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Thermodynamic functions of activation for viscous flow of cholesterol in some non-aqueous solutions

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Abstract

The viscosities of solutions of cholesterol in benzene, toluene, carbon tetrachloride, chloroform and 1,2-dichloroethane up to 0.4 mol kg^{-1} at 293, 298, 303, 313, 323 and 333 K have been measured. On the basis of Eyring's theory of rate processes, the molar thermodynamic functions of activation for viscous flow of solution, i.e. the molar Gibbs free energy $\Delta\#\overline{G}_{1,2}$, molar enthalpy, $\Delta\#\overline{H}_{1,2}$ and molar entropy, $\Delta\#\overline{S}_{1,2}$, and corresponding partial molar quantities of activation for viscous flow of solute and solvent have been determined. Additionally, the viscosity coefficients B and D and their temperature derivatives are calculated and correlated with solvent dielectric parameter β. The influence of the "solvent effect" on the above parameters is discussed on the basis of Eyring's theory of the transition state and the structure of solution.

INTRODUCTION

Non-aqueous cholesterol systems attract attention in physical and biophysical chemistry [1–11]. In these systems, solute–solute and solute–solvent interactions occur, which depend on the solvent electric permittivity, the proton acceptor and donor abilities of the solute and solvent, the stereochemical properties of the solute, etc. It was shown that the cholesterol molecules can aggregate either by hydrogen bonding [1–4,6,10,12] or hydrophobic interactions [13]. It seems that the most important role in these processes is played by the hydroxylic group of the cholesterol molecule, its planar structure, as well as the alkyl side chain of the cholesterol molecule with all possible conformations. Due to their specific structure, cholesterol molecules play an important role in the formation of cell membranes and interactions among them. In this way, the cholesterol molecules maintain the permeability and fluidity of biological membranes.

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However, the deposition of cholesterol in the arteriosclerotic plaque has not been elucidated completely. For a deeper insight into these processes, therefore, it is instructive to determine some physicochemical properties of such systems. In the present study the thermodynamic functions of activation for viscous flow of cholesterol molecules in some aprotic solvents are determined, with the aim of elucidating the solvent effect on these parameters.

EXPERIMENTAL

Materials

Cholesterol (Sigma) was used without any purification and stored in a desiccator over P_2O_5. Solvents used were supplied from Merck. Benzene, toluene and chloroform were shaken with concentrated sulphuric acid, washed twice with water, then with a 10% aqueous solution of sodium carbonate, again with water to neutral reaction, dried over calcium chloride and distilled [14]. Carbon tetrachloride was shaken with an aqueous-ethanol solution of potassium hydroxide for half an hour at 50–60°C, rinsed with water to neutrality, dried over calcium chloride and distilled [14]. 1,2-Dichloroethane was used without any purification, except distillation. All solvents were kept under molecular sieves (4 Å).

Viscosity measurements

The viscosity of the investigated solutions was determined with a Cannon–Fenske viscometer. The absolute viscosity of solution, $\eta_{1,2}$ (Pl) was calculated by means of the equation [15]

$$\eta_{1,2} = Cd_{1,2}t - \frac{Ed_{1,2}}{t^2} \qquad (1)$$

where $d_{1,2}$ (kg m^{-3}) is the density of solution, t(s) is the flow time and C and E are constants characteristic of the viscometer. The viscometer was calibrated with water. Hence the values of $C = (1.1370 \pm 0.0007) \times 10^{-8}$ m^2 s^{-2} and $E = (8.37 \pm 0.29) \times 10^{-5}$ m^2 s were determined by a least squares fit to eqn. (1), using the absolute viscosity and density data of water [14], and the flow times at the experimental temperatures. The bath temperature was maintained to ±0.02°C. The viscosities of solutions were determined with an accuracy better than 3×10^{-6} Pl.

RESULTS AND DISCUSSION

For the interpretation of the experimental viscosity data, which are given in Tables 1–5, the theory of rate processes to viscous flow is applied [16].

TABLE 1

Absolute viscosities of benzene solutions of cholesterol in the concentration and temperature range studied

m (mol kg^{-1})	$\eta_{1,2} \times 10^4$ [a] (Pl) 293 K	298 K	303 K	313 K	323 K	333 K
0.0000	6.43	5.96	5.57	4.89	4.35	3.90
0.0444	6.65	6.17	5.74	5.06	4.48	4.02
0.0575	6.71	6.24	5.79	5.09	4.53	4.05
0.0971	6.95	6.43	5.98	5.25	4.66	4.16
0.1136	7.02	6.51	6.07	5.29	4.72	4.20
0.1654	7.38	6.81	6.33	5.52	4.89	4.37
0.1944	7.56	6.98	6.47	5.65	4.99	4.45
0.2098	7.68	7.08	6.57	5.71	5.04	4.48
0.2472	7.94	7.33	6.77	5.88	5.17	4.60
0.3016	8.42	7.73	7.14	6.14	5.41	4.80

[a] Literature values of $\eta_1^\ominus \times 10^4$ (Pl) [14]: 6.487 (293 K); 6.028 (298 K); 5.621 (303 K); 4.923 (313 K).

Thereby, the molar Gibbs free energy of activation for viscous flow of a solution, $\Delta\#\overline{G}_{1,2}$ (J mol^{-1}) is calculated from

$$\Delta\#\overline{G}_{1,2} = RT \ln\left[\frac{\overline{V}_{1,2}\eta_{1,2}}{hN_A}\right] \tag{2}$$

where R is the gas constant, h is Planck's constant, N_A is Avogadro's constant and $\overline{V}_{1,2}$ (cm^3 mol^{-1}) is the volume of one mole of solution

$$\overline{V}_{1,2} = \frac{1000 + mM_2}{d_{1,2}(n_1 + m)} \tag{3}$$

TABLE 2

Absolute viscosities of toluene solutions of cholesterol in the concentration and temperature range studied

m (mol kg^{-1})	$\eta_{1,2} \times 10^4$ [a] (Pl) 293 K	298 K	303 K	313 K	323 K	333 K
0.0000	5.80	5.46	5.15	4.61	4.18	3.79
0.0414	6.01	5.67	5.34	4.78	4.32	3.92
0.0697	6.15	5.79	5.46	4.88	4.40	4.01
0.1179	6.43	6.04	5.69	5.08	4.58	4.15
0.1489	6.60	6.16	5.79	5.15	4.64	4.19
0.1885	6.82	6.39	5.99	5.33	4.76	4.32
0.2395	7.20	6.72	6.28	5.56	4.97	4.49
0.3054	7.72	7.16	6.68	5.91	5.23	4.71
0.3919	8.54	7.87	7.31	6.40	5.62	5.03

[a] Literature values of $\eta_1^\ominus \times 10^4$ (Pl) [14]: 5.859 (293 K); 5.525 (298 K).

TABLE 3

Absolute viscosities of carbon tetrachloride solutions of cholesterol in the concentration and temperature range studied

m (mol kg^{-1})	$\eta_{1,2} \times 10^4$ [a] (Pl)					
	293 K	298 K	303 K	313 K	323 K	333 K
0.0000	9.65	8.99	8.38	7.35	6.53	5.84
0.0379	10.58	9.83	9.12	7.97	7.05	6.28
0.0642	11.25	10.40	9.62	8.36	7.38	6.54
0.0810	11.75	10.77	9.96	8.58	7.53	6.68
0.1025	12.39	11.36	10.45	8.98	7.85	6.92
0.1302	13.32	12.19	11.20	9.53	8.26	7.29
0.1661	14.61	13.28	12.12	10.24	8.81	7.72
0.2131	16.45	14.91	13.55	11.34	9.60	8.34

[a] Literature values of $\eta_1^\ominus \times 10^4$ (Pl) [14]: 9.785 (293 K); 9.004 (298 K); 8.45 (303 K).

TABLE 4

Absolute viscosities of chloroform solutions of cholesterol in the concentration and temperature range studied

m (mol kg^{-1})	$\eta_{1,2} \times 10^4$ [a] (Pl)					
	293 K	298 K	303 K	313 K	323 K	333 K
0.0000	5.61	5.38	5.17	4.79	4.47	4.18
0.0240	5.82	5.57	5.34	4.94	4.59	4.29
0.0404	5.96	5.70	5.47	5.04	4.68	4.36
0.0684	6.22	5.94	5.68	5.22	4.83	4.49
0.1172	6.70	6.38	6.08	5.55	5.11	4.73
0.1490	7.03	6.67	6.35	5.78	5.29	4.89
0.1911	7.49	7.09	6.73	6.09	5.55	5.10
0.2457	8.12	7.66	7.24	6.52	5.89	5.40
0.3185	9.03	8.48	7.98	7.12	6.37	5.82

[a] Literature values of $\eta_1^\ominus \times 10^4$ (Pl) [14]: 5.357 (298 K); 5.14 (303 K).

TABLE 5

Absolute viscosities of 1,2-dichloroethane solutions of cholesterol in the concentration and temperature range studied

m (mol kg^{-1})	$\eta_{1,2} \times 10^4$ [a] (Pl)					
	293 K	298 K	303 K	313 K	323 K	333 K
0.0000	8.23	7.70	7.22	6.39	5.73	5.17
0.0311	8.49	7.94	7.43	6.59	5.87	5.30
0.0524	8.68	8.12	7.61	6.73	5.99	5.42
0.0659	8.83	8.25	7.72	6.82	6.08	5.48
0.0831	9.02	8.40	7.85	6.92	6.19	5.57

[a] Literature values of $\eta_1^\ominus \times 10^4$ (Pl) [14]: 7.30 (303 K).

TABLE 6

Regression coefficients of eqn. (4) with standard error of the estimate s for benzene solutions of cholesterol in the temperature range studied

T (K)	$\Delta^{\#}G_1^{\ominus}$ [a] (J mol^{-1})	β_G (J mol^{-1})	γ_G (J mol^{-1})	s (J mol^{-1})
293	12101	30823	244950	3
298	12136	31466	195940	3
303	12180	31428	168730	3
313	12280	31884	103750	5
323	12393	33100	42603	18
333	12514	32396	40131	6

[a] $\Delta^{\#}G_1^{\ominus}$ (J mol^{-1}) values calculated from density and viscosity data of pure solvent [14]: 12122 (293 K); 12162 (298 K); 12205 (303 K).

where m (mol kg^{-1}) is the molality of solution, $n_1 = 1000/M_1$ is the number of moles of solvent and M_1 and M_2 are the molecular weights of solvent and solute, respectively. The values of $d_{1,2}$ for the systems studied are taken from ref. 11. It was found that at a definite temperature the concentration dependence of $\Delta^{\#}\overline{G}_{1,2}$ may be given by [17]

$$\Delta^{\#}\overline{G}_{1,2} = \Delta^{\#}G_1^{\ominus} + \beta_G X_2 + \gamma_G X_2^2 + \ldots \tag{4}$$

where $\Delta^{\#}G_1^{\ominus}$ is the molar Gibbs free energy of activation for viscous flow of pure solvent, β_G and γ_G are coefficients depending on solute, solvent and temperature, and X_2 is the mole fraction of solute. The coefficient β_G is defined as

$$\beta_G = \left(\frac{\delta \Delta^{\#}\overline{G}_{1,2}}{\delta X_2} \right)_{X_2 \to 0} \tag{5}$$

The concentration dependence of $\Delta^{\#}\overline{G}_{1,2}$ versus X_2 is linear, i.e. $\gamma_G = 0$ for chloroform and 1,2-dichloroethane solutions of cholesterol, while for the other solutions studied this dependence is quadratic. The values of $\Delta^{\#}G_1^{\ominus}$, β_G and γ_G, obtained by the method of least squares via eqn. (4), together with the standard errors of the estimate, s, are given in Tables 6–10. The linear regression coefficients, r, are greater than 0.999. The values of $\Delta^{\#}G_1^{\ominus}$ in the temperature range studied are close to the molar Gibbs free energy of activation for viscous flow of pure solvents, obtained from their viscosity and density data [14].

The temperature dependence of coefficients β_G is expressed analytically as

$$\beta_G = a_0 + a_1(T - T_0) + a_2(T - T_0)^2 \tag{6}$$

where a_i is the regression coefficient and $T_0 = 298$ K. The values of coefficient a_i are given in Table 11. However, as in the case of benzene,

TABLE 7

Regression coefficients of eqn. (4) with standard error of the estimate s for toluene solutions of cholesterol in the temperature range studied

T (K)	$\Delta^{\#}G_1^{\ominus}$ [a] (J mol^{-1})	β_G (J mol^{-1})	γ_G (J mol^{-1})	s (J mol^{-1})
293	12290	26686	181430	6
298	12367	26202	165690	7
303	12441	26187	146830	9
313	12596	26282	124450	11
323	12764	26003	90970	10
333	12925	26529	63146	11

[a] $\Delta^{\#}G_1^{\ominus}$ (J mol^{-1}) values calculated from density and viscosity data of pure solvent [14]: 12310 (293 K); 12388 (298 K).

toluene and 1,2-dichloroethane solutions of cholesterol, the values of coefficient β_G can be considered to be temperature independent, so the values of a_0 for these solutions are the average values of coefficient β_G. The temperature dependence of coefficient β_G is linear in the case of chloroform, whereas in the case of carbon tetrachloride solutions of cholesterol this dependence is quadratic.

The coefficient β_G is related to coefficients β_H and β_S through [17]

$$\beta_G = \beta_H - T\beta_S \tag{7}$$

where $\beta_S = -(\delta\beta_G/\delta T)_P$. The coefficients β_S and β_H, like coefficient β_G, depend on the solute, solvent and temperature. Relative to the temperature dependence of coefficient β_G (see eqn. (6)), the values of coefficient β_S are zero for benzene, toluene and 1,2-dichloroethane solutions of cholesterol, while the values of coefficient β_S are temperature independent for chloroform solutions; i.e. $\beta_S = -a_1$. In the case of carbon tetrachloride

TABLE 8

Regression coefficients of eqn. (4) with standard error of the estimate s for carbon tetrachloride solutions of cholesterol in the temperature range studied

T (K)	$\Delta^{\#}G_1^{\ominus}$ [a] (J mol^{-1})	β_G (J mol^{-1})	γ_G (J mol^{-1})	s (J mol^{-1})
293	13290	45243	90634	5
298	13357	43144	111400	8
303	13420	41924	109620	7
313	13559	39559	97432	10
323	13715	38231	35344	17
333	13860	38376	3369	11

[a] $\Delta^{\#}G_1^{\ominus}$ (J mol^{-1}) values calculated from density and viscosity data of pure solvent [14]: 13325 (293 K); 13361 (298 K); 13440 (303 K).

TABLE 9

Regression coefficients of eqn. (4) with standard error of the estimate s for chloroform solutions of cholesterol in the temperature range studied

T (K)	$\Delta \# G_1^{\ominus}$ (J mol^{-1})	β_G (J mol^{-1})	s (J mol^{-1})
293	11516	40597	1
298	11625	39809	2
303	11735	38981	1
313	11958	37510	1
323	12193	35531	2
333	12421	34707	3

[a] $\Delta \# G_1^{\ominus}$ (J mol^{-1}) values calculated from density and viscosity data of pure solvent [14]: 11614 (298 K); 11720 (303 K).

solutions of cholesterol, the temperature dependence of coefficient β_S is linear, i.e. $\beta_S = -a_1 - 2a_2(T - T_0)$. The values of coefficient β_H at 298 K are given in Table 11. In calculations of coefficient β_H via relation (7), the values of coefficient a_0 and a_1 from Table 11 were used to obtain β_G and β_S values, respectively.

The molar entropy, $\Delta \# \bar{S}_{1,2}$ (J mol^{-1} K^{-1}), as well as molar enthalpy, $\Delta \# \bar{H}_{1,2}$ (J mol^{-1}), of activation for viscous flow of a solution can be given by the following relations:

$$\Delta \# \bar{S}_{1,2} = \Delta \# S_1^{\ominus} + \beta_S X_2 + \gamma_S X_2^2 + \ldots \tag{8}$$

$$\Delta \# \bar{H}_{1,2} = \Delta \# H_1^{\ominus} + \beta_H X_2 + \gamma_H X_2^2 + \ldots \tag{9}$$

where $\Delta \# S_1^{\ominus}$ and $\Delta \# H_1^{\ominus}$ are the molar entropy and molar enthalpy of activation for viscous flow of pure solvent, respectively.

TABLE 10

Regression coefficients of eqn. (4) with standard error of the estimate s for 1,2-dichloroethane solutions of cholesterol in the temperature range studied

T (K)	$\Delta \# G_1^{\ominus}$ [a] (J mol^{-1})	β_G (J mol^{-1})	s (J mol^{-1})
293	12409	36785	5
298	12474	36099	3
303	12536	35954	3
313	12666	35958	2
323	12806	35779	7
333	12954	36215	4

[a] $\Delta \# G_1^{\ominus}$ (J mol^{-1}) values calculated from density and viscosity data of pure solvent [14]: 12565 (303 K).

TABLE 11

Regression coefficients of eqn. (6) and values of coefficient β_H at 298 K

Solvent	a_0	a_1	a_2	β_H (J mol^{-1})
Benzene	31850 ± 329			31850
Toluene	26315 ± 250			26315
Carbon tetrachloride	43339 ± 91	−341 ± 14	5.7 ± 0.4	145008
Chloroform	39767 ± 140	−153 ± 7		85384
1,2-Dichloroethane	36132 ± 350			36132

Thus, the partial molar functions of activation for viscous flow of the solute at infinite dilution, $\Delta\#\bar{Y}_{2,0}$, can be calculated from [18]

$$\Delta\#\bar{Y}_{2,0} = \Delta\#Y_1^{\ominus} + \beta_Y \qquad Y \equiv G,\ H \text{ or } S \tag{10}$$

From this relation it follows that the parameter β_Y may be considered as the difference of the partial molar function of activation for viscous flow of a solute at infinite dilution and the respective molar quantity of the pure solvent.

The partial molar parameters of activation for viscous flow of the investigated solute at infinite dilution and 298 K, i.e. $\Delta\#\bar{G}_{2,0}$, $\Delta\#\bar{S}_{2,0}$ and $\Delta\#\bar{H}_{2,0}$, calculated via relation (10), are presented in Table 12, using the values of the molar functions of activation for viscous flow for pure solvents from Table 13. Hence, the values of molar Gibbs free energy of activation for viscous flow of pure solvents in the temperature range from 293 to 333 K were calculated via relation (2), using the densities of pure solvents from ref. 11 and their viscosities from Tables 1–5. From the temperature dependence of $\Delta\#G_1^{\ominus}$, the entropy and then via the Gibbs–Helmholz relation the enthalpies of activation for viscous flow of the pure solvents were estimated. In the temperature range studied the values of $\Delta\#S_1^{\ominus}$ depend linearly on the temperature.

TABLE 12

Values of partial molar parameters of activation for viscous flow of cholesterol in investigated solvents at infinite dilution and 298 K

Solvent	$\Delta\#\bar{G}_{2,0}$ (J mol^{-1})	$\Delta\#\bar{S}_{2,0}$ (J mol^{-1} K^{-1})	$\Delta\#\bar{H}_{2,0}$ (J mol^{-1})
Benzene	43983	−8.3	41515
Toluene	38675	−15.0	34200
Carbon tetrachloride	56695	328	154589
Chloroform	51391	133	91009
1,2-Dichloroethane	48609	−12.3	44942

TABLE 13

Values of molar functions of activation for viscous flow of investigated solvents at 298 K

Solvent	$\Delta^{\#}G_1^{\ominus}$ (J mol^{-1})	$-\Delta^{\#}S_1^{\ominus}$ (J mol^{-1} K^{-1})	$\Delta^{\#}H_1^{\ominus}$ (J mol^{-1})
Benzene	12133	8.3	9665
Toluene	12360	15.0	7885
Carbon tetrachloride	13356	12.7	9581
Chloroform	11624	20.1	5625
1,2-Dichloroethane	12477	12.3	8810

The values of $\Delta^{\#}\bar{Y}_{2,0}$ can be interpreted in terms of the relative effects of a solute on the ground and transition state solvent [19,20]. If a solute is completely coordinated in the ground state solvent, formation of the transition state involves solute–solvent bond breaking and a reduction in the coordination number of the solute. However, if the ground state solvent is highly structured and thus resists the complete coordination of the solute, then the additional solute–solvent bonds can be formed in the less rigid transition state solvent with an increase in the coordination number of the solute.

From Tables 12 and 13 it follows that the values of $(\Delta^{\#}\bar{G}_{2,0} - \Delta^{\#}G_1^{\ominus})$ are positive. As $\Delta^{\#}\bar{G}_{2,0} > \Delta^{\#}G_1^{\ominus}$, it may be anticipated that in the systems studied the solute–solvent bonds are stronger than the solvent–solvent bonds in the transition state. In the case of chlorinated hydrocarbons, the values of $(\Delta^{\#}\bar{G}_{2,0} - \Delta^{\#}G_1^{\ominus})$ increase with the molar volumes or molecular weights of the solvents, as well as with the values of viscosity coefficient B. In contrast, for both aromatic solvents the lower value of $(\Delta^{\#}\bar{G}_{2,0} - \Delta^{\#}G_1^{\ominus})$ belongs to the solvent with the higher value of $V_1^{\ominus}$ and M_1, while the viscosity coefficients B are practically equal for both solvents.

According to the transition state theory of viscosity, the values of $\Delta^{\#}\bar{G}_{2,0}$ do not contain any contributions from the changes of solvent–solvent interactions caused by the molecule of solute. The value of $\Delta^{\#}\bar{G}_{2,0}$ and the viscosity coefficient B depend only on the difference in the solute–solvent interactions in the ground and transition state. In contrast, the changes of the corresponding enthalpies, $\Delta^{\#}\bar{H}_{2,0}$, and entropies, $\Delta^{\#}\bar{S}_{2,0}$, are affected not only by the changes of solute–solvent interactions but also by the changes of solvent–solvent interactions. In general, the changes of solute–solvent interactions can be attributed either to the breaking or making of solute–solvent bonds in the transition state, leading to a decrease or an increase of order, respectively. For a system where solute molecules are coordinated completely or nearly so in the ground state, $\Delta^{\#}\bar{S}_{2,0}$ is only slightly negative, while $\Delta^{\#}\bar{H}_{2,0}$ is positive [20].

From Table 12, it can be seen that $\Delta^{\#}\bar{G}_{2,0}$ values are positive and differ over a range of 18 kJ mol^{-1}; the lowest value of $\Delta^{\#}\bar{G}_{2,0}$ is in the case of toluene and the highest in the case of carbon tetrachloride as a solvent. The values of $\Delta\#\bar{S}_{2,0}$ are positive for carbon tetrachloride and chloroform solutions and follow the same order as the molecular weights of the solvents. For these solvents bond-breaking may be assumed in the transition state. However, in the case of benzene, toluene and 1,2-dichloroethane as solvents, the slightly negative values of $\Delta\#\bar{S}_{2,0}$ indicate nearly complete coordination in the ground state solvent. The values of $\Delta\#\bar{H}_{2,0}$, given in Table 12, are all positive and, except for benzene solutions of cholesterol, increase with the molecular weight of solvent. The relatively high values of $\Delta\#\bar{H}_{2,0}$ may suggest that these values contain an additional contribution from solvent–solvent bond breaking, required for the movement of cholesterol molecules from one equilibrium position to another. In all cases, the values of $\Delta\#\bar{H}_{2,0}$ are higher than $T\Delta\#\bar{S}_{2,0}$ values; i.e. $\Delta\#\bar{H}_{2,0} > T\Delta\#\bar{S}_{2,0}$ which is characteristic for a non-structured solvent, which offers little resistance to the solvation of solute molecules in the ground state, and where the solute–solvent bonds can largely be broken in the transition state.

By contrast, the relative viscosity, η_r, of a non-electrolyte solution at moderate to higher concentrations of solute can be given by [21]

$$\eta_r = \frac{\eta_{1,2}}{\eta_1^{\ominus}} = 1 + Bm + Dm^2 \tag{11}$$

where $\eta_1^{\ominus}$ is the absolute viscosity of pure solvent, and the coefficients B and D are empirical constants, characteristic of a given solute–solvent pair. Thus, the viscosity coefficient B is considered to reflect mainly the effects of the size and shape of the solute molecule, as well as the solute–solvent interactions on viscous flow. The coefficient D, besides the solute–solute interactions, also reflects that part of the solute–solvent interactions which are not included in the viscosity coefficient B.

Considering Eyring's theory of rate processes applied to viscous flow, the relation of viscosity coefficient B is [18]

$$B = d_1^{\ominus}\left(V_1^{\ominus} - \bar{V}_{2,0}\right) + \frac{\beta_G M_1}{RT} \tag{12}$$

where $d_1^{\ominus}$ is the density and $V_1^{\ominus}$ the molar volume of pure solvent, and $\bar{V}_{2,0}$ is the partial molar volume of solute at infinite dilution. From relation (12) it is evident that the solvent structure can influence the viscosity coefficient B in two terms: the volumetric term, which gives a negative contribution if $V_1^{\ominus} < \bar{V}_{2,0}$, and the term depending on changes of partial molar Gibbs free energy of activation for viscous flow of solute at infinite dilution and pure solvent. For a system in which $\Delta\#G_1^{\ominus} < \Delta\#\bar{G}_{2,0}$ this term gives a positive contribution to the B value. Thus, eqn. (12) allows the comparison of viscosity coefficients B in different solvents at a definite temperature.

For the investigated systems the viscosity coefficients B were calculated via eqn. (12), using the partial molar volumes of solute from ref. 11. In calculating viscosity coefficients B, the average values of coefficient β_G in the temperature range studied were used for benzene, toluene and 1,2-dichloroethane solutions of cholesterol, (i.e. $\beta_G = a_0$ from Table 11), while for carbon tetrachloride and chloroform solutions the β_G values at the temperatures studied are taken from Tables 8 and 9, respectively. However, the viscosity coefficients D were calculated on the basis of eqn. (11), using the calculated values of viscosity coefficients B, and the viscosity data from Tables 1–5. The values of viscosity coefficients B and D in the temperature range studied are given in Table 14. From Table 14 it can be seen that the values of viscosity coefficient B are positive, which means that the second term of the right-hand side of eqn. (12) prevails over the first one. Furthermore, it can be seen that in the case of aromatic solvents the values found for B are nearly equal, while for chlorinated hydrocarbons the values of viscosity coefficient B increase from solvent to solvent with the increasing molecular weight of the solvent. Since the viscosity coefficients B and D are characteristic for a given solute–solvent pair, it may be concluded that the investigated systems differ in their solute–solvent as well as solute–solute interactions.

From Tables 12 and 14, it can be seen that for chlorinated hydrocarbons the values of $\Delta\#\overline{G}_{2,0}$ follow the same order as the values of viscosity coefficients B and D; i.e. a large and positive $\Delta\#\overline{G}_{2,0}$ value results in large and positive values of viscosity coefficients B and D. This means that the solvent structure influences both viscosity coefficients B and D much more than the $\Delta\#\overline{G}_{2,0}$ values. In contrast, in the case of aromatic solvents, practically the same values of viscosity coefficient B are associated with rather different values of $\Delta\#\overline{G}_{2,0}$, while the values of viscosity coefficient D are slightly different and the value of D is higher at lower values of $\Delta\#\overline{G}_{2,0}$.

The viscosity coefficients B and D can be correlated with the dielectric parameter β of the solvent, defined as [22]

$$\beta = \left(\frac{2N_A^2}{3\epsilon_0}\right)\left(\frac{\mu_1^{\ominus 2}}{V_1^{\ominus}}\right) \tag{13}$$

where ϵ_0 is the dielectric permittivity of a vacuum and $\mu_1^{\ominus}$ is the dipole moment of the solute molecule. From Table 14, it can be seen that in the case of chlorinated hydrocarbons, with increasing values of the dielectric parameter β, from β(carbon tetrachloride) = 0, β(chloroform) = 4.90 kJ mol^{-1} to β(1,2-dichloroethane) = 12.68 kJ mol^{-1} at 298 K, the values of viscosity coefficients B and D decrease. In the case of aromatic hydrocarbons, practically the same values of the viscosity coefficient B are observed at nearly the same dielectric parameter β: β(benzene) = 0 and β(toluene)

TABLE 14

Values of viscosity coefficients B (kg mol^{-1}) and D (kg^2 mol^{-2}) of eqn. (12) for investigated solutions of cholesterol in the temperature range from 293 to 333 K

Solvent	293 K		298 K		303 K		313 K		323 K		333 K	
	B	D	B	D	B	D	B	D	B	D	B	D
Benzene	0.752	0.909	0.737	0.821	0.722	0.705	0.694	0.509	0.669	0.461	0.645	0.398
Toluene	0.749	1.165	0.733	1.004	0.718	0.899	0.690	0.768	0.664	0.549	0.639	0.500
Carbon tetrachloride	2.387	4.316	2.211	4.125	2.094	3.759	1.880	3.132	1.738	2.197	1.686	1.515
Chloroform	1.525	1.222	1.456	1.109	1.386	1.006	1.263	0.830	1.129	0.712	1.052	0.565
1,2-Dichloroethane	1.065	1.084	1.042	0.626	1.021	0.349	0.976	0.266	0.938	0.200	0.900	0.190

TABLE 15

Values of temperature derivative of viscosity coefficients B and D for investigated solutions of cholesterol

Solvent	$-\mathrm{d}B/\mathrm{d}T$ (kg mol^{-1} K^{-1})	$-\mathrm{d}D/\mathrm{d}T$ (kg^{2} mol^{-2} K^{-1})
Benzene	0.003	0.013
Toluene	0.003	0.017
Carbon tetrachloride	0.030	0.072
Chloroform	0.013	0.016
1,2-Dichloroethane	0.005	0.019

= 0.25 kJ mol^{-1}, while the D value for a toluene solution of cholesterol is slightly higher than for a benzene solution.

The temperature dependence of viscosity coefficient B is calculated from [18]

$$\frac{\mathrm{d}B}{\mathrm{d}T} = \alpha_1^{\ominus} d_1^{\ominus}\left(\bar{V}_{2,0} - V_1^{\ominus}\right) - d_1^{\ominus}\left(\bar{E}_{2,0} - E_1^{\ominus}\right) - \frac{\beta_{\mathrm{H}} M_1}{RT^2} \tag{14}$$

where $\alpha_1^{\ominus}$ is the thermal expansion coefficient of pure solvent, $\bar{E}_{2,0}$ the partial molar expansibility of solute at infinite dilution, and $E_1^{\ominus}$ is the molar expansibility of pure solvent. In calculations of $\mathrm{d}B/\mathrm{d}T$, the $\alpha_1^{\ominus}$ and $d_1^{\ominus}$ values were taken from ref. 14, and $\bar{V}_{2,0}$ and $\bar{E}_{2,0}$ from ref. 11. The values of $\mathrm{d}B/\mathrm{d}T$ are given in Table 15. These values are, within experimental error, equal to those obtained from the temperature dependence of B values, given in Table 14. From Table 15 it can be seen that the temperature dependence of viscosity coefficients B and D is negative, as can be expected due to the decrease of intermolecular interactions either between solute–solvent or solute–solute molecules with an increase of temperature. The highest values of $\mathrm{d}B/\mathrm{d}T$ and $\mathrm{d}D/\mathrm{d}T$ are observed for carbon tetrachloride solutions of cholesterol and the lowest for benzene solutions. It is interesting to note that the absolute values of $\mathrm{d}B/\mathrm{d}T$ for chlorinated hydrocarbons increase with decreasing values of the dielectric parameter β of the solvent. In the case of aromatic solvents, with nearly the same dielectric parameter β, the same values of $\mathrm{d}B/\mathrm{d}T$ are observed.

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