

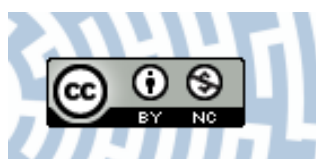


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**Title:** Volumetric properties of binary mixtures of 2,4,6-trimethylpyridine with 1,2-ethanediol, methanol, and water, and the association energies of the O-H...N bonded complexes

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# Volumetric Properties of Binary Mixtures of 2,4,6-Trimethylpyridine with 1,2-Ethanediol, Methanol, and Water, and the Association Energies of the O–H···N Bonded Complexes

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**Abstract** 2,4,6-Trimethylpyridine forms 1:1 complexes with methanol, 1,2-ethanediol, and water due to the O–H···N bonds. The association energy of the complexes was calculated using MP2 and DFT methods. The complexes with 1,2-ethanediol and water aggregate in the liquid phase as a result of the O–H···O bonds. In spite of the higher O–H···N bond energy, the aggregation of the ethanediolic complexes is less pronounced than that of the aqueous ones. That is probably caused by the weaker induction effect due to the C–C chain separating the hydroxyl groups in the diol molecule. Aggregation is impossible in the methanolic system, because of the lack of proton-donating functional groups. Differences in the hydrogen bond energy and in the ability to aggregate are manifested in the volumetric properties of the mixtures.

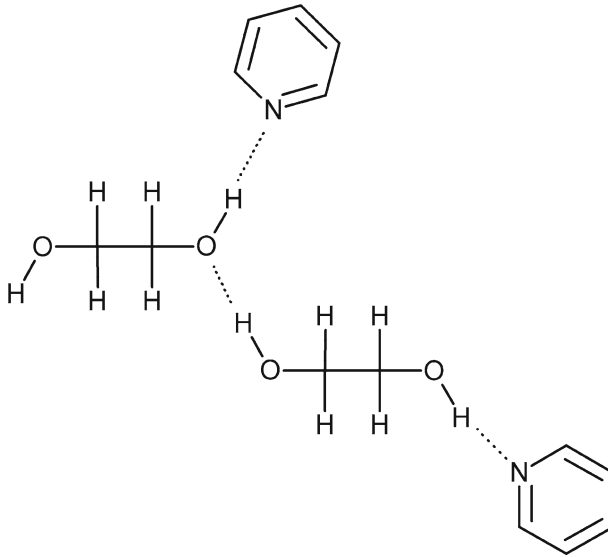
**Keywords** Association energy · Hydrogen-bonded complexes · Molar expansion · Molar volume · Partial functions · Thermodynamic excess

## 1 Introduction

In a paper published recently, we suggested that hydrogen-bonded complexes of pyridine and its methyl derivatives with 1,2-ethanediol,  $\text{RN} \cdots \text{H}-\text{OC}_2\text{H}_4\text{OH}$ , aggregate in the liquid mixtures in a way as sketched in Fig. 1 [1]. Similar structures occur also in aqueous solutions of the pyridines, as results from small-angle neutron scattering, infrared, thermodynamic, and ultrasonic absorption experiments [2, 3]. Direct evidence of the aggregation through the O–H···O bonds between water molecules in the crystalline trihydrates of pyridine and 4-methylpyridine was obtained by X-ray diffraction [4, 5]. Thus, solvophilic solvation consisting mainly of the formation of the O–H···N

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**Fig. 1** Association of the pyridine–1,2-ethanediol complexes

bonds, as well as the association of the complexes, is a characteristic for aqueous and 1,2-ethanediolic solutions of pyridine and its derivatives. Similar to water, 1,2-ethanediol forms a three-dimensional, hydrogen-bonded network in crystals [6–8]. This supports the idea of the solvent-induced aggregation of pyridines in both solvents. Two questions seem of particular interest: first, the influence of the  $\text{O-H} \cdots \text{N}$  bond energy on the properties of the liquid mixtures and second, the co-operative strengthening of  $\text{O-H} \cdots \text{O}$  bonds in the neighborhood of the  $\text{O-H} \cdots \text{N}$  bond.

In the present work, we report results of volumetric studies of binary mixtures of 2,4,6-trimethylpyridine with 1,2-ethanediol and methanol compared with previously published data for the aqueous system [9]. Association energies of the 1:1 complexes of the amine with the proton-donating molecules were calculated using different methods of quantum chemistry. The two approaches made it possible to suggest an explanation of similarities and differences in the molar excesses of volume and expansions as well as those in the partial molar volumes.

## 2 Experimental

### 2.1 Chemicals

2,4,6-Trimethylpyridine (Aldrich, purity 99 %), methanol (POCH, for HPLC, min. 99.9 %), and 1,2-ethanediol (Fluka, min. 99.5 %), were used as supplied by the manufacturer. The purity of the liquid samples is evidenced by the measured densities that are very close to literature data (Table 1). The chemicals were stored in dark

**Table 1** Densities  $\rho$  of 2,4,6-trimethylpyridine, methanol, and 1,2-ethanediol at  $T = 298.15$  K used in this study and reported in the literature

Liquid	$\rho$ ( $\text{kg} \cdot \text{m}^{-3}$ )	
	This work	Literature
2,4,6-Trimethylpyridine	909.838	909.80 [21], 909.97 [9]
Methanol	786.549	786.37 [22], 786.4 [23], 786.49 [24], 786.5 [25, 26], 786.6 [27], 786.64 [28], 786.65 [29], 786.654 [30]
1,2-Ethanediol	1109.868	1109.6 [31], 1109.7 [32], 1109.87 [33], 1109.88 [34], 1109.90 [35], 1109.91 [36]

glass flasks, the alcohols at room temperature, while 2,4,6-trimethylpyridine, which is chemically unstable, in a refrigerator.

The mixtures were prepared by mass using an Acculab ATL-224-V analytical balance with an accuracy of  $\pm 1 \times 10^{-3}$  g. Before measurements, every sample was degassed in an ultrasonic cleaner, Unitra Unima UM4. The solutions were used immediately after they were prepared.

## 2.2 Apparatus

The densities were measured by a vibrating-tube densimeter (Anton Paar DMA 5000) with an uncertainty of  $5 \times 10^{-2}$   $\text{kg} \cdot \text{m}^{-3}$ . The uncertainty was estimated from the results of measurements of density standards: pure organic liquids and aqueous solutions of salts.

## 3 Results

Densities of pure liquids and their binary mixtures, measured at temperatures from 276.15 K to 313.15 K, are reported in Table 2. Their temperature dependences were approximated by second-order polynomials:

$$\rho/(\text{kg} \cdot \text{m}^{-3}) = \sum_{i=0}^2 a_i (T/\text{K} - 273.15)^i \quad (1)$$

where  $T$  is the absolute temperature and  $a_i$ 's are the polynomial coefficients calculated by the least-squares method and collected in Table 3. Since the mean deviations from the regression lines were smaller than the measurement uncertainty, the densities obtained from Eq. 1 rather than the raw experimental data were used in further calculations.

From the densities given by Eq. 1, the molar volumes  $V$  were calculated:

$$V = (M_1 x_1 + M_2 x_2) / \rho, \quad (2)$$

**Table 2** Densities measured by the vibrating tube densimeter

$x_1$	$T$ (K)	$\rho$ (kg · m <sup>-3</sup> )	$T$ (K)	$\rho$ (kg · m <sup>-3</sup> )	$T$ (K)	$\rho$ (kg · m <sup>-3</sup> )	$T$ (K)	$\rho$ (kg · m <sup>-3</sup> )	$T$ (K)	$\rho$ (kg · m <sup>-3</sup> )
2,4,6-Trimethylpyridine (1) + Methanol (2)										
0.0000	276.15	807.18	277.15	806.25	283.15	800.64	288.15	795.96	293.15	791.26
0.0204	276.15	816.99	277.15	816.06	283.15	810.47	288.15	805.79	293.15	801.11
0.0511	276.15	830.47	277.15	829.54	283.15	823.96	288.15	819.30	293.15	814.63
0.0997	276.15	848.99	277.15	848.07	283.15	842.50	288.15	837.86	293.14	833.20
0.1940	276.15	875.69	277.15	874.77	283.15	869.23	288.15	864.59	293.15	859.94
0.2957	276.15	895.63	277.15	894.71	283.14	889.20	288.15	884.59	293.15	879.97
0.3884	276.15	907.79	277.15	906.88	283.14	901.42	288.15	896.86	293.15	892.28
0.4890	276.15	916.36	277.15	915.47	283.15	910.10	288.15	905.60	293.15	901.10
0.5852	276.15	921.51	277.15	920.64	283.14	915.35	288.15	910.93	293.15	906.50
0.6949	276.15	925.01	277.15	924.15	283.15	918.95	288.15	914.61	293.15	910.25
0.7971	276.15	926.99	277.15	926.14	283.14	921.01	288.15	916.72	293.15	912.41
0.8889	276.15	928.16	277.15	927.31	283.15	922.22	288.15	917.96	293.15	913.69
1.0000	276.15	928.45	277.15	927.61	283.15	922.54	288.15	918.32	293.14	914.08
2,4,6-Trimethylpyridine (1) + Methanol (2)										
0.0000	298.15	786.55	303.15	781.83	308.15	777.08	313.14	772.31		
0.0204	298.15	796.41	303.15	791.70	308.15	786.96	313.14	782.20		
0.0511	298.14	809.94	303.15	805.24	308.15	800.51	313.14	795.75		
0.0997	298.15	828.52	303.15	823.83	308.14	819.11	313.14	814.36		
0.1940	298.15	855.28	303.15	850.60	308.14	845.89	313.15	841.15		
0.2957	298.15	875.33	303.15	870.67	308.15	865.99	313.15	861.28		
0.3884	298.15	887.69	303.15	883.08	308.14	878.45	313.15	873.79		
0.4890	298.15	896.57	303.15	892.04	308.14	887.48	313.14	882.90		

Table 2 continued

$x_1$	$T$ (K)	$\rho$ (kg·m <sup>-3</sup> )	$T$ (K)	$\rho$ (kg·m <sup>-3</sup> )	$T$ (K)	$\rho$ (kg·m <sup>-3</sup> )	$T$ (K)	$\rho$ (kg·m <sup>-3</sup> )	$T$ (K)	$\rho$ (kg·m <sup>-3</sup> )
0.5852	298.15	902.05	303.15	897.58	308.14	893.10	313.15	888.59	293.15	1113.37
0.6949	298.14	905.88	303.15	901.49	308.14	897.08	313.14	892.65	293.15	1104.68
0.7971	298.15	908.10	303.14	903.77	308.14	899.42	313.15	895.05	293.15	1094.67
0.8889	298.14	909.41	303.14	905.12	308.15	900.82	313.15	896.49	293.14	1078.26
1.0000	298.15	909.84	303.15	905.58	308.15	901.31	313.15	897.03	293.15	1052.33
2,4,6-Trimethylpyridine (1) + 1,2-Ethanediol (2)										
0.0000	276.15	1125.17	277.15	1124.48	283.15	1120.32	288.15	1116.86	293.15	1029.98
0.0227	276.15	1116.64	277.15	1115.94	283.15	1111.72	288.15	1108.21	293.15	1010.15
0.0509	276.15	1106.81	277.15	1106.10	283.15	1101.82	288.15	1098.26	293.15	993.97
0.1024	276.15	1090.72	277.16	1090.00	283.16	1085.61	288.15	1081.94	293.15	976.33
0.1996	276.15	1065.35	277.15	1064.61	283.15	1060.10	288.15	1056.23	293.15	960.96
0.2983	276.15	1043.61	277.15	1042.81	283.15	1038.02	288.15	1034.02	293.15	945.20
0.4014	276.15	1024.29	277.15	1023.47	283.15	1018.50	288.15	1014.34	293.15	930.36
0.4958	276.15	1008.47	277.15	1007.63	283.16	1002.53	288.15	998.27	293.15	913.30
0.5984	276.15	991.05	277.15	990.18	283.15	985.00	288.15	980.68	293.15	897.03
0.6974	276.15	975.68	277.15	974.81	283.16	969.63	288.15	965.31	293.15	882.65
0.7927	276.15	959.81	277.15	958.95	283.15	953.81	288.15	949.52	293.15	868.59
0.8896	276.15	944.84	277.15	944.00	283.15	938.89	288.15	934.64	293.15	854.53
2,4,6-Trimethylpyridine (1) + 1,2-Ethanediol (2)										
0.0000	298.14	1109.87	303.15	1106.36	308.15	1102.84	313.15	1099.30	293.15	1078.26
0.0227	298.14	1101.13	303.15	1097.58	308.15	1094.01	313.15	1090.43	293.15	1052.33
0.0509	298.14	1091.07	303.15	1087.45	308.15	1083.83	313.15	1080.18	293.15	1029.98
0.1024	298.14	1074.55	303.15	1070.84	308.15	1067.10	313.14	1063.34	293.15	1010.15

Table 2 continued

$x_1$	$T$ (K)	$\rho$ ( $\text{kg} \cdot \text{m}^{-3}$ )	$T$ (K)	$\rho$ ( $\text{kg} \cdot \text{m}^{-3}$ )	$T$ (K)	$\rho$ ( $\text{kg} \cdot \text{m}^{-3}$ )	$T$ (K)	$\rho$ ( $\text{kg} \cdot \text{m}^{-3}$ )	$T$ (K)	$\rho$ ( $\text{kg} \cdot \text{m}^{-3}$ )
0.1996	298.15	1048.43	303.15	1044.52	308.15	1040.64	313.14	1036.74		
0.2983	298.14	1025.93	303.15	1021.84	308.15	1017.74	313.14	1013.62		
0.4014	298.15	1005.94	303.15	1001.71	308.14	997.46	313.14	993.19		
0.4958	298.14	989.66	303.15	985.33	308.15	980.98	313.14	976.61		
0.5984	298.15	971.96	303.15	967.57	308.14	963.16	313.14	958.73		
0.6974	298.15	956.59	303.15	952.20	308.15	947.78	313.15	943.35		
0.7927	298.15	940.86	303.15	936.51	308.15	932.13	313.15	927.74		
0.8896	298.14	926.07	303.15	921.76	308.15	917.43	313.15	913.09		

**Table 3** Coefficients of the density polynomials (Eq. 1) and mean deviations from the regression line  $\delta$ 

$x_1$	$a_0$	$a_1 \times 10^1$	$a_2 \times 10^3$	$\delta$
2,4,6-Trimethylpyridine + methanol				
0.0000	809.969 ± 0.008	-9.297 ± 0.010	-0.294 ± 0.023	0.009
0.0204	819.767 ± 0.008	-9.266 ± 0.009	-0.317 ± 0.021	0.008
0.0511	833.232 ± 0.008	-9.235 ± 0.009	-0.336 ± 0.020	0.008
0.0997	851.750 ± 0.007	-9.207 ± 0.008	-0.351 ± 0.020	0.008
0.1940	878.441 ± 0.006	-9.176 ± 0.007	-0.365 ± 0.020	0.006
0.2957	898.365 ± 0.005	-9.129 ± 0.006	-0.352 ± 0.015	0.006
0.3884	910.498 ± 0.005	-9.041 ± 0.005	-0.339 ± 0.013	0.005
0.4890	919.031 ± 0.004	-8.903 ± 0.004	-0.327 ± 0.010	0.004
0.5852	924.141 ± 0.004	-8.758 ± 0.005	-0.324 ± 0.011	0.004
0.6949	927.593 ± 0.002	-8.613 ± 0.003	-0.307 ± 0.007	0.003
0.7971	929.543 ± 0.003	-8.509 ± 0.003	-0.286 ± 0.008	0.003
0.8889	930.691 ± 0.003	-8.450 ± 0.004	-0.251 ± 0.009	0.003
1.0000	930.975 ± 0.003	-8.409 ± 0.004	-0.195 ± 0.008	0.003
2,4,6-Trimethylpyridine + 1,2-ethanediol				
0.0000	1127.239 ± 0.004	-6.890 ± 0.005	-0.239 ± 0.011	0.004
0.0227	1118.740 ± 0.003	-6.991 ± 0.003	-0.214 ± 0.007	0.003
0.0509	1108.932 ± 0.004	-7.075 ± 0.004	-0.284 ± 0.010	0.004
0.1024	1092.905 ± 0.004	-7.260 ± 0.005	-0.330 ± 0.011	0.004
0.1996	1067.667 ± 0.040	-7.594 ± 0.046	-0.365 ± 0.108	0.042
0.2983	1045.989 ± 0.002	-7.918 ± 0.003	-0.439 ± 0.007	0.003
0.4014	1026.759 ± 0.002	-8.217 ± 0.002	-0.444 ± 0.005	0.003
0.4958	1011.009 ± 0.002	-8.437 ± 0.002	-0.410 ± 0.005	0.002
0.5984	993.616 ± 0.003	-8.568 ± 0.004	-0.388 ± 0.009	0.004
0.6974	978.248 ± 0.002	-8.570 ± 0.002	-0.387 ± 0.005	0.002
0.7927	962.365 ± 0.002	-8.512 ± 0.003	-0.362 ± 0.006	0.002
0.8896	947.374 ± 0.003	-8.443 ± 0.004	-0.324 ± 0.008	0.003

where  $M$  is the molar mass,  $x$  is the mole fraction, and subscripts 1 and 2 stand for 2,4,6-trimethylpyridine and methanol or 1,2-ethanediol, respectively. The molar isobaric expansions,

$$E_p \equiv (\partial V / \partial T)_p, \quad (3)$$

were calculated by differentiation of Eq. 2 with  $\rho$  given by Eq. 1.

The thermodynamic excesses of volume and expansion were calculated from the definition,

$$Y^E = Y - Y^{\text{id}} \quad (4)$$



where  $Y$  is  $V$  or  $E_p$ , superscript “id” stands for the ideal mixture, and  $Y^{\text{id}} = x_1 Y_1^* + x_2 Y_2^*$ ; asterisks denote pure substances.

The mole fraction dependences of the excess volumes at constant temperature were approximated by the Redlich-Kister polynomials,

$$V^E = x_1 x_2 \sum_{i=0}^3 a_i (x_2 - x_1)^i, \quad (5)$$

where  $a_i$ 's are the regression coefficients, calculated by the least-squares method and reported in Table 4. As was evidenced by the  $t$  test, only four coefficients for each isotherm were statistically significant. Although the excess expansions are temperature-derivatives of  $V^E$ , the calculations of  $E_p^E$  from Eq. 5 gave rather poor result. Thus, the Redlich-Kister polynomials of the form analogous to Eq. 5 were fitted independently to the experimental excess expansions. Their coefficients are given in Table 4 as well. The  $V^E$  and  $E_p^E$  functions are plotted in Figs. 2 and 3, together with the excesses for the aqueous system. From among the latter,  $V^E$ 's were reported earlier, while  $E_p^E$ 's were calculated from the density polynomials [9].

The partial molar volumes of 2,4,6-trimethylpyridine were calculated from the Redlich-Kister polynomials (Eq. 5);

$$V_1 = V^{\text{id}} + V^E + x_2 \frac{\partial V^{\text{id}}}{\partial x_1} + x_2 \frac{\partial V^E}{\partial x_1}, \quad (6)$$

and from the following approximate formula:

$$V_1 \approx V + (1 - \bar{x}_1) \frac{\Delta V}{\Delta x_1}, \quad (7)$$

where  $\Delta V$  and  $\Delta x_1$  are differences between two consecutive molar volumes and mole fractions of the systems ordered according to the increasing value of  $x_1$ , while  $\bar{x}_1$  is the arithmetic mean of the two mole fractions. In this way, the derivatives of the Redlich-Kister polynomials were verified as good approximations of the partial volume isotherms. The results are plotted in Fig. 4.

#### 4 Theoretical Calculations

Association energies and structural parameters of the 1:1 complexes of 2,4,6-trimethylpyridine with methanol and water were calculated using the Gaussian09 program package [10]. Similarly, as in a previous study [1], density functional theory (DFT) and second-order Møller–Plesset perturbation theory (MP2) were applied. For both methods, the Dunning's augmented correlation consistent polarized valence double- $\xi$  (aug-cc-pVDZ) basis set [11, 12] was employed. The DFT calculations were carried out using the B3LYP exchange-correlation functional [13, 14]. First, equilibrium geometries of the isolated monomers and the 1:1 complexes were fully optimized at the DFT/B3LYP level of theory. Next, energies of the equilibrium structures were

**Table 4** Coefficients of the Redlich-Kister polynomials (Eq. 5) for the molar excesses of volume and isobaric expansion, and mean deviations from the regression lines  $\delta$ 

$T$ (K)	$a_0$	$a_1$	$a_2$	$a_3$	$\delta$
$V^E \times 10^6$ (m <sup>3</sup> · mol <sup>-1</sup> )					
2,4,6-Trimethylpyridine + methanol					
277.02	-6.258 ± 0.017	-1.194 ± 0.067	0.997 ± 0.077	1.325 ± 0.163	0.0077
283.15	-6.280 ± 0.017	-1.159 ± 0.067	0.954 ± 0.077	1.286 ± 0.164	0.0077
288.15	-6.296 ± 0.018	-1.132 ± 0.067	0.920 ± 0.077	1.255 ± 0.165	0.0077
293.15	-6.310 ± 0.018	-1.104 ± 0.068	0.888 ± 0.078	1.224 ± 0.166	0.0078
298.15	-6.323 ± 0.018	-1.078 ± 0.068	0.856 ± 0.078	1.192 ± 0.167	0.0078
303.15	-6.334 ± 0.018	-1.051 ± 0.069	0.826 ± 0.079	1.161 ± 0.168	0.0079
308.15	-6.343 ± 0.018	-1.026 ± 0.069	0.797 ± 0.080	1.129 ± 0.169	0.0079
313.15	-6.351 ± 0.018	-1.001 ± 0.070	0.769 ± 0.080	1.097 ± 0.171	0.0080
2,4,6-Trimethylpyridine + 1,2-ethanediol					
277.02	-7.606 ± 0.048	3.263 ± 0.185	1.563 ± 0.216	-1.269 ± 0.455	0.0214
283.15	-7.595 ± 0.049	3.195 ± 0.187	1.485 ± 0.218	-1.192 ± 0.460	0.0216
288.15	-7.582 ± 0.050	3.137 ± 0.189	1.424 ± 0.220	-1.135 ± 0.465	0.0218
293.15	-7.565 ± 0.050	3.078 ± 0.191	1.365 ± 0.223	-1.082 ± 0.470	0.0221
298.15	-7.545 ± 0.051	3.018 ± 0.193	1.307 ± 0.225	-1.034 ± 0.474	0.0223
303.15	-7.520 ± 0.051	2.956 ± 0.195	1.252 ± 0.227	-0.991 ± 0.479	0.0225
308.15	-7.491 ± 0.052	2.892 ± 0.197	1.199 ± 0.230	-0.953 ± 0.485	0.0228
313.15	-7.458 ± 0.052	2.827 ± 0.199	1.148 ± 0.232	-0.920 ± 0.490	0.0230
$E_p^E \times 10^9$ (m <sup>3</sup> · mol <sup>-1</sup> · K <sup>-1</sup> )					
2,4,6-Trimethylpyridine + methanol					
277.02	-3.77 ± 0.04	5.71 ± 0.15	-7.07 ± 0.17	-6.21 ± 0.37	0.02
283.15	-3.39 ± 0.04	5.59 ± 0.15	-6.82 ± 0.17	-6.24 ± 0.37	0.02
288.15	-3.06 ± 0.04	5.50 ± 0.15	-6.61 ± 0.18	-6.26 ± 0.38	0.02
293.15	-2.72 ± 0.04	5.40 ± 0.16	-6.40 ± 0.18	-6.28 ± 0.39	0.02
298.15	-2.37 ± 0.04	5.29 ± 0.17	-6.18 ± 0.19	-6.30 ± 0.41	0.02
303.15	-2.02 ± 0.05	5.19 ± 0.18	-5.95 ± 0.20	-6.32 ± 0.43	0.02
308.15	-1.65 ± 0.05	5.08 ± 0.19	-5.71 ± 0.22	-6.35 ± 0.46	0.02
313.15	-1.28 ± 0.05	4.97 ± 0.20	-5.47 ± 0.23	-6.37 ± 0.50	0.02
2,4,6-Trimethylpyridine + 1,2-ethanediol					
277.02	1.59 ± 0.17	-10.40 ± 0.65	-13.44 ± 0.75	11.67 ± 1.59	0.07
283.15	2.46 ± 0.16	-10.86 ± 0.62	-12.91 ± 0.71	10.85 ± 1.52	0.07
288.15	3.19 ± 0.16	-11.26 ± 0.62	-12.46 ± 0.71	10.16 ± 1.50	0.07
293.15	3.94 ± 0.16	-11.66 ± 0.62	-12.00 ± 0.72	9.45 ± 1.52	0.07
298.15	4.70 ± 0.17	-12.08 ± 0.65	-11.54 ± 0.74	8.71 ± 1.58	0.07
303.15	5.49 ± 0.18	-12.52 ± 0.69	-11.06 ± 0.79	7.96 ± 1.67	0.08
308.15	6.29 ± 0.19	-12.97 ± 0.74	-10.56 ± 0.85	7.19 ± 1.80	0.08
313.15	7.12 ± 0.21	-13.43 ± 0.80	-10.06 ± 0.92	6.39 ± 1.95	0.09

recalculated in the MP2 method, applying these geometries. In the DFT and MP2 calculations, the supermolecule approach was applied. Additionally, double hybrid B2PLYP calculations [15] were performed, which included geometry optimization. The results were corrected taking into account the basis set superposition error (BSSE) and zero-point vibrational energies (ZPE). Calculated association energies and geometries of the 1:1 complexes are provided in Table 5. To verify the obtained results for 2,4,6-trimethylpyridine complexes, the association energies for monohydrates of pyridine, monomethylpyridines, and 2,6-dimethylpyridine were also calculated by the DFT and MP2 methods. They proved to be equal to the values reported by Papai and Jancsó [16], within a  $\pm 0.1 \text{ kJ} \cdot \text{mol}^{-1}$  uncertainty interval.

## 5 Discussion

Excess molar volumes of the three systems are negative, with the largest absolute values for the aqueous system and the smallest for the methanolic one (Fig. 2). In the previous study, we reported positive correlation between the negative excess volumes and the association energies in the 1:1 complexes of 1,2-ethanediol with pyridine and its derivatives [1]. Present results do not follow that pattern, since the energies increase in the order  $\Delta E(\text{H}_2\text{O}) < \Delta E(\text{CH}_3\text{OH}) < \Delta E(\text{C}_2\text{H}_4(\text{OH})_2)$  independent of the method used in the calculations, provided the BSSE and ZPE corrections were taken into account. Thus, the formation of the O–H $\cdots$ N bonds is not the only reason for the negative excess volume.

The largest negative excess volume of the aqueous system may result from the aggregation of the 1:1 hydrates into clusters,  $(\text{C}_8\text{H}_{11}\text{N} \cdot \text{H}_2\text{O})_n$ , in a way similar to that found for hydrates of pyridine, 2-methylpyridine, and 2,6-dimethylpyridine [2]. Since no aggregation of that kind is possible for  $\text{C}_8\text{H}_{11}\text{N} \cdot \text{CH}_3\text{OH}$  because of the lack of proton-donating groups in the complex, the excess is smaller for the methanolic system than for the aqueous one, in spite of the higher association energy in the former. The excess volume isotherms for the 2,6-dimethylpyridine–1,2-ethanediol system may reflect two phenomena. The first is the aggregation, albeit undoubtedly weaker than that in the aqueous system because of the weakened induction effect due to the C–C chains that separate the hydroxyl groups in the 1,2-ethanediol molecule. Consequently, the co-operative effects in the vicinity of the O–H $\cdots$ N bonds are less pronounced. The second is the formation of other complexes. One molecule of diol may join two molecules of 2,4,6-trimethylpyridine through hydrogen bonds that would lead to  $(\text{C}_8\text{H}_{11}\text{N})_2 \cdot \text{C}_2\text{H}_4(\text{OH})_2$  complexes apart from the  $\text{C}_8\text{H}_{11}\text{N} \cdot \text{C}_2\text{H}_4(\text{OH})_2$  ones. Strong O–H $\cdots$ N bonds would compensate for the unfavorable entropy change. In aqueous solutions, the  $\text{C}_8\text{H}_{11}\text{N} \cdot \text{H}_2\text{O}$  complexes predominate because of the significant decrease of entropy that accompanies binding another amine molecule to the existing monohydrate. The negative change of entropy is obviously smaller in the 1,2-ethanediol system, as the  $(\text{C}_8\text{H}_{11}\text{N})_2 \cdot \text{C}_2\text{H}_4(\text{OH})_2$  complex is less rigid than the similar aqueous one. Although restricted in the translational motions, the amine molecules in the former may still rotate around the C–C axis. Another argument for the complexation equilibrium shifted towards the  $(\text{C}_8\text{H}_{11}\text{N})_2 \cdot \text{C}_2\text{H}_4(\text{OH})_2$  complexes is that the extrema of the excess volume isotherms are located at an amine mole fraction

**Table 5** Association energies and selected structural parameters <sup>a</sup> of the 1:1 complexes of 2,4,6-trimethylpyridine with water, methanol, and 1,2-ethanediol <sup>b</sup>

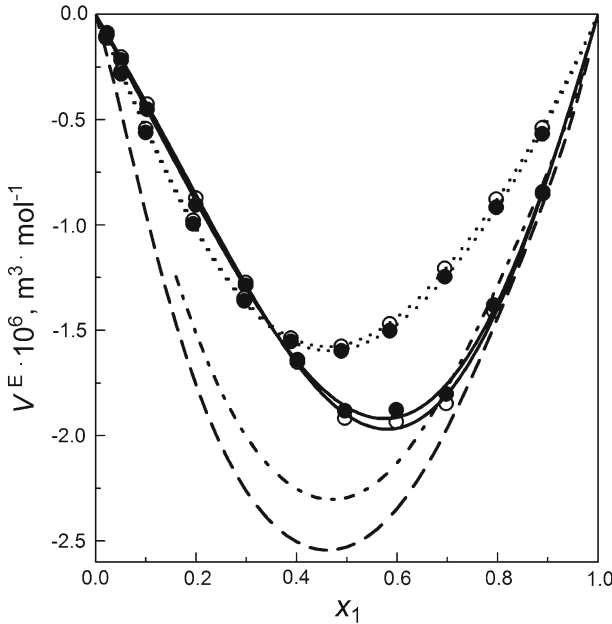
	DFT/B3LYP			MP2 <sup>c</sup>			B2PLYP		
	$\Delta E$	$\Delta E_{\text{BSSE}}$	$\Delta E_{\text{BSSE+ZPE}}$	$\Delta E$	$\Delta E_{\text{BSSE}}$	$\Delta E_{\text{BSSE+ZPE}}$	$\Delta E$	$\Delta E_{\text{BSSE}}$	$\Delta E_{\text{BSSE+ZPE}}$
H <sub>2</sub> O	29.1	26.9	18.9	37.5	29.9	21.9	32.5	28.7	20.8
CH <sub>3</sub> OH	28.4	25.1	19.6	41.6	32.2	26.6	33.6	28.4	23.2
C <sub>2</sub> H <sub>4</sub> (OH) <sub>2</sub>	30.2	26.7	21.5	45.6	34.7	29.5	37.7	32.1	27.7
$R_{\text{N}\cdots\text{H}}$		$\alpha_{\text{C}(4)\text{NH}}$	$\alpha_{\text{NHO}}$				$R_{\text{N}\cdots\text{H}}$	$\alpha_{\text{C}(4)\text{NH}}$	$\alpha_{\text{NHO}}$
H <sub>2</sub> O	1.908	170.5	173.4				1.902	169.3	173.0
CH <sub>3</sub> OH	1.921	174.0	171.7				1.904	173.4	172.8
C <sub>2</sub> H <sub>4</sub> (OH) <sub>2</sub>	1.902	174.3	172.1				1.856	170.6	171.5

*B3LYP* corrected for the basis set superposition error, *ZPE* corrected for the zero-point vibrational energy

<sup>a</sup> Energies  $\Delta E$  in  $\text{kJ}\cdot\text{mol}^{-1}$ , bond lengths  $R$  in  $\text{\AA}$ , valence angles  $\alpha$  in  $^\circ$

<sup>b</sup> Data for the complexes with 1,2-ethanediol were published earlier [1] and are reported here for the readers' convenience

<sup>c</sup> Results obtained for single-point calculations from the DFT/B3LYP optimized geometries



**Fig. 2** Excess molar volumes of the systems: 2,4,6-trimethylpyridine (1) + a proton-donating substance (2). Substance: methanol—dotted lines, 1,2-ethanediol—solid lines. Points—experimental results: open symbols— $T = 277.02$  K, filled symbols— $T = 313.15$  K. Lines—Redlich-Kister polynomials, Eq. 5 (this work). Aqueous system: dashed line— $T = 277.02$  K, dotted-dashed line— $T = 303.15$  K [9]. The phase separation of the aqueous system at  $T > 278.85$  K causes the last isotherm to be broken

close to 0.6 rather than to 0.5 (Fig. 2). For the 1:1 complexes, that mole fraction would be  $x_1 \approx 0.5$ , while for the 2:1 ones,  $x_1 \approx 0.67$  could be expected.

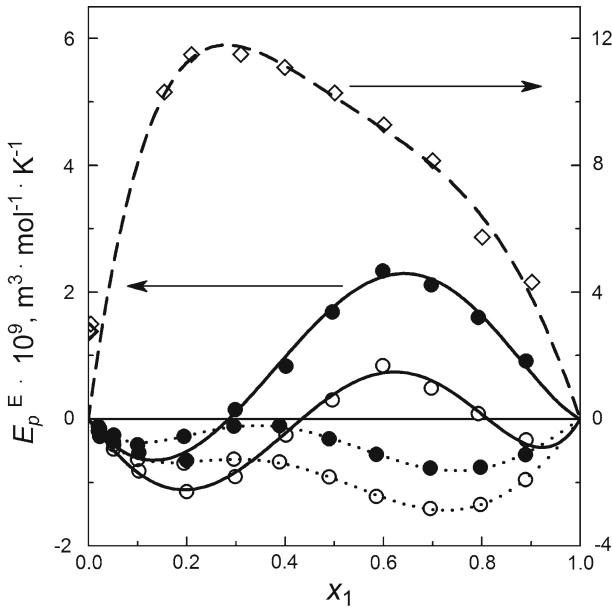
The ability for aggregation for the complexes is probably reflected in the excess expansions (Fig. 3). The excess expansion for the aqueous system is positive over the whole concentration range, while it is negative for the methanolic mixtures. The positive excess seems to be due to the disintegration of the hydrate clusters caused by the increasing temperature. The effect is less pronounced in the 2,4,6-trimethylpyridine + 1,2-ethanediol system, since the solvate clusters are weaker. As a result, the  $E_p^E(x_1)$  isotherms are S-shaped for that mixture, with much lower positive extrema at  $x_1 \approx 0.6$ .

The excess isobaric expansion may be related to the change in the excess entropy caused by pressure. For the systems with positive  $E_p^E$ , the excess entropy decreases with increasing pressure:

$$dp > 0 \Rightarrow dS^E < 0, \tag{8}$$

because of the following thermodynamic relationship:

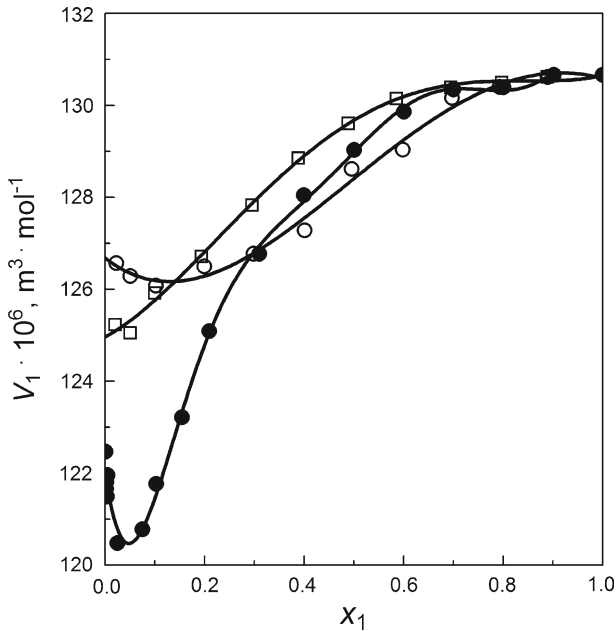
$$dS^E = -E_p^E dp, \tag{9}$$



**Fig. 3** Excess molar isobaric expansions of the systems: 2,4,6-trimethylpyridine (1) + a proton-donating substance (2). Substance: methanol—dotted lines, 1,2-ethanediol—solid lines, water—dashed line. Points—experimental results: open circles— $T = 283.15$  K, filled circles— $T = 313.15$  K, diamonds— $T = 277.15$  K. Lines—Redlich-Kister polynomials

which is valid for  $T = \text{const}$ . This points to the shift of the aggregation equilibrium towards products at higher pressures. As could be expected, the tendency to pressure-induced aggregation is stronger in an aqueous system than in the 1,2-ethanediolic one, while not observed in the methanolic mixtures.

The similarity of aqueous and 1,2-ethanediolic systems is revealed also in the partial molar volumes of 2,4,6-trimethylpyridine. The  $V_1(x_1)$  isotherms for the two systems show minima, while  $V_1$  in the methanolic mixture increases monotonically with increasing  $x_1$  (Fig. 4). In the clathrate hydrate model, the minima of  $V_1(x_1)$  are interpreted as a result of stabilization of the adjoining cavities in the water structure occupied by guest molecules [17]. The model applies to aqueous solutions of non-electrolytes, e.g., alcohols. Although the minimum of  $V_1$  of 2,4,6-trimethylpyridine for the 1,2-ethanediolic system is much shallower than that for the aqueous one, it still resembles that for the partial volume of ethanol in water. A hydrophobic-like solvation was postulated to account for the positron annihilation in the solutions of non-electrolytes in 1,2-ethanediol. However, ultrasonic experiments (speed and absorption) did not confirm that finding [18–20]. It seems probable, that the U-shaped isotherms of  $V_1$  may reflect the association of complexes rather than solvent-separated solvation. The strong volume contraction caused by aggregation would result in the decrease of the partial volume of 2,4,6-trimethylpyridine as its mole fraction increases in the mixture with 1,2-ethanediol.



**Fig. 4** Partial molar volume of 2,4,6-trimethylpyridine in the mixtures with water (●), 1,2-ethanediol (○), and methanol (□) at  $T = 277.02$  K. Points—values calculated from Eq. 7, lines—Eq. 6

## 6 Conclusions

The 1:1 hydrates of 2,4,6-trimethylpyridine,  $\text{C}_8\text{H}_{11}\text{N} \cdot \text{H}_2\text{O}$ , aggregate into clusters in aqueous solutions as a result of the  $\text{O}-\text{H} \cdots \text{O}$  bonds. Similar aggregates of  $\text{C}_8\text{H}_{11}\text{N} \cdot \text{C}_2\text{H}_4(\text{OH})_2$  probably arise in the 2,4,6-trimethylpyridine–1,2-ethanediol system, apart from the  $(\text{C}_8\text{H}_{11}\text{N})_2 \cdot \text{C}_2\text{H}_4(\text{OH})_2$  complexes. However, the propensity to aggregation of the ethanediolic complexes is less pronounced than that of the aqueous ones in spite of the higher  $\text{O}-\text{H} \cdots \text{N}$  bond energy since the induction effect is weaker due to the C–C chain separating the OH groups in the diol molecule. The aggregation evidently influences the volumetric properties of the two systems, as can be inferred from a comparison with those of the methanolic one. Is it obvious that the  $\text{C}_8\text{H}_{11}\text{N} \cdot \text{CH}_3\text{OH}$  complexes cannot aggregate because of the lack of functional groups capable of forming the hydrogen bonds.

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