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Volumetric investigations of solute–solvent interactions of cytosine and their methyl-, methoxy-, and hydroxy-derivatives in methanol and *N*,*N*-dimethylformamide at 25 °C

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Abstract

Experimentally determined densities of cytosine and their methyl-, methoxy-, and hydroxy-derivatives at 25 °C in methanol and *N*,*N*-dimethylformamide are presented. The apparent molar volumes and then the partial molar volumes V_2^0 were calculated. Together with previously obtained V_2^0 for aqueous solutions of compounds studied: (1) the transfer functions $\Delta V_{2,\mathrm{tr}}^0$ water–methanol, water–*N*,*N*-dimethylformamide; (2) the contributions to V_2^0 value which correspond to substitution on cytosine moiety of a hydrogen atom on a N, O, C atom by CH_3 group and replacement of a hydrogen on N^4 by an OH group were determined and discussed.

Structural parameters: molecular accessible surface S^{M} areas and their atomic partition S_{N}, S_{O}, $S_{\mathrm{H(N,O)}}$, molecular volumes V_2^{M} of compounds studied were calculated. Its enables to determine the correlations between volumetric properties and structural parameters according to the model which is based on the assumptions that density of solvation shell α depends on polarity P and the structure of the hydrophobic compounds. The transfer functions $\Delta V_{2,\mathrm{tr}}^0$ water–methanol, water–*N*,*N*-dimethylformamide were also calculated and discussed.

Keywords: Partial molar volume; Molecular volume; Methyl-, methoxy-, and hydroxy-cytosines; Relative density of solvation shell

1. Introduction

Previously [1] were presented the results of enthalpic investigations of cytosine and some methylated, hydroxy- and methoxy-derivatives of cytosine in nonaqueous solutions. The subject of this paper was the determination of partial molar volumes of these compounds in nonaqueous solvents (*N*,*N*-dimethylformamide and methanol). The purpose of these investigations was to enlarge the conclusions from our determination of the enthalpy of solvation. It was demonstrated, that in the aqueous solutions both acceptors and donors of protons are involved into the specific solute–solvent interactions; methanol, which is more active as a donor of protons interacts with the oxygen and nitrogen atoms, whereas DMF interacts solely with the hydrogen atom of the solute. These assumptions were made using the model of solute–solvent interactions, which postulates that density of solvation shell depends on the structure and polarity of compounds studied.

The obtained results of V_2^0 were elaborated using:

(1) the general addivity scheme giving the possibilities to determine the contributions to V_2^0 value

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identified as $Z_{CH_2(N)}$, $Z_{CH_2(C)}$, $Z_{CH_2(O)}$ and Z_O which correspond to substitution on cytosine moiety of a hydrogen atom on a N, O, C atom by CH_3 group and replacement of a hydrogen on N^4 by an OH group;

(2) the transfer functions $\Delta V^0_{2,tr}$ water–methanol, water–*N*,*N*-dimethylformamide;
(3) structural parameters: molecular accessible surface areas S^M, their atomic partition S_N, S_O, $S_{H(N,O)}$ and molecular volumes V^M_2 of compounds studied;
(4) the model, which is based on assumption that density of solvation shell depends on structure and polarity of the compounds studied.

2. Experimental

2.1. The objectives

The compounds studied are: cytosine (Cyt), 1-methylcytosine (m^{1}Cyt), 1,5-dimethylcytosine (m^{1,5}Cyt), 1-methyl-N^4-hydroxycytosine (m$^1N^4$OHCyt), 1,5-dimethyl-N^4-hydroxycytosine (m$^{1,5}N^4$OHCyt), 1-methyl-N^4-methoxycytosine (m$^1N^4$OmCyt), 1,5-dimethyl-N^4-methoxycytosine (m$^{1,5}N^4$OmCyt), 1,N^4-dimethylcytosine (m$^1N^4$Cyt), 1,N^4-dimethyl-5-ethylcytosine (m$^1N^4$e^{4}Cyt), 1,N^4-dimethyl-5-propylcytosine (m$^1N^4$p^{4}Cyt), and 1,N^4-dimethyl-5-butylcytosine (m$^1N^4$b^{4}Cyt), of the structure given on Fig. 1. Cytosine (Lot 16H1023), 1-methylcytosine (Lot 93H0377), 1,5-dimethylcytosine (Lot 83F0667) were obtained from Sigma. The remaining compounds were individually synthesised in the Institute of Basic Sciences, Military School of Medicine, Lodz, Poland. The compounds were tested by elementary analysis; the mass-spectra analysis using LKB 9000S device with the application of ionic beams of 15 and 20 eV: the 1H^{1}NMR spectra were obtained with Brucker 300 MHz apparatus, X-ray measurements on CAD-4 diffractometer with a graphite monochromator using w-20 scan technique. The compounds were thoroughly purified by repeated crystallisation and repeated vacuum sublimation and were carefully dried for several days. Their identity and purity (better

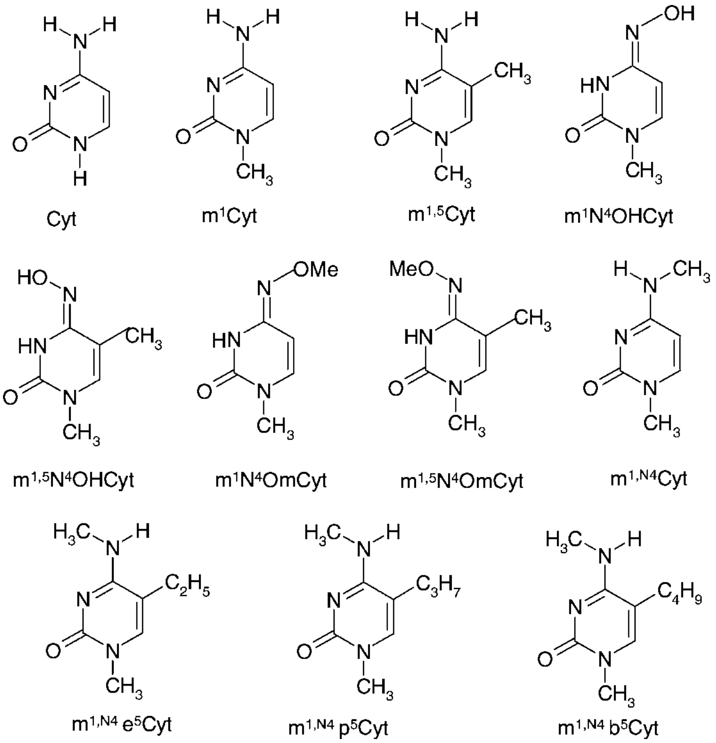

Fig. 1. Structural formulas of the compounds studied.

than 99.4%) was checked by the use of a DSC Du Pont Thermal Analysis System and chromatographic analysis in several solvent systems.

Methanol (POCh Gliwice, Poland) was dehydrated by distillation and stored in an inert gas atmosphere in hermetically sealed ampoules of volume 2.5 ml. The ampoules were opened immediately before the volumetric measurement. The moisture content determined by the Fischer method was 0.01%. Chemically pure *N*,*N*-dimethylformamide (POCh Gliwice, Poland) was distilled at a reduced pressure and stored over 4A type molecular sieves. Its moisture content was 0.01%.

2.2. Methods

Densities of the solutions relative to the density of pure solvent were measured with an Anton Paar DMA 60/602 digital densimeter at 25 °C. For each systems five or six density experiments were carried out. The apparent molar volumes V_ϕ of the solute were calculated from solution densities d using following relation:

$$V_\phi = \frac{M}{d} - \frac{1000(d - d_0)}{m\,d\,d_0} \tag{1}$$

where d_0 is the density of pure solvents, m the molality, and M the molar mass of the solute. The geometrical parameters of each molecule were determined by the method of molecular mechanics according to the SYBYL program [2], whereas molecular volumes V_2^{M}, volumes of solvation shell $V_{1,\mathrm{solv}}$ as well as molecular accessible surface areas S^{M} and its atomic partitions S_{A} were calculated with help of GEPOL Version 12.1 [3] by using a standard set of atomic radii. Surface accessible areas for solvent was calculated according to the method given by Lee and Richards [4] as the surface generated by the center of the solvent, considered as a rigid sphere rolled over Van der Waals surface (external surface build from a set a rigid spheres centered on the atoms or group of atoms forming the molecule). As was shown [1] according to the both quantum mechanical calculations [5], UV spectroscopic [6], X-ray data [7] and H^{1}NMR-data [1] of N^4-methoxy and N^4-hydroxy-derivatives were analysed in either *trans* or *cis* conformation.

The volume of solvation shell $V_{1,\mathrm{solv}}$ was calculated as equal to the volume determined by rolling sphere of diameter of one solvent over the surface of the solute. The relative densities of salvation shell α [8,9], characterising the structure of solvent around the solute molecules and expressed as a ratio of the difference between partial molar volume V_2^0 and molecular volume V_2^{M} divided by the volume $V_{1,\mathrm{solv}}$ of the solvation shell were calculated according to the Eq. (2):

$$\alpha = \frac{V_2^{\mathrm{M}} - V_2^0}{V_{1,\mathrm{solv}}} \tag{2}$$

Relative density of solvation shell was correlated with the polarity P. Polarity P was defined as a ratio of molecular surface of polar groups and atoms exposed to the total molecular surface of the solute molecule and according to the assumptions made before was calculated for aqueous solutions as: $S_{\mathrm{O}} + S_{\mathrm{N}} + S_{\mathrm{H(N,O)}}$, for methanol solutions as $S_{\mathrm{O}} + S_{\mathrm{N}}$: and for *N*,*N*-dimethylformamide: $S_{\mathrm{H(N,O)}}$.

The results of the partial molar volumes are analyzed on the basis of the group additivity scheme according to the following formula:

$$X = X_0 + \sum_i n_i Z_i \tag{3}$$

where X_0 is a constant; Z_i the additive value for group i; and n_i the number of groups type i. In our calculations, X_0 corresponds to partial molar volumes of cytosine; the groups i are CH_2(N), CH_2(C), CH_2(O) and O. Values X_0 and Z_i were estimated using standard multilinear regression based on least squares.

The molar volumes of transfer water(L_1)–methanol (L_2), water(L_1)-*N*,*N*-dimethylformamide(L_2) were determined according to the relation:

$$\Delta V_{2,\mathrm{tr}}^0(L_1 \to L_2) = V_2^0(L_2) - V_2^0(L_1) \tag{4}$$

3. Results and discussion

The apparent molar volumes are collected in Tables 1 and 2, respectively, for methanol and *N*,*N*-dimethylformamide, where m is molality, d the density of solution and V_ϕ the apparent molar volume. Within the range of experimental concentrations apparent molar volume was found to be unrelated to concentration. Therefore, the average apparent molar volumes were assumed to be identical with the partial molar volumes at infinite dilution. The data of partial

Table 1
Apparent molar volumes V_ϕ of cytosine and their derivatives at 25 °C in methanol

m (mol kg^{-1})	d (g cm^{-3})	V_ϕ (cm^3 mol^{-1})
Cyt		
0.019000	0.787576	58.11
0.016054	0.787417	58.91
0.014389	0.787340	58.07
0.013994	0.787317	58.40
0.008470	0.787036	58.07
m^{1}Cyt		
0.028936	0.787963	82.77
0.011648	0.787261	83.79
0.009475	0.787042	83.60
0.008279	0.786988	83.22
0.005584	0.786860	83.76
m^{1,5}Cyt		
0.015689	0.787310	103.68
0.013528	0.787213	103.60
0.012643	0.787173	103.59
0.010945	0.787095	103.76
0.009767	0.787048	102.72
0.007999	0.786966	102.92
m$^1N^4$OHCyt		
0.013739	0.787413	83.70
0.013504	0.787399	83.67
0.012817	0.787359	83.64
0.011896	0.787306	83.43
0.010508	0.787225	83.21
0.008080	0.787084	82.56
m$^{1,5}N^4$OHCyt		
0.018102	0.787628	104.07
0.015678	0.787491	103.82
0.012831	0.787328	104.24
0.012098	0.787290	103.73
0.010403	0.787192	103.94
0.009090	0.787118	103.82
m$^1N^4$OmCyt		
0.032684	0.788342	110.81
0.023954	0.787882	110.57
0.021800	0.787768	110.50
0.017744	0.787550	110.59
0.012860	0.787291	110.31
m$^{1,5}N^4$OmCyt		
0.019966	0.787667	128.21
0.018152	0.787574	128.21
0.015667	0.787439	128.40
0.014495	0.787377	128.09
0.010566	0.787164	128.64
m$^1N^4$e^{5}Cyt		
0.013289	0.787300	131.11
0.013616	0.787330	131.44
0.015595	0.787420	131.92
0.018002	0.787544	132.65
0.023654	0.787821	131.84
0.024000	0.787843	131.48
m$^1N^4$p^{5}Cyt		
0.010099	0.787281	147.56
0.012747	0.787291	146.35
0.013902	0.787499	147.74
0.015828	0.787441	147.20
0.017200	0.787509	147.43
m$^1N^4$b^{5}Cyt		
0.008696	0.786986	174.63
0.009456	0.787020	174.62
0.011482	0.787112	174.59
0.011676	0.787127	174.52
0.011815	0.787130	174.27
m$^1N^4$Cyt		
0.016965	0.787492	101.18
0.016452	0.787471	100.71
0.013350	0.787297	104.14
0.012802	0.787302	100.32
0.011293	0.787227	100.89

molar volumes V_2^0 data for aqueous [10], methanol and *N*,*N*-dimethylformamide solutions together with the calculated values of molecular volume V_2^M, volume of solvation shell $V_{1,\mathrm{solv}}$, molecular accessible surface areas S^M of the molecule, surface of nitrogen S_N oxygen S_O and hydrogen atoms $S_{H(N,O)}$ of the cytosine skeleton, and the relative density of solvation shell are presented in Table 3.

The contributions to V_2^0 value identified as $Z_{CH_2(N)}$, $Z_{CH_2(C)}$, $Z_{CH_2(O)}$ and Z_O which correspond to substitution on cytosine moiety of a hydrogen atom on a N, O, C atom by CH_3 group and replacement of a hydrogen on N^4 by an OH group were determined and the results were given in Table 4. The inspection in data for methyl-, methoxy-, and hydroxy-derivatives collected in Table 4 shows that:

(1) The increment in the partial molar values depends strongly on the placement of substitution of the CH_2 groups, while $Z_{CH_2(O)} > Z_{CH_2(N)} > Z_{CH_2(C)}$. For all solvents the most significant contribution to the partial molar volumes is brought by the substitution of a hydrogen atom on O^4 atom by a CH_3 group and the least by substitution of a hydrogen atom on C atom by a CH_3 group.

Table 2
Apparent molar volumes V_ϕ of cytosine and their derivatives at 25 °C in *N*,*N*-dimethylformamide

m (mol kg^{-1})	d (g cm^{-3})	V_ϕ (cm^3 mol^{-1})
Cyt		
0.009674	0.944295	68.36
0.008566	0.944241	68.98
0.007441	0.944195	68.66
0.006351	0.944146	68.91
0.006121	0.944136	68.91
0.005882	0.944126	68.67
$\mathrm{m}^{1}\mathrm{Cyt}$		
0.014638	0.944409	91.05
0.010796	0.944264	91.54
0.010280	0.944256	90.36
0.009629	0.944224	91.25
0.008305	0.944175	91.29
$\mathrm{m}^{1,5}\mathrm{Cyt}$		
0.007994	0.944150	108.09
0.007413	0.944124	108.79
0.006977	0.944113	108.40
0.005995	0.944078	108.47
0.004744	0.944036	108.14
$\mathrm{m}^{1}N^{4}\mathrm{OHCyt}$		
0.013913	0.944518	97.21
0.011507	0.944404	97.42
0.006709	0.944190	96.02
0.006431	0.944170	97.09
0.005186	0.944116	96.36
0.004286	0.944069	97.26
$\mathrm{m}^{1}N^{4}\mathrm{Cyt}$		
0.018975	0.944701	111.36
0.014183	0.944526	112.82
0.013646	0.944522	111.79
0.013246	0.944509	111.82
0.012696	0.944468	112.95
0.010808	0.944433	111.79
$\mathrm{m}^{1,5}N^{4}\mathrm{OHCyt}$		
0.028846	0.945059	116.92
0.024076	0.944868	116.68
0.014250	0.944452	117.38
0.013770	0.944430	117.64
0.013419	0.944421	117.20
0.011188	0.944414	117.77
$\mathrm{m}^{1}N^{4}\mathrm{OmCyt}$		
0.016024	0.944469	122.36
0.015099	0.944448	122.37
0.012289	0.944331	122.22
0.011373	0.944298	122.06
0.009946	0.944242	122.33
0.008947	0.944202	122.78
$\mathrm{m}^{1,5}N^{4}\mathrm{OmCyt}$		
0.020605	0.944538	142.74
0.013618	0.944306	143.24
0.013410	0.944303	142.94
0.009073	0.944163	142.96
0.008047	0.944131	142.86
0.007337	0.944107	142.96
0.005625	0.944053	142.71
$\mathrm{m}^{1}N^{4}\mathrm{e}^{5}\mathrm{Cyt}$		
0.011737	0.994462	145.38
0.011656	0.944487	145.02
0.010528	0.944432	146.61
0.010417	0.944452	145.07
0.009481	0.944417	145.12
0.008568	0.944395	145.64
$\mathrm{m}^{1}N^{4}\mathrm{p}^{5}\mathrm{Cyt}$		
0.017560	0.944507	158.90
0.016054	0.944459	159.21
0.012584	0.944356	159.52
0.009955	0.944287	159.36
0.008248	0.944157	158.74
$\mathrm{m}^{1}N^{4}\mathrm{b}^{5}\mathrm{Cyt}$		
0.012052	0.944233	176.90
0.010685	0.944190	177.68
0.009312	0.944162	176.78
0.008976	0.944158	176.21

(2) The specificity of substitution of hydrogen by CH_3 on N^1 or C^5 atoms of the cytosine skeleton is evident for methanol and water.

(3) Substitution of hydrogen of an OH group by a CH_3 group gives for water and DMF the highest increment value.

(4) The contribution Z_{O} for water and DMF are similar, whereas for the methanol solutions the obtained Z_{O} values is negligibly small. It may be explained by strong interactions between methanol and oxygen of cytosine skeleton, resulting from donor properties of methanol.

(5) The contribution in partial molar volume, corresponding to replacement of a hydrogen atom on the N^4 atom by an OH group is higher for DMF solutions than for aqueous solutions. It is result of acceptors properties of *N*,*N*-dimethylformamide.

(6) The obtained values are in good agreement with literature data [11]: $Z_{\mathrm{CH_2}} = 16.0 \pm$

Table 3
Structural parameters S^{M} S_{N}, S_{O}, $S_{\mathrm{H(N,O)}}$, V_2^{M} and partial molar volumes V_2^0 of cytosine and their derivatives in water [1], methanol and *N*,*N*-dimethylformamide

	Volume ($\mathrm{cm^3\,mol^{-1}}$)			Surface (A^2)				α	P
	V_2^0	V_2^{M}	$V_{1,\mathrm{solv}}$	S_{O}	S_{N}	$S_{\mathrm{H(N,O)}}$	S^{M}		
Cyt									
Water	73.7	46.9	431.5	14.6	24.6	20.6	102.0	−0.062	0.586
Methanol	58.31 ± 0.08	47.2	671.8	14.6	24.4	20.3	100.4	−0.017	0.388
DMF	68.75 ± 0.05	47.6	1146.7	14.5	23.8	19.8	98.1	−0.018	0.202
m^1Cyt									
Water	91.91 ± 0.02	56.2	477.7	13.3	22.6	13.8	116.5	−0.075	0.427
Methanol	83.43 ± 0.08	56.7	738.3	13.2	22.4	13.6	108.5	−0.036	0.328
DMF	91.10 ± 0.06	57.2	1247.1	12,9	21.7	13,3	111.1	−0,027	0.119
$\mathrm{m}^{1,5}$Cyt									
Water	107.46 ± 0.03	65.5	518.4	13.3	22.4	12.5	130.3	−0.081	0.369
Methanol	103.38 ± 0.09	66.1	794.6	13.2	22.0	12.2	127.6	−0.046	0.276
DMF	108.38 ± 0.06	66.8	1334.1	12.9	21.4	11.9	124.1	−0.031	0.096
m^1N^4Cyt									
Water	109.29 ± 0.08	65.3	528.8	13.3	18.0	6.4	131.6	−0.084	0.286
Methanol	101.44 ± 0.34	65.6	818.4	13.2	17.4	6.2	116.7	−0.044	0.262
DMF	112.09 ± 0.13	66.7	1347.4	12.9	18.0	6.3	111.9	−0.034	0.056
$\mathrm{m}^1N^4\mathrm{e}^5$Cyt									
Water	142.4 ± 0.1	84.7	607.0	13.3	17.1	4.5	156.9	−0.095	0.222
Methanol	131.74 ± 0.11	85.2	913.7	13.1	18.1	6.6	129.6	−0.051	0.221
DMF	145.47 ± 0.12	87.0	1515.7	12.9	17.2	6.0	148.8	−0.039	0.048
$\mathrm{m}^1N^4\mathrm{p}^5$Cyt									
Water	156.7 ± 0.1	93.7	649.2	13.4	17.1	4.5	164.1	−0.097	0.213
Methanol	147.26 ± 0.07	95.5	972.9	13.2	18.1	6.1	138.9	−0.054	0.204
DMF	159.15 ± 0.11	97.5	1621,9	12,9	17.1	5.9	153,7	−0.038	0.044
$\mathrm{m}^1N^4\mathrm{b}^5$Cyt									
Water	172.0 ± 0.1	103.3	693.8	13.3	17.0	4.6	175.8	−0.099	0.199
Methanol	174.53 ± 0.08	105.6	1036.1	13.1	17.8	6.1	146.9	−0.067	0.193
DMF	176.89 ± 0.15	108.1	1699.5	12.9	17.2	5.9	161.1	−0.043	0.041
m^1N^4OHCyt									
Water	97.7 ± 0.05	60.7	504.5	23.9	19.9	14.1	124.7	−0.073	0.464
Methanol	83.37 ± 0.04	61.3	778.2	23.6	19.4	13.8	121.9	−0.028	0.369
DMF	96.89 ± 0.12	61.8	1307.0	23.0	18.6	13.5	118.5	−0.027	0.114
$\mathrm{m}^{1,5}N^4$OHCyt									
Water	113.72	69.9	542.7	23.8	19.5	12.9	138.3	−0.081	0.406
Methanol	103.94 ± 0.09	70.4	826.0	23.4	19.0	12.6	138.9	−0.040	0.310
DMF	117.27 ± 0.09	71.3	1405.5	22.8	18.3	12.1	131.0	−0.033	0.092
m^1N^4OmCyt									
Water	119.92 ± 0.04	70.1	567.1	21.5	19.2	5.8	142.2	−0.088	0.327
Methanol	110.56 ± 0.04	70.5	863.5	21.1	18.7	5.4	139.4	−0.046	0.286
DMF	122.35 ± 0.09	71.2	1443.2	20.6	17.8	5.2	135.5	−0.035	0.038
$\mathrm{m}^{1,5}N^4$OmCyt									
Water	135.08 ± 0.1	78.9	602.2	21.5	18.8	4.4	156.2	−0.093	0.286
Methanol	128.31 ± 0.09	79.7	915.3	21.0	18.2	4.1	152.4	−0.053	0.257
DMF	142.92 ± 0.04	80.7	1530.7	20.4	17.4	3.8	148.3	−0.041	0.026

Table 4
Contribution of Z_i for CH_2(N), CH_2(C), CH_2(O) and O substitutents in the V_2^0 values for water, methanol and *N*,*N*-dimethylformamide solutions

	X_0	$Z_{CH_2(N)}$	$Z_{CH_2(C)}$	$Z_{CH_2(O)}$	Z_O	R
Water	73.7 ± 0.6	18.1 ± 0.4	15.6 ± 0.2	21.8 ± 0.6	6.0 ± 0.5	0.9997
Methanol	61.8 ± 4.7	19.1 ± 3.0	17.9 ± 1.4	25.8 ± 4.7	3.8 ± 3.6	0.9880
DMF	69.5 ± 2.1	21.3 ± 1.3	16.3 ± 0.6	25.5 ± 2.1	8.1 ± 1.7	0.9975

Table 5
Contribution of Z_i for CH_2(N), CH_2(C) substitutents in the V_2^0 values for methanol and *N*,*N*-dimethylformamide solutions of cytosine and uracil

	Methanol				*N*,*N*-dimethylformamide			
	X_0	$Z_{CH_2(C)}$	$Z_{CH_2(N)}$	R	X_0	$Z_{CH_2(C)}$	$Z_{CH_2(N)}$	R
Uracil[a]	70.5 ± 3.1	14.9 ± 1.8	18.8 ± 1.3	0.994	72.4 ± 3.6	16.1 ± 2.1	19.9 ± 1.5	0.997
Cytosine	61.8 ± 4.7	17.9 ± 1.4	19.1 ± 3.0	0.988	69.5 ± 2.1	16.3 ± 0.6	21.3 ± 1.3	0.998

[a] From [12].

$0.5\,cm^3\,mol^{-1}$, $Z_O = 7.6 \pm 0.1\,cm^3\,mol^{-1}$ (water); $Z_{CH_2} = 18.21 \pm 0.01\,cm^3\,mol^{-1}$, $Z_O = 7.5 \pm 0.2\,cm^3\,mol^{-1}$ (DMF); $Z_{CH_2} = 17.72 \pm 0.01\,cm^3\,mol^{-1}$, $Z_O = -1.1 \pm 0.2\,cm^3\,mol^{-1}$ (methanol).

In Table 5 the previously obtained data of Z_{CH_2} for alkylated derivatives of uracil were collected. Data reported in Table 5 shows the specificity of substitution of hydrogen atom by CH_3 on N or C atoms of the pyrimidine skeleton.

The linear relations between relative densities α of solvation shell and polarity P were found according to Eq. (5) similarly as in the case of alkylated derivatives of uracil [12] and other series of aqueous solutions of hydrophobic compounds [8].

$$\alpha = \alpha_0 + bP \tag{5}$$

The obtained values α_0 and b are presented in Table 6. It can be assumed that, the α_0 values contain the correction for the change of the solvent density caused by introducing of completely apolar solute. The higher is α_0 value, the less disturbed is the structure of solvent in solvation sphere. Between the values of α_0 obtained for water, methanol and *N*,*N*-dimethylformamide solutions the distinct differences are observed. The least change in density of solvation shell is caused by introducing of cytosine derivatives to *N*,*N*-dimethylformamide solutions of the compounds studied and the highest changes in aqueous solutions.

Table 6
The values of α_o, *i*, *b* for water, methanol *i* *N*,*N*-dimethylformamide

	α_o	b	R
Water	−0.117 ± 0.003	0.093 ± 0.007	0.957
Methanol	−0.100 ± 0.004	0.200 ± 0.022	0.904
DMF	−0.043 ± 0.002	0.126 ± 0.011	0.939

The transfer functions $\Delta V_{2,tr}^0$ are reported in Table 7. The obtained results of $\Delta V_{2,tr}^0$ water–methanol are more negative than water–DMF. The results of $\Delta V_{2,tr}^0$ water–methanol, water–DMF are in agreement with the following sequences: Cyt < m^1Cyt <

Table 7
Partial molar volumes of transfer $\Delta V_{2,tr}^0$ water–methanol, water–*N*,*N*-dimethylformamide

	$\Delta V_{2,tr}^0$ ($cm^3\,mol^{-1}$)	
	(Water–methanol)	(Water–DMF)
Cyt	−15.39	−4.95
m^1Cyt	−8.48	−0.81
$m^{1,5}$Cyt	−4.08	0.98
m^1N^4OHCyt	−14.33	−0.81
$m^{1,5}N^4$OHCyt	−9.78	3.55
m^1N^4OmCyt	−9.36	2.43
$m^{1,5}N^4$OmCyt	−6.77	7.84

$m^{1,5}$Cyt < m^1N^4OHCyt < $m^{1,5}N^4$OHCyt < m^1N^4OmCyt < $m^{1,5}N^4$OmCyt.

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