293.4	177.10	326.3	37.52	347.5	16.59
298.1	138.20	331.0	31.31	349.9	15.46
302.8	108.95	335.8	25.92	352.2	14.44
307.5	87.05	338.1	23.34	354.6	13.38
312.2	69.46	340.5	21.92	356.9	12.37
316.9	55.34	342.8	20.10	359.3	11.47
321.6	46.10	345.2	18.29		
<i>n</i> = 8					
331.0	32.91	342.8	20.59	354.6	13.46
333.4	29.86	345.2	18.77	356.9	12.41
335.8	27.07	347.5	17.20	359.3	11.54
338.1	25.02	349.9	15.92		
340.5	22.48	352.2	14.55		
<i>n</i> = 9					
314.6	77.43	331.0	36.76	347.5	19.29
316.9	68.36	333.4	33.41	349.9	17.71
319.3	62.03	335.8	30.39	352.2	16.29
321.6	55.67	338.1	27.67	354.6	14.73
324.0	50.19	340.5	25.17	356.9	13.64
326.3	46.36	342.8	22.88	359.3	12.67
328.7	40.59	345.2	20.99		
<i>n</i> = 10					
345.2	21.82	352.2	16.41	359.3	12.88
347.5	19.95	354.6	15.05		
349.9	18.22	356.9	13.92		

shows some peculiarities similar to those observed in the isothermal viscosity dependence on *n*. Figure 3 shows the *n* dependence of the viscosity of studied diols at three temperatures. In all cases the $\eta(n)$ dependence is, in a good approximation, linear (as in the case of the previously studied mesogenic compounds^{1,2}), but for *n* = 6 one observes a significant change in the slope of the lines. As seen in Figure 4, the effect manifests itself also in the *D*(*n*), *T*₀(*n*), and η_{∞} (*n*) dependences.

The presented results show that 1,6-hexanediol divides the series of HO(CH₂)_{*n*}OH diols into two parts (for *n* < 6

Table 3. Values of the Parameters η_{∞} , *D*, and *T*₀ Corresponding to the Best Fitting of Eq 1 to the Viscosity Experimental Data for 1,*n*-Alkanediols and the Standard Deviation *σ* (eq 2)

<i>n</i>	$\eta_{\infty}/\text{mPa}\cdot\text{s}$	<i>D</i>	<i>T</i> ₀ /K	<i>σ/mPa·s</i>
2	0.030 345	7.1779	138.940	0.12
3	0.012 824	12.0507	119.151	0.19
4	0.008 494	14.7435	112.766	0.20
5	0.004 201	19.3944	101.672	0.24
6	0.002 824	22.0371	97.507	0.12
7	0.001 286	34.5023	74.947	0.30
8	0.000 413	54.2447	57.011	0.12
9	0.000 189	85.8919	41.133	0.35
10	0.000 053	124.1500	31.500	0.14

**Figure 3.** *n* dependence of the viscosity of the 1,*n*-alkanediols at different temperatures.**Figure 4.** *n* dependence of the parameters *D*, *T*₀, and η_{∞} corresponding to the best fitting of eq 1 to the experimental values of the viscosity of 1,*n*-alkanediols.

and *n* > 6), of a quite different change of the shear viscosity due to the addition of a successive CH₂ group in the diol molecule.

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