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Partial molar volumes and partial molar expansibilities of cholesterol in some aprotic solvents

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Abstract

The densities of solutions of cholesterol (up to 0.4 mol kg^{-1}) in benzene, toluene, carbon tetrachloride, chloroform or 1,2-dichloroethane were measured at 293, 298, 303, 313, 323 and 333 K. The partial molar volumes and partial molar expansibilities of the solute were found to be independent of concentration. The thermal expansion coefficients of the solute in the studied solvents tended to decrease slightly with increasing temperature. The thermal expansion coefficients of the investigated solutions decreased with increasing concentration. In addition, the partial molar volumes of the solute at infinite dilution are discussed on the basis of scaled particle theory. The "solvent effect" on the partial molar volume of the solute was found to be due mainly to cavity formation and intermolecular dispersion forces.

INTRODUCTION

Cholesterol is one of the main constituents of many biological substances, such as lipoproteins, biological membranes, gallstones etc. Therefore physico-chemical investigations of aqueous and non-aqueous solutions of cholesterol are important in the fields of chemistry and biophysical chemistry, and have received considerable attention in recent years [1–6]. It has been found that cholesterol molecules undergo self-association via hydrogen bond formation. The structure of non-aqueous solutions of cholesterol has been studied by infrared spectroscopy [1–3], nuclear magnetic resonance [2], thermochemical methods [4,5] and vapour pressure osmometry [6] with the aim of elucidating the self-association of cholesterol molecules and the binding of cholesterol molecules to phospholipids and neutral triacylglycerols in non-polar media via hydrogen bonds. However, the volumetric investigations give valuable parameters for obtaining a deeper insight into the behaviour of such systems where solute–solute as well as solute–solvent interactions may exist. Surprisingly enough, there are only a few reports on volumetric data of cholesterol solution [7–9].

In the present study, some volumetric properties of cholesterol have been determined in several aprotic solvents differing in electric permittivity and dipole moment. Subsequently, the partial molar volume of the solute at infinite dilution is discussed on the basis of scaled particle theory [10], i.e. in terms of cavity formation and possible "shrinking" of the cavity.

EXPERIMENTAL

Materials

Cholesterol (Sigma) was used without any purification and was stored in a desiccator over P_2O_5.

The solvents used were supplied by Merck. Benzene, toluene and chloroform were shaken with concentrated sulphuric acid, washed twice with water, then with 10% aqueous solution of sodium carbonate, again with water to neutral reaction, dried over calcium chloride and distilled [11]. Carbon tetrachloride was shaken with an aqueous ethanol solution of potassium hydroxide for 0.5 h at 50–60 ° C, rinsed with water to neutrality, dried over calcium chloride and distilled [11]. 1,2-Dichloroethane was used without purification apart from distillation. All solvents were kept over molecular sieve 4A.

The densities and refractive indices of the purified solvents, given in Table 1, are close to the values from ref. 11.

Density measurements

For the investigated systems except carbon tetrachloride solutions, the densimeter was calibrated by means of dry air [12] and water [13]. In the case of carbon tetrachloride solutions of cholesterol the densimeter was calibrated with dry air and carbon tetrachloride [14].

RESULTS AND DISCUSSION

The volumes of the investigated solutions, $V_{1,2}$ (cm^3), containing m moles of solute per kilogram of solvent, were calculated from

$$V_{1,2} = \frac{1000 + mM_2}{d_{1,2}} \tag{1}$$

TABLE 1

Densities and refractive indices of purified solvents at 298 K

Solvent	d_1^0 (g cm^{-3})	n_D
Benzene	0.87294	1.4978
Toluene	0.86213	1.4941
Carbon tetrachloride	1.58457	1.4574
Chloroform	1.47945	1.4430
1,2-Dichloroethane	1.24580	1.4421

TABLE 2

Densities of benzene solutions of cholesterol in the concentration and temperature ranges studied

m (mol kg^{-1})	$d_{1,2}$ (g cm^{-3})					
	293 K	298 K	303 K	313 K	323 K	333 K
0.0000	0.8790	0.8736	0.8683	0.8574	0.8451	0.8332
0.0444	0.8805	0.8752	0.8699	0.8592	0.8470	0.8352
0.0575	0.8810	0.8756	0.8704	0.8597	0.8476	0.8358
0.0971	0.8823	0.8770	0.8718	0.8612	0.8492	0.8376
0.1136	0.8828	0.8776	0.8724	0.8618	0.8499	0.8383
0.1654	0.8845	0.8793	0.8742	0.8638	0.8519	0.8405
0.1944	0.8854	0.8802	0.8751	0.8648	0.8531	0.8417
0.2098	0.8859	0.8807	0.8756	0.8654	0.8537	0.8423
0.2472	0.8870	0.8819	0.8768	0.8667	0.8551	0.8438
0.3016	0.8886	0.8835	0.8786	0.8685	0.8571	0.8459

where M_2 (g mol^{-1}) is the solute molecular weight and $d_{1,2}$ (g cm^{-3}) is the density of the solution. The values of $d_{1,2}$ for the investigated systems are given in Tables 2–6.

The concentration dependence of $V_{1,2}$ can be described by [15]

$$V_{1,2} = V_S^0 + \bar{V}_{2,0}m + v_{22}m^2 + v_{222}m^3 + \dots \tag{2}$$

where $V_S^0 = 1000/d_1^0$, d_1^0 (g cm^{-3}) is the density of the pure solvent, $\bar{V}_{2,0}$ (cm^3 mol^{-1}) is the partial molar volume of the solute at infinite dilution, and v_{22}, v_{222}, etc. are the virial coefficients according to the McMillan–Mayer theory of solution [16], and represent the contributions to the excess thermodynamic properties of pair, triplet and higher order solute aggregates.

TABLE 3

Densities of toluene solutions of cholesterol in the concentration and temperature ranges studied

m (mol kg^{-1})	$d_{1,2}$ (g cm^{-3})					
	293 K	298 K	303 K	313 K	323 K	333 K
0.0000	0.8668	0.8621	0.8573	0.8474	0.8376	0.8282
0.0414	0.8685	0.8638	0.8591	0.8492	0.8395	0.8302
0.0697	0.8697	0.8650	0.8603	0.8505	0.8408	0.8315
0.1179	0.8716	0.8670	0.8622	0.8525	0.8429	0.8337
0.1489	0.8727	0.8682	0.8635	0.8538	0.8442	0.8350
0.1885	0.8742	0.8698	0.8650	0.8554	0.8459	0.8367
0.2395	0.8761	0.8716	0.8670	0.8574	0.8479	0.8388
0.3054	0.8784	0.8740	0.8694	0.8599	0.8505	0.8416
0.3919	0.8813	0.8769	0.8724	0.8630	0.8538	0.8450

TABLE 4

Densities of carbon tetrachloride solutions of cholesterol in the concentration and temperature ranges studied

m (mol kg^{-1})	$d_{1,2}$ (g cm^{-3}) 293 K	298 K	303 K	313 K	323 K	333 K
0.0000	1.5940	1.5843	1.5746	1.5550	1.5351	1.5150
0.0379	1.5801	1.5706	1.5611	1.5421	1.5227	1.5031
0.0642	1.5708	1.5615	1.5521	1.5334	1.5145	1.4951
0.0810	1.5651	1.5558	1.5463	1.5281	1.5093	1.4902
0.1025	1.5578	1.5487	1.5394	1.5213	1.5029	1.4840
0.1302	1.5488	1.5398	1.5306	1.5129	1.4948	1.4762
0.1661	1.5375	1.5286	1.5196	1.5024	1.4847	1.4665
0.2131	1.5233	1.5147	1.5059	1.4892	1.4720	1.4543

TABLE 5

Densities of chloroform solutions of cholesterol in the concentration and temperature ranges studied

m (mol kg^{-1})	$d_{1,2}$ (g cm^{-3}) 293 K	298 K	303 K	313 K	323 K	333 K
0.0000	1.4891	1.4797	1.4706	1.4511	1.4313	1.4112
0.0240	1.4822	1.4729	1.4639	1.4446	1.4251	1.4053
0.0404	1.4776	1.4684	1.4594	1.4403	1.4210	1.4014
0.0684	1.4699	1.4608	1.4519	1.4331	1.4141	1.3948
0.1172	1.4570	1.4482	1.4395	1.4211	1.4026	1.3838
0.1490	1.4490	1.4403	1.4317	1.4136	1.3954	1.3770
0.1911	1.4388	1.4303	1.4218	1.4041	1.3862	1.3682
0.2457	1.4262	1.4179	1.4096	1.3924	1.3749	1.3575
0.3185	1.4105	1.4025	1.3944	1.3776	1.3608	1.3439

TABLE 6

Densities of 1,2-dichloroethane solutions of cholesterol in the concentration and temperature ranges studied

m (mol kg^{-1})	$d_{1,2}$ (g cm^{-3}) 293 K	298 K	303 K	313 K	323 K	333 K
0.0000	1.2535	1.2457	1.2382	1.2230	1.2072	1.1923
0.0311	1.2491	1.2414	1.2340	1.2189	1.2033	1.1885
0.0407	1.2478	1.2401	1.2328	1.2176	1.2021	1.1874
0.0524	1.2462	1.2385	1.2312	1.2162	1.2007	1.1860
0.0659	1.2444	1.2367	1.2295	1.2145	1.1991	1.1845
0.0831	1.2421	1.2345	1.2273	1.2123	1.1971	1.1825

For the investigated solutions, it was found that the volumes of solutions at a definite temperature in each solvent studied are, within the experimental errors, linearly dependent on the concentration of solute. Therefore the partial molar volumes of solute in the solvents studied at infinite dilution, given in Table 7, are the average values obtained at a definite temperature from $\bar{V}_{2,0} = (V_{1,2} - V_1^0)/m$. The indicated errors of $\bar{V}_{2,0}$ are the standard errors of the mean values of $\bar{V}_{2,0}$ at a given temperature.

The partial molecular volumes at infinite dilution $\bar{v}_{2,0}$ (cm^3 molecule^{-1}) for the investigated solute in the solvents studied at 293 K, calculated from $\bar{v}_{2,0} = \bar{V}_{2,0}/N$ (where N is Avogadro's constant), are given in Table 8. The molecular volume of the solid solute $v_2^0 = 6.017 \times 10^{-22}$ cm^3 molecule^{-1} at 293 K was calculated from $v_2^0 = M_2/d_2^0 N$, where d_2^0 (g cm^{-3}) is the density of the pure solute [17]. A comparison of the partial molecular volumes of cholesterol in different solvents at infinite dilution with its molecular volume shows that the former are greater than the latter, and that the average value of their ratios $\bar{v}_{2,0}/v_2^0$ at 293 K is 1.09 ± 0.01. The values of partial excess molecular volumes $\bar{v}_{2,0}^{\text{ex}} = \bar{v}_{2,0} - v_2^0$ (cm^3 molecule^{-1}), which characterize the volume changes associated with the transfer of one molecule of solute from the pure solute to solution at infinite dilution and are given in Table 8, are positive and relatively high.

With an assumption that the molar volume of a pure solute V_2^0 consists of a volume $Nv_{2,\text{w}}$, where $v_{2,\text{w}}$ is the van der Waals molecular volume, plus a varying amount of empty space between solute molecules, the ratio of the molar volume of pure solute to the van der Waals molar volume $V_{2,\text{w}}$ varies from compound to compound. Thus the empty volume in the crystal depends on the shape of the molecules, their ability of vibrational motion and hydrogen bonding between solute molecules. For relatively non-polar compounds, it was found that the ratio $V_2^0/V_{2,\text{w}}$ is about 1.5 [18]. For cholesterol, this ratio is 1.41 ($v_{2,\text{w}} = 426.1 \times 10^{-24}$ cm^3 molecule^{-1} [18]), which is fairly low; the low ratio can be ascribed to the flat shape of the cholesterol molecule, which allows good packing of cholesterol molecules in the crystal, and to the hydrogen bonding between cholesterol molecules, which brings them closer together [19]. From the obtained values of the ratio $\bar{v}_{2,0}/v_{2,\text{w}}$, which are almost constant for the investigated solutions, it may be concluded that the empty volume of cholesterol is essentially independent of the nature of the solvents studied and close to that in the crystalline state (see Table 8).

In Fig. 1 the temperature dependence of the partial molar volumes of cholesterol at infinite dilution in the solvents studied is presented. From Fig. 1 it can be seen that this dependence is linear

$$\bar{V}_{2,0} = a_0 + a_1(T - T_0) \tag{3}$$

where a_0 and a_1 are empirical constants and T is the absolute tempera-

TABLE 7

Partial molar volumes of cholesterol in the investigated solvents at infinite dilution and at the temperatures studied

Solvent	$\bar{V}_{2,0}$ (cm^3 mol^{-1})					
	293 K	298 K [a]	303 K	313 K	323 K	333 K
Benzene	394.51 ± 0.15	395.07 ± 0.15	395.74 ± 0.16	395.62 ± 0.12	396.25 ± 0.13	397.28 ± 0.15
Toluene	390.22 ± 0.16	390.78 ± 0.20	391.57 ± 0.14	393.45 ± 0.08	395.15 ± 0.09	396.66 ± 0.14
Carbon tetrachloride	390.47 ± 0.06	391.49 ± 0.07	392.84 ± 0.13	392.78 ± 0.10	393.54 ± 0.07	395.11 ± 0.05
Chloroform	391.50 ± 0.07	392.45 ± 0.06	394.05 ± 0.06	396.14 ± 0.06	397.75 ± 0.06	399.20 ± 0.09
1,2-Dichloroethane	399.49 ± 0.11	401.03 ± 0.10	401.31 ± 0.21	405.70 ± 0.27	407.55 ± 0.15	410.83 ± 0.22

[a] The literature data of $\bar{V}_2$, calculated from the partial specific volumes of cholesterol in the solvents studied, at 298 K are: $\bar{V}_2$ (cm^3 mol^{-1}) = 394.78 for benzene [7], 390.53 for toluene [8,9], 390.89 for carbon tetrachloride [9] and 391.69 for chloroform [9].

TABLE 8

Partial molecular volumes and excess partial molecular volumes of cholesterol in the investigated solvents at infinite dilution and the ratio of partial molecular volume to van der Waals molecular volume at 293 K

Solvent	$\bar{v}_{2,0} \times 10^{22}$ (cm^3 molecule^{-1})	$\bar{v}^{ex}_{2,0} \times 10^{22}$ (cm^3 molecule^{-1})	$\frac{\bar{v}_{2,0}}{v_{2,w}}$
Benzene	6.56	0.54	1.54
Toluene	6.48	0.46	1.52
Carbon tetrachloride	6.48	0.47	1.52
Chloroform	6.50	0.48	1.53
1,2-Dichloroethane	6.63	0.62	1.56

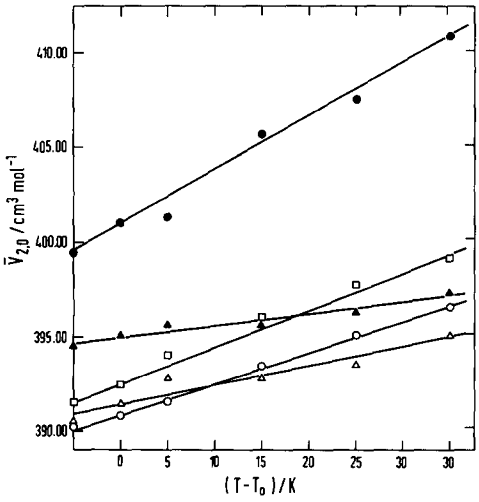

Fig. 1. Temperature dependence of the partial molar volumes of cholesterol in (●) 1,2-dichloroethane; (▲) benzene; (□) chloroform; (○) toluene and (△) carbon tetrachloride.

TABLE 9

Regression coefficients of eqns. (3) and (8)

Solvent	a_0	a_1	$-(\alpha_{2,0} - \alpha_1^0) \times 10^4$ (K^{-1})
Benzene	395.00 ± 0.17	0.059 ± 0.009	10.62
Toluene	390.96 ± 0.08	0.162 ± 0.004	6.42
Carbon tetrachloride	391.46 ± 0.30	0.099 ± 0.016	9.76
Chloroform	392.74 ± 0.22	0.195 ± 0.012	7.86
1,2-Dichloroethane	400.78 ± 0.30	0.283 ± 0.016	4.44

ture; $T_0 = 298$ K. The coefficients a_0 and a_1, determined by the method of least squares, are given in Table 9.

As the partial molar volumes of cholesterol in the solvents studied are concentration independent and equal to their volumes at infinite dilution, so the values of partial molar expansibility of the solute $\bar{E}_2 = (\delta \bar{V}_2/\delta T)_P$ (cm^3 mol^{-1} K^{-1}) are also concentration independent and equal to their values at infinite dilution ($\bar{E}_2 = \bar{E}_{2,0}$).

The partial molar expansibility of the solute at infinite dilution is equal to the regression coefficient a_1 of eqn. (3), and the thermal expansion coefficient of the solute at infinite dilution $\alpha_{2,0}$ (K^{-1}) defined as

$$\alpha_{2,0} = \frac{1}{\bar{V}_{2,0}} \left(\frac{\delta \bar{V}_{2,0}}{\delta T} \right)_P = \frac{\bar{E}_{2,0}}{\bar{V}_{2,0}} \tag{4}$$

is equal to the ratio a_1/a_0 at 298 K. The values of $\alpha_{2,0}$ tend to decrease slightly with increasing temperature. On the other hand, the thermal expansion coefficient of solution $\alpha_{1,2}$ (K^{-1}) is defined by

$$\alpha_{1,2} = \frac{1}{V_{1,2}} \left(\frac{\delta V_{1,2}}{\delta T} \right)_P \tag{5}$$

Thus the thermal expansion coefficients of the investigated solutions were calculated from

$$\alpha_{1,2} = \frac{1}{V_{1,2}} \left(\frac{10^3}{d_1^0} \alpha_1^0 + m\bar{E}_{2,0} \right) \tag{6}$$

where α_1^0 (K^{-1}) is the thermal expansion coefficient of pure solvent.

In Fig. 2 the dependence of $(\alpha_{1,2} - \alpha_1^0)$ against the volume fraction of solute Φ_2 is shown. The values of α_1^0 were taken from ref. 11. The volume fraction was used instead of molality or mole fraction of solute to allow for the effects of size differences of solute and solvent molecules. The volume fraction of solute was calculated from

$$\Phi_2 = \frac{m\bar{V}_{2,0}}{1000/d_1^0 + m\bar{V}_{2,0}} \tag{7}$$

From Fig. 2, it is shown that the dependence of $(\alpha_{1,2} - \alpha_1^0)$ vs. Φ_2 is linear. This dependence may be expressed in the form

$$\alpha_{1,2} - \alpha_1^0 = (\alpha_{2,0} - \alpha_1^0)\Phi_2 \tag{8}$$

The calculated values of $(\alpha_{2,0} - \alpha_1^0)$ at 298 K are given in Table 9. From Fig. 2 and Table 9 it can be seen that the values of the thermal expansion coefficient of the investigated solutions are lower than those of the pure solvents, and the values of $(\alpha_{1,2} - \alpha_1^0)$ decrease with increasing concentration of solute. The values of $(\alpha_{2,0} - \alpha_1^0)$ are lowest in the case of 1,2-dichloroethane and highest in the case of benzene as solvent.

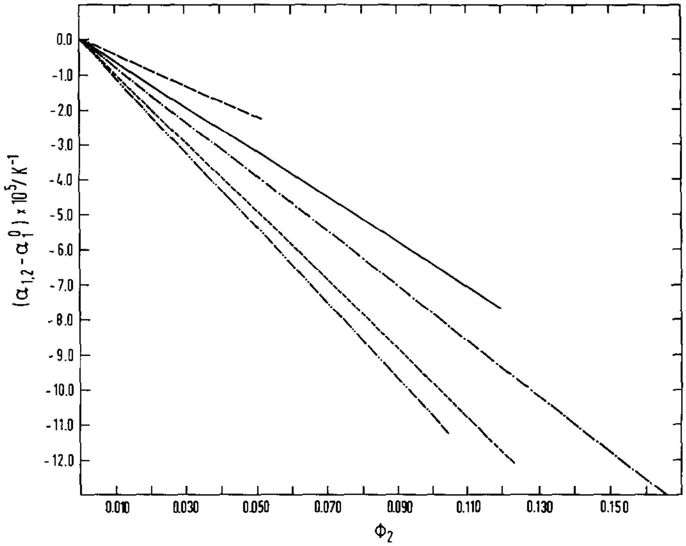

Fig. 2. Dependence of $(\alpha_{1,2} - \alpha_1^0)$ on volume fraction of solute for solvents studied at 298 K: (— — —) 1,2-dichloroethane; (———) toluene; (–·–·–) chloroform; (------) carbon tetrachloride and (– –··) benzene.

On the other hand, as was shown previously, the thermal expansion coefficient of a solution may be given as the sum of two terms [20]

$$\alpha_{1,2} = \alpha_{1,2}^{\mathrm{id}} + \alpha_{1,2}^{\mathrm{ex}} \tag{9}$$

where $\alpha_{1,2}^{\mathrm{id}}$ is the thermal expansion coefficient considering the ideal part and $\alpha_{1,2}^{\mathrm{ex}}$ is the excess part of the thermal expansion coefficient of the solution. The term $\alpha_{1,2}^{\mathrm{ex}}$ includes contributions due to the specific and non-specific interactions associated with the self-association process as well as solute–solvent interactions. From equation (9) and the results presented in Fig. 2 it may be concluded that the values of $\alpha_{1,2}^{\mathrm{ex}}$ increase linearly with increasing concentration of solute.

The partial molar volume of a solute at infinite dilution, where only solute–solvent interactions exist, can be assumed to be the sum of a number of contributions, e.g. the intrinsic volume of the non-solvated molecules and terms which take into account the volume changes undergone by the solvent molecules in the solvation process [15]. According to the scaled particle theory, the expression for partial molar volume of a solute at infinite dilution can be given by [10,21,22]

$$\bar{V}_{2,0} = \bar{V}_{\mathrm{cav}} + \bar{V}_{\mathrm{int}} + \kappa_1^0 RT \tag{10}$$

where $\bar{V}_{\mathrm{cav}}$ (cm^3 mol^{-1}) is the volume contribution to the partial molar volume of solute associated with cavity formation in the liquid, and $\bar{V}_{\mathrm{int}}$ (cm^3 mol^{-1}) is the volume contribution due to the solute–solvent interactions; κ_1^0RT (cm^3 mol^{-1}) arises from the changes in the standard state between gas and solution; κ_1^0 is the isothermal compressibility of a solvent, and R is the gas constant.

The creation of a cavity is by definition a positive contribution to the partial molar volume of a solute, whereas the attractive forces between the solute and the surrounding solvent cause a negative contribution by "shrinking" the cavity [21].

The expression for calculation of $\bar{V}_{\text{cav}}$ is [23]

$$\bar{V}_{\text{cav}} = \kappa_1^0 RT\left(\frac{y}{1-y} + \frac{3yz(1+z)}{(1-y)^2} + \frac{9y^2z^2}{(1-y)^3}\right) + \frac{\Pi\sigma_2^3 N}{6} \tag{11}$$

where y is the ratio of the volume occupied by one mole of hard sphere solvent molecules to the molar volume of the solvent, and z is the ratio of solute σ_2 and solvent σ_1 hard sphere diameters

$$y = \frac{\Pi\sigma_1^3 N}{6V_1^0} \tag{12}$$

and

$$z = \frac{\sigma_2}{\sigma_1} \tag{13}$$

From relation (11) it may be concluded that the cavity contribution depends on the intrinsic size of the solute and the solvent molecule, and also on the isothermal compressibility of the solvent.

In order to get a consistent set of data for hard sphere diameters of the investigated solvents, the values of y were calculated from [22]

$$\kappa_1^0 = \frac{V_1^0(1-y)^4}{RT(1+2y)^2} \tag{14}$$

and then the hard sphere diameters of solvents were obtained via relation (12). The values of κ_1^0 for the solvents studied were taken from ref. 11. The obtained values of y and σ_1 are given in Table 10. The hard sphere diameters so obtained for the solvents are slightly lower than those given in the literature; e.g. 0.526 nm for benzene [21], 0.537 nm for carbon tetrachloride [21] and 0.564 nm for toluene [24] at 298 K. The hard sphere diameter of the solute molecule, $\sigma_2 = 0.961$ nm, was calculated from De Ligny's empirical formula [25], using the van der Waals volume of cholesterol from ref. 18. The calculated values of $\bar{V}_{\text{cav}}$ for the investigated systems are positive and large (see Table 10). The $\bar{V}_{\text{cav}}$ values can be correlated with the normalized empirical solvent polarity parameter E_T^N [26] given in Table 10. From Table 10 it can be seen that the $\bar{V}_{\text{cav}}$ values decrease with the increasing values of E_T^N.

TABLE 10

Solvent data for the scaled particle theory and values of $\bar{V}_{\mathrm{cav}}$, $\bar{V}_{\mathrm{int}}$ and $\Delta\Delta H^{\mathrm{int}}$ at 298 K

Solvent	V_1^0 (cm^3 mol^{-1})	$\kappa_1^0 RT$ (cm^3 mol^{-1})	σ_1 (nm)	y	$\bar{V}_{\mathrm{cav}}$ (cm^3 mol^{-1})	$-\bar{V}_{\mathrm{int}}$ (cm^3 mol^{-1})	E_T^N	P_{i} (atm)	$-\Delta\Delta H^{\mathrm{int}}$ (kJ mol^{-1})
Benzene	89.42	2.39	0.501	0.44433	430.41	37.73	0.111	3695	30.8
Toluene	106.87	2.26	0.542	0.46910	431.52	43.00	0.099	3445	31.3
Carbon tetrachloride	97.09	2.68	0.514	0.44086	436.59	47.78	0.052	3349	21.7
Chloroform	80.68	2.40	0.479	0.42963	429.74	39.69	0.259	3715	45.8
1,2-Dichloroethane	79.40	2.10	0.482	0.44546	423.27	24.34	0.327	3969	–

Another macroscopic property related to the cohesive forces and molecular order of liquids is the internal pressure P_i defined as [27]

$$P_i \approx T\frac{\alpha_1^0}{\kappa_1^0} \tag{15}$$

which, for systems where chemical interactions (e.g. hydrogen bonding) are negligible and non-chemical interactions (e.g. polar or non-polar forces) are more important, can be related to the volume of cavity formation in the liquid and the volume associated with the solute–solvent interactions.

Alternatively, the interaction volume may be considered as the sum of volume contributions due to the dispersion interactions $\bar{V}_{disp}$, dipole–dipole $\bar{V}_{dip}$, and dipole–induced dipole interactions $\bar{V}_{induc}$, respectively; i.e. [22]

$$\bar{V}_{int} = \bar{V}_{disp} + \bar{V}_{dip} + \bar{V}_{induc} \tag{16}$$

Because the interaction term is difficult to predict accurately, the $\bar{V}_{int}$ values are calculated from eqn. (10). It is evident that $\bar{V}_{int}$ values depend upon the accuracy of $\bar{V}_{2,0}$ as well as $\bar{V}_{cav}$ determination. The obtained values of $\bar{V}_{int}$ are negative and, together with $\bar{V}_{cav}$ are given in Table 10. From Table 10 it is seen that when $\bar{V}_{cav}$ becomes more positive the $\bar{V}_{int}$ term compensates by becoming more negative. The variations in $\bar{V}_{cav}$ are greater than variations in $\bar{V}_{2,0}$.

In the investigated systems some solvents are apolar (benzene, carbon tetrachloride) and the others are slightly polar [11]; $\mu_1 = 1.83$ D for 1,2-dichloroethane, 1.15 D for chloroform and 0.31 D for toluene. Since the solute molecule is also slightly polar, $\mu_2 = 1.66$ D for cholesterol [3], it may be concluded that the contribution to the $\bar{V}_{int}$ value arises primarily from the intermolecular dispersion forces [22].

Recently, Góralski et al. [5] determined the interaction enthalpies of cholesterol with various solvents relative to cyclohexane. The measured values of $\Delta\Delta H^{int}$ are given in Table 10. From Table 10 it is seen that the greatest value of $\Delta\Delta H^{int}$ is for the chloroform solution of cholesterol, where also the contributions from hydrogen bonding between the acidic proton of chlorinated hydrocarbons and the oxygen atom of the cholesterol molecule must be taken into account [2]. On the other hand, the lowest $\Delta\Delta H^{int}$ value is obtained for carbon tetrachloride, which is an inert solvent. For both aromatic solvents $\Delta\Delta H^{int}$ values lie between these limiting values and are practically the same for both solvents. These values demonstrate the weak intermolecular interactions between the Π-electronic system of the aromatic ring of either solvent and the cholesterol molecule.

From the above arguments, the so called "solvent effect" on the partial molar volume of cholesterol at infinite dilution in the solvents studied may be described mainly by the cavity formation and by solute–solvent interactions, arising from the intermolecular dispersion forces and from weak dipole–dipole interactions and hydrogen bonding.

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