Shear Viscosity of Mixtures of α-Tocopherol with Nonpolar Solvents†

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Shear viscosities (η) of the binary mixtures of α-tocopherol (vitamin E) with 4-*n*-propylcyclohexyl-4′-*n*-pentylphenyl and mesitilene, two nonpolar solvents composed of the molecules of essentially different shape, have been measured in the temperature range from (278 to 353) K. In the whole concentration range of α-tocopherol in both solvents, the dependence of η on T can be well described by the Vogel−Fulcher−Tammann equation. The viscosity deviations from the additive behavior are strongly negative, and their concentration dependence was fitted to the Redlich−Kister equation.

Introduction

Tocopherols and tocotrienols belong to the family of vitamin E compounds. Natural vitamin E comprises eight different forms (α-, β-, γ-, and δ-) of both tocols, which differ from each other by the number and location of the CH_3 groups. The tocotrienols have an unsaturated isoprenoid side chain.[1] Although all these tocopherols are present in biological materials, α-tocopherol and its acetate derivative are reputed to have the highest biological activity.[2,3] As an in vivo antioxidant,[4] they protect the cells against free radicals and prevent the peroxidation of body fats. Tocopherols are the active compounds used in cosmetic products for hair and skin care and as effective moisturizing agents. They are particularly suitable for use in sun-protection products.

Tocopherols are the subject of numerous physicochemical studies.[1] As they are rather highly viscous liquids, their ability to flow at different conditions, related to the temperature and the flow velocity, is one of the fundamental properties of tocopherols. The flow ability can be quantitatively represented by the shear viscosity, which is defined as a proportionality coefficient between the shear stress and the shear rate (velocity gradient). As in practice tocopherols are often used in solutions, we present the results of the temperature and concentration dependence of the shear viscosity measured for binary mixtures of α-tocopherol dissolved in two solvents composed of nonpolar molecules of different shape. To the best of our knowledge, the viscosity for α-tocopherol measured over a large temperature range has not been published.

Experimental Section

Materials. The compounds studied, D,L-α-tocopherol from SERVA (purity ≥ 97 %) and mesitilene from MERCK (purity ≥ 98 %), were used as supplied, and 4-*n*-propylcyclohexyl-4′-*n*-pentylphenyl (3CyPh5) was synthesized and purified (purity ≥ 99 %) at the Institute of Chemistry, Military Technical University, Warsaw, Poland. The chemical structures of the compounds are presented in Figure 1.

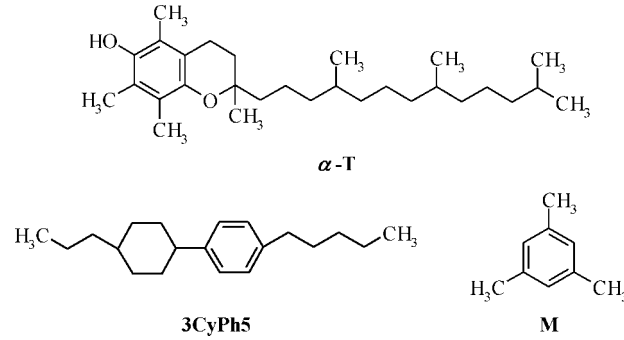

Figure 1. Chemical structure of α-tocopherol (α-T), 4-*n*-propylcyclohexyl-4'-*n*-pentylphenyl (3CyPh5), and mesitilene (M).

Apparatus and Procedure. The shear viscosity was measured with a Haake Modular Advanced Rheometer System (MARS) II with a double-cone sensor DC60/1Ti with a small cone angle $\alpha = 1.004°$. The cone diameter was 63.564 mm. The gap size between the cones, h, is 53 μm. The sensor allows one to measure the torque (resulting from the liquid viscous flow) up to $M_{max} = 0.2$ Nm, and for a viscosity of about 10 Pa·s, it corresponds to the limit of the shear rate $D_{max} \approx 100\ s^{-1}$ that can be applied. The viscosity values presented in the paper were measured at the shear rate (velocity gradient) of 10 s^{-1}. All the samples studied show the Newtonian behavior up to the shear rate of 100 s^{-1}. The sample volume necessary for the measurement amounts to 2.7 cm^3. The apparatus allows one to measure the shear viscosity from the range of about 50 Pa·s to about 1 mPa·s. The temperature was stabilized with the use of a Haake Universal Temperature Controller (UTC) with a Peltier system. The temperature uncertainty was ± 0.1 K, and the uncertainty of the viscosity determination was 0.3 %.

Results and Discussion

The results of the viscosity measurements performed for the mixtures of α-tocopherol (α-T) + 4-*n*-propylcyclohexyl-4′-*n*-

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Table 1. Viscosities η and Viscosity Deviations $\Delta\eta$ for the Binary Mixtures of x α-Tocopherol + (1 − x)4-*n*-Propylcyclohexyl-4′-*n*-pentylphenyl at Different Temperatures

	η	$\Delta\eta$		η	$\Delta\eta$		η	$\Delta\eta$
x	Pa·s	Pa·s	x	Pa·s	Pa·s	x	Pa·s	Pa·s
	T = 278.15 K			T = 284.15 K			T = 290.15 K	
0.0000	0.02774	0.000	0.0000	0.02148	0.000	0.0000	0.01695	0.000
0.2058	0.07595	−7.587	0.2058	0.05348	−3.100	0.2058	0.03825	−1.288
0.4023	0.38428	−14.57	0.4023	0.23160	−5.913	0.4023	0.14552	−2.431
0.6026	1.2706	−21.11	0.6026	0.79438	−8.399	0.6026	0.44194	−3.409
0.8018	7.4719	−22.30	0.8018	3.4882	−8.737	0.8018	1.6699	−3.449
1.0000	37.128	0.000	1.0000	15.242	0.000	1.0000	6.3800	0.000
	T = 296.15 K			T = 302.15 K			T = 308.15 K	
0.0000	0.01350	0.000	0.0000	0.01109	0.000	0.0000	0.00921	0.000
0.2058	0.02810	−0.6036	0.2058	0.02157	−0.3023	0.2058	0.01680	−0.1582
0.4023	0.09637	−1.126	0.4023	0.06592	−0.5566	0.4023	0.04614	−0.2872
0.6026	0.26641	−1.557	0.6026	0.16327	−0.7637	0.6026	0.10633	−0.3883
0.8018	0.91116	−1.511	0.8018	0.48533	−0.7444	0.8018	0.27853	−0.3766
1.0000	3.0175	0.000	1.0000	1.5310	0.000	1.0000	0.81481	0.000
	T = 314.15 K			T = 320.15 K			T = 325.15 K	
0.0000	0.00764	0.000	0.0000	0.00658	0.000	0.0000	0.00601	0.000
0.2058	0.01317	−0.08645	0.2058	0.01098	−0.05260	0.2058	0.00933	−0.03403
0.4023	0.03391	−0.1535	0.4023	0.02601	−0.09200	0.4023	0.02065	−0.05838
0.6026	0.07105	−0.2059	0.6026	0.05166	−0.1218	0.6026	0.03936	−0.07602
0.8018	0.17309	−0.1929	0.8018	0.12077	−0.1079	0.8018	0.08286	−0.06868
1.0000	0.45458	0.000	1.0000	0.28356	0.000	1.0000	0.18751	0.000
	T = 330.15 K			T = 335.15 K			T = 340.15 K	
0.0000	0.00519	0.000	0.0000	0.00457	0.000	0.0000	0.00413	0.000
0.2058	0.00798	−0.02273	0.2058	0.00685	−0.01585	0.2058	0.00604	−0.01109
0.4023	0.01686	−0.03822	0.4023	0.01403	−0.02597	0.4023	0.01175	−0.01780
0.6026	0.03020	−0.04972	0.6026	0.02408	−0.03357	0.6026	0.01947	−0.02274
0.8018	0.06104	−0.04358	0.8018	0.04615	−0.02904	0.8018	0.03524	−0.01956
1.0000	0.12920	0.000	1.0000	0.09265	0.000	1.0000	0.06732	0.000
	T = 345.15 K			T = 350.15 K				
0.0000	0.00368	0.000	0.0000	0.00329	0.000			
0.2058	0.00537	−0.007839	0.2058	0.00470	−0.005610			
0.4023	0.00997	−0.01234	0.4023	0.00855	−0.008463			
0.6026	0.01610	−0.01548	0.6026	0.01330	−0.01054			
0.8018	0.02732	−0.01348	0.8018	0.02224	−0.008399			
1.0000	0.04998	0.000	1.0000	0.03740	0.000			

pentylphenyl (3CyPh5) are summarized in Table 1 and Figure 2 and for α-tocopherol + mesitilene (M) in Table 2 and Figure 3. Like most highly viscous liquids, tocopherol belongs to glass-forming materials.[5,6] Numerous temperature-dependent physical quantities concerning that class of compounds can be quite well described with the empirical Vogel−Fulcher−Tammann (VFT) equation[7]

$$\eta(T) = A \exp \frac{B}{T - T_o} \tag{1}$$

where A, B, and T_o are adjustable parameters. As can be seen in Figures 2 and 3, the temperature dependence of the viscosity of pure α-tocopherol and its solutions in low-viscous solvents can also be reproduced with the VFT equation (solid lines in the figures). The values of the fitting parameters are gathered in Table 3 together with the values of the standard deviation σ calculated with the following formula

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

where n_d and n_p denote the number of the experimental points and the number of the parameters, respectively. As the glass transition temperature T_g of α-tocopherol equals about 220 K, the results presented in Table 3 show that the difference $T_g - T_0$ is very close to predictions of some models discussed in ref 7.

Tables 1 and 2 also contain the data on the viscosity deviations from the additive mole fraction behavior in the mixtures studied, calculated from the following

$$\Delta\eta(x) = \eta_{\mathrm{exp}} - [x\eta_1 + (1 - x)\eta_2] \tag{3}$$

where η_{exp} is the measured viscosity; x is the mole fraction of α-tocopherol in the mixture; and η_1 and η_2 are the viscosity of

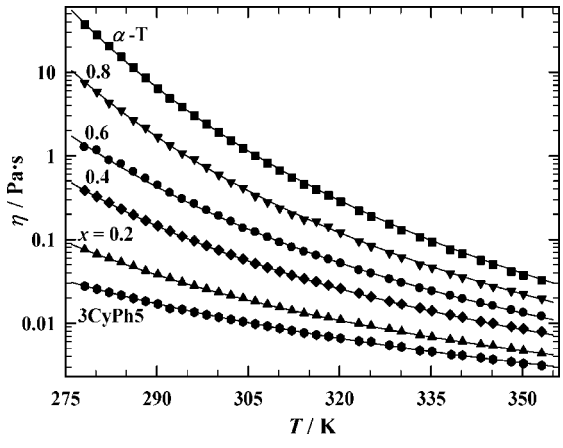

Figure 2. Temperature dependence of the shear viscosity of the mixtures of α-tocopherol (α-T) + 4-*n*-propylcyclohexyl-4'-*n*-pentylphenyl (3CyPh5). x denotes the mole fraction of α-T. The solid lines represent the best fit of Vogel−Fulcher−Tammann eq 1 to the experimental data.

Table 2. Viscosities η and Viscosity Deviations $\Delta\eta$ for the Binary Mixtures of x α-Tocopherol + (1 − x)Mesitilene at Different Temperatures

	η	$\Delta\eta$		η	$\Delta\eta$		η	$\Delta\eta$
x	Pa·s	Pa·s	x	Pa·s	Pa·s	x	Pa·s	Pa·s
	T = 278.15 K			T = 284.15 K			T = 290.15 K	
0.0000	0.00085	0.000	0.0000	0.00080	0.000	0.0000	0.00075	0.000
0.2025	0.00685	−7.512	0.2025	0.00555	−3.082	0.2025	0.00460	−1.288
0.4036	0.14808	−14.84	0.4036	0.09232	−6.060	0.4036	0.05698	−2.519
0.5972	1.2536	−20.92	0.5972	0.65851	−8.445	0.5972	0.35726	−3.453
0.7955	5.9447	−23.59	0.7955	3.0376	−9.088	0.7955	1.5332	−3.542
1.0000	37.128	0.000	1.0000	15.242	0.000	1.0000	6.3801	0.000
	T = 296.15 K			T = 302.15 K			T = 308.15 K	
0.0000	0.00063	0.000	0.0000	0.00057	0.000	0.0000	0.00053	0.000
0.2025	0.00388	−0.6077	0.2025	0.00324	−0.3073	0.2025	0.00294	−0.1625
0.4036	0.03800	−1.180	0.4036	0.02665	−0.5916	0.4036	0.01906	−0.3101
0.5972	0.21082	−1.592	0.5972	0.13099	−0.7836	0.5972	0.08396	−0.4029
0.7955	0.81967	−1.581	0.7955	0.47736	−0.7407	0.7955	0.27612	−0.3722
1.0000	3.0175	0.000	1.0000	1.5310	0.000	1.0000	0.81481	0.000
	T = 314.15 K			T = 320.15 K			T = 325.15 K	
0.0000	0.00049	0.000	0.0000	0.00046	0.000	0.0000	0.00044	0.000
0.2025	0.00239	−0.09005	0.2025	0.00214	−0.05565	0.2025	0.00196	−0.03636
0.4036	0.01443	−0.1693	0.4036	0.01142	−0.1033	0.4036	0.00928	−0.06666
0.5972	0.05552	−0.2162	0.5972	0.04057	−0.1290	0.5972	0.03055	−0.08161
0.7955	0.17398	−0.1877	0.7955	0.11600	−0.1097	0.7955	0.08201	−0.06724
1.0000	0.45458	0.000	1.0000	0.28356	0.000	1.0000	0.18751	0.000
	T = 330.15 K			T = 335.15 K			T = 340.15 K	
0.0000	0.00041	0.000	0.0000	0.00040	0.000	0.0000	0.00039	0.000
0.2025	0.00183	−0.02466	0.2025	0.00172	−0.01737	0.2025	0.00165	−0.01230
0.4036	0.00775	−0.04464	0.4036	0.00656	−0.03108	0.4036	0.00559	−0.02181
0.5972	0.02373	−0.05359	0.5972	0.01889	−0.03660	0.5972	0.01533	−0.02503
0.7955	0.06010	−0.04276	0.7955	0.04563	−0.02816	0.7955	0.03446	−0.01917
1.0000	0.12920	0.000	1.0000	0.09265	0.000	1.0000	0.06732	0.000
	T = 345.15 K			T = 350.15 K				
0.0000	0.00035	0.000	0.0000	0.00034	0.000			
0.2025	0.00152	−0.008882	0.2025	0.00137	−0.006476			
0.4036	0.00481	−0.01557	0.4036	0.00425	−0.01105			
0.5972	0.01233	−0.01766	0.5972	0.01050	−0.01197			
0.7955	0.02647	−0.01336	0.7955	0.02144	−0.008382			
1.0000	0.04998	0.000	1.0000	0.03740	0.000			

pure α-tocopherol and the other component, respectively. Figures 4 and 5 present the dependences of $\Delta\eta$ on the mole fraction of α-tocopherol in 3CyPh5 and mesitilene solutions, respectively, at several temperatures. The mole fraction dependences of $\Delta\eta$ at different temperatures were fitted to the Redlich−Kister polynomial equation[8]

$$\Delta\eta(x) = x(1-x)\sum_{i=0}^{k} A_i(2x-1)^i \qquad (4)$$

where A_i are adjustable parameters. The solid lines in Figures 4 and 5 represent the best fit of eq 4 to the experimental $\Delta\eta(x)$ data. The fitting parameters (A_i) as well as the corresponding standard deviations (σ) are gathered in Table 4, and Figure 6 presents the temperature dependences of the parameters obtained for the two solutions studied.

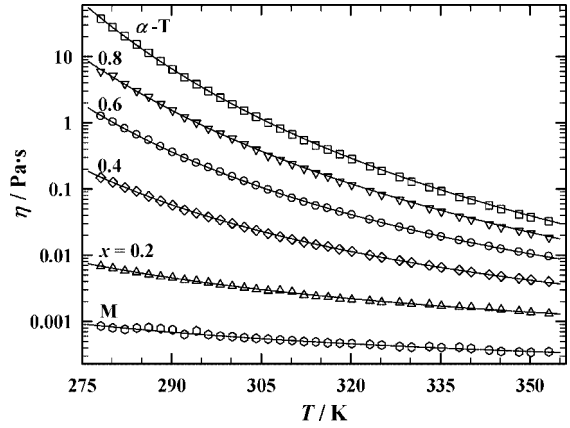

Figure 3. Temperature dependence of the shear viscosity of the mixtures of α-tocopherol (α-T) + mesitilene (M). x denotes the mole fraction of α-T. The solid lines represent the best fit of Vogel−Fulcher−Tammann eq 1 to the experimental data.

The presented data show that in the studied temperature range (278 to 353) K the shear viscosity of α-tocopherol varies in an exceptionally large extent (from mPa·s to Pa·s), and its temperature dependence can be perfectly reproduced with the Vogel−Fulcher−Tammann equation. The usefulness of the equation concerns also the viscosity temperature dependence measured for the mixtures of α-tocopherol and two nonpolar solvents of low viscosity. The viscosities of the mixtures studied exhibit a very strong negative deviation from the additive rule,

Table 3. Coefficients of the Vogel−Fulcher−Tammann Equation 1 and Standard Deviation for Viscosity of the Binary Mixtures of α-Tocopherol + Nonpolar Solvents

α-T + 3CyPh5						
	3CyPh9	x = 0.2058	x = 0.4023	x = 0.6026	x = 0.8018	α-T
A/Pa·s	$6.30\cdot10^{-5}$	$8.00\cdot10^{-5}$	$4.50\cdot10^{-5}$	$1.61\cdot10^{-5}$	$1.08\cdot10^{-5}$	$3.95\cdot10^{-6}$
B/K	822.3	721.1	889.1	1183.2	1264.9	1549.4
T_0/K	143.2	172.9	179.9	173.9	184.2	181.8
σ/Pa·s	$1.49\cdot10^{-4}$	$4.88\cdot10^{-4}$	$1.50\cdot10^{-3}$	$2.46\cdot10^{-2}$	$4.35\cdot10^{-2}$	0.208
α-T + M						
	M	x = 0.2025	x = 0.4036	x = 0.5972	x = 0.7955	α-T
A/Pa·s	$9.36\cdot10^{-5}$	$1.55\cdot10^{-4}$	$6.45\cdot10^{-5}$	$2.78\cdot10^{-5}$	$5.68\cdot10^{-6}$	$3.95\cdot10^{-6}$
B/K	237.0	372.3	650.2	952.7	1463.4	1549.4
T_0/K	171.2	179.9	194.3	189.5	173.1	181.8
σ/Pa·s	$2.81\cdot10^{-5}$	$5.78\cdot10^{-5}$	$7.68\cdot10^{-4}$	$7.29\cdot10^{-3}$	$8.97\cdot10^{-2}$	0.208

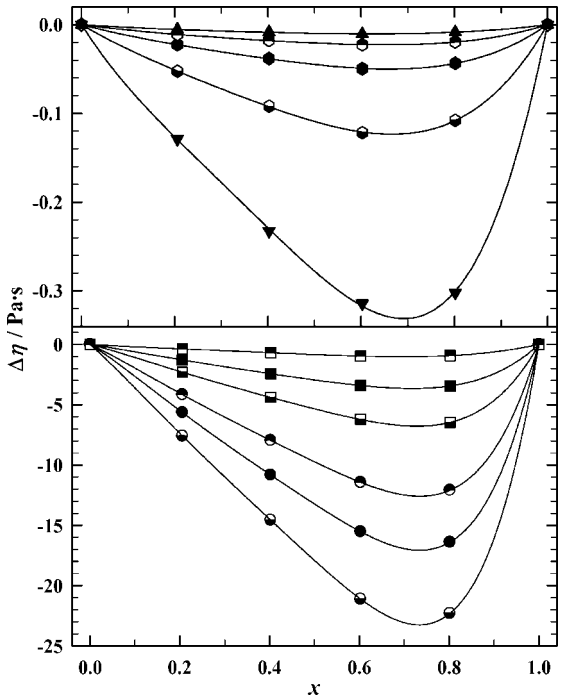

Figure 4. Viscosity deviation $\Delta\eta$ from the mole fraction additivity in the mixtures of α-tocopherol with 4-*n*-propylcyclohexyl-4'-*n*-pentylphenyl. *x* denotes the mole fraction of α-tocopherol, and the solid lines represent the best fit of Redlich−Kister eq 4 to the experimental data. ◓, 278.15 K; ●, 280.15 K; ◒, 282.15 K; ⬓, 286.15 K; ■, 290.15 K; ⬒, 300.15 K; ▼, 310.15 K; bottom filled hexagon, 320.15 K; ⬢, 330.15 K; top filled hexagon, 340.15 K; ▲, 350.15 K.

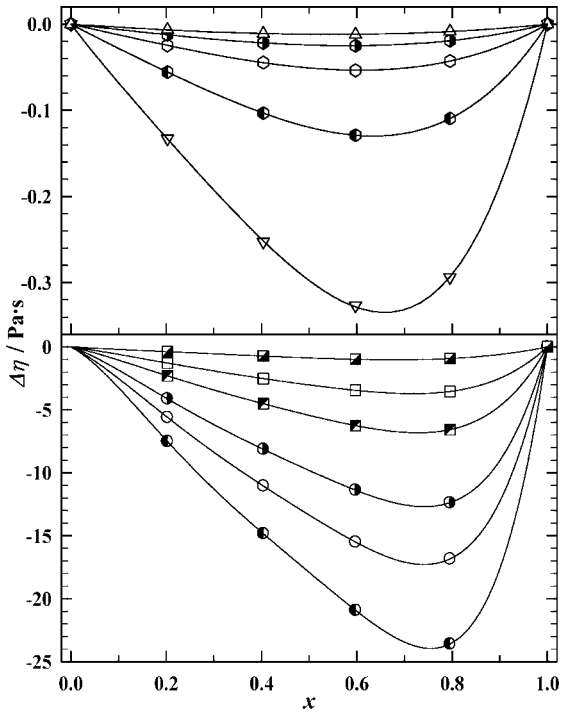

Figure 5. Viscosity deviation $\Delta\eta$ from the mole fraction additivity in the mixtures of α-tocopherol with mesitilene. *x* denotes the mole fraction of α-tocopherol, and the solid lines represent the best fit of Redlich−Kister eq 4 to the experimental data. ◑, 278.15 K; ○, 280.15 K; ◐, 282. 15 K; ◩, 286.15 K; □, 290.15 K; ◪, 300.15 K; ▽, 310.15 K; left filled hexagon, 320.15 K; ⬡, 330.15 K; right filled hexagon, 340.15 K; △, 350.15 K.

and the effect is observed for both nonpolar admixtures used, independently of the shape of the molecules.

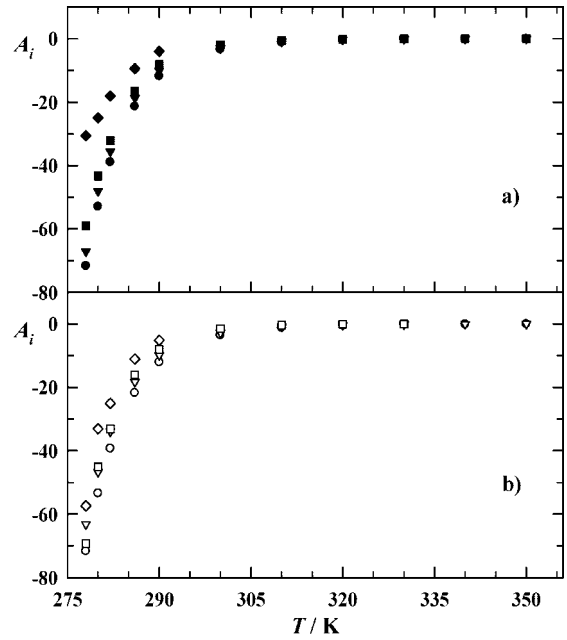

Figure 6. Temperature dependence of the coefficients A_i of the Redlich−Kister eq 4 for the mixtures of α-tocopherol with (a) 4-*n*-propylcyclohexyl-4'-*n*-pentylphenyl (●, A_0; ▼, A_1; ■, A_2; ◆, A_3) and (b) mesitilene (○, A_0; ▽, A_1; □, A_2; ◇, A_3).

Table 4. Coefficients of the Redlich−-Kister Equation 4 and Standard Deviation for Viscosity Deviations $\Delta\eta(x)$ for the Binary Mixtures of α-Tocopherol + Nonpolar Solvents, at Several Temperatures

α-T + 3CyPh5					
T/K	A_0	A_1	A_2	A_3	σ/Pa·s
278.15	−71.66	−67.04	−59.00	−30.56	$2.0\cdot10^{-7}$
280.15	−52.93	−48.05	−43.29	−24.97	$7.1\cdot10^{-6}$
282.15	−38.93	−35.56	−32.17	−18.08	$1.2\cdot10^{-7}$
286.15	−21.37	−18.70	−16.44	−9.430	$3.5\cdot10^{-7}$
290.15	−11.80	−10.06	−8.128	−3.973	$7.2\cdot10^{-6}$
300.15	−3.365	−2.937	−1.987	-	$8.1\cdot10^{-3}$
310.15	−1.112	−0.9125	−0.6281	-	$2.4\cdot10^{-3}$
320.15	−0.4371	−0.2994	−0.1721	-	$5.9\cdot10^{-4}$
330.15	−0.1795	−0.1136	−0.07462	-	$1.9\cdot10^{-3}$
340.15	−0.08270	−0.04676	−0.03541	-	$2.2\cdot10^{-4}$
350.15	−0.03885	−0.01650	−0.01349	-	$2.3\cdot10^{-4}$

α-T + M					
T/K	A_0	A_1	A_2	A_3	σ/Pa·s
278.15	−71.65	−63.15	−69.28	−57.38	$3.2\cdot10^{-5}$
280.15	−53.44	−46.64	−45.05	−33.07	$2.0\cdot10^{-6}$
282.15	−39.28	−33.91	−33.16	−25.05	$7.9\cdot10^{-3}$
286.15	−21.77	−18.25	−16.01	−11.07	$3.6\cdot10^{-6}$
290.15	−12.10	−9.846	−7.973	−5.179	$2.6\cdot10^{-6}$
300.15	−3.524	−2.813	−1.492	-	$7.2\cdot10^{-3}$
310.15	−1.191	−0.8257	−0.3539	-	$1.2\cdot10^{-3}$
320.15	−0.4792	−0.2779	−0.08731	-	$7.4\cdot10^{-5}$
330.15	−0.2035	−0.09339	−0.01336	-	$1.2\cdot10^{-4}$
340.15	−0.09721	−0.03516	-	-	$2.4\cdot10^{-5}$
350.15	−0.04702	−0.009890	-	-	$1.9\cdot10^{-4}$

Acknowledgment

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