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Density and partial molar volumes of the liquid mixture water + methanol + ethanol + 2-propanol at 298.15 K and 0.1 MPa

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Abstract

The density of the quaternary mixture water + methanol + ethanol + propan-2-ol as well as its four ternary and six binary subsystems is measured over a wide composition range at ambient temperature and pressure, i.e. 298.15 K and 0.1 MPa. The resulting molar volume data are correlated with a response surface model, consisting of linear, quadratic, bilinear and trilinear interaction terms. The density values obtained with that correlation are compared to molecular simulation results and experimental literature data. Further, the excess molar volume and the partial molar volumes are determined for the ternary and quaternary mixtures. The analytical solution for the partial molar volumes of a quaternary mixture for the response surface model is also given.

Keywords: density, partial molar volume, water, alcohol

Introduction

The understanding of thermodynamic volumetric properties, such as density, excess and partial molar volumes, is of importance to understand and describe solvation and mixing effects of liquid mixtures. Several engineering design and optimization problems in the chemical industry require quantitative information on the density of multicomponent liquid mixtures. For example, partial molar volumes are required to convert Fick diffusion coefficients between different velocity reference frames. Solutions of water with alcohols in binary, ternary and quaternary systems are expected to show a complex behavior due to the presence of strong intermolecular interactions and self-association by hydrogen bonding. Thus, their study is of interest for the development and evaluation of thermodynamic models for the description of the mixing behavior of polar solutions. Further, mixtures containing alcohols are an important field of investigation due to their use as sustainable energy carriers^{1,2}.

This work is part of a systematic research on transport and volumetric properties of aqueous mixtures with short alcohols based on experiments and molecular simulations³⁻⁶. Here, the density, excess and partial molar volumes of the quaternary mixture water + methanol + ethanol + propan-2-ol and all of its four ternary subsystems are presented. The six binary subsystems have been thoroughly studied in the literature, e.g. in Refs.⁷⁻¹⁶, therefore only selected compositions of these were measured for validation purposes.

Experimental measurements of the volumetric properties of the quaternary mixture under consideration have been reported in the literature¹⁷, however, only 34 different compositions were measured and no attempt was made to correlate these data. Further, molecular simulation results for the density of ten compositions of the quaternary mixture were reported in previous work⁶. The volumetric properties of the ternary subsystem water + methanol + ethanol has been studied thoroughly in the literature^{10,11,18-20} and Zarei et al.¹⁰ as well as Mori et al.¹¹ proposed Redlich-Kister- and NRTL-type correlations for its excess volume. Wei and Rowley⁷ studied the density and kinematic viscosity of the ternary mixture methanol + ethanol + propan-2-ol, but only correlated the latter. The density of the ternary mixtures water + methanol + propan-2-ol and wa-

ter + ethanol + propan-2-ol at 298.15 K and 0.1 MPa has been reported by Chen and Hou¹⁷, but the data were not correlated.

Experimental

Materials

The purity of the employed anhydrous methanol, ethanol and propan-2-ol is given in Table 1. Water deionized by reverse osmosis was used to prepare the mixture samples. The alcohols were dried by chemical sieves before each set of measurements.

Table 1: Chemical formula, CAS registry number and mass fraction purity of the employed chemicals.

Substance	Formula	CAS Reg. No.	suppliers	purity mass fraction	method
methanol	CH ₄ O	67-56-1	VWR chemicals	≥ 0.999	GC ^a
ethanol	C ₂ H ₆ O	64-17-5	VWR chemicals	≥ 0.998	GC ^a
propan-2-ol	C ₃ H ₈ O	67-63-0	Seccosolv [®] Millipore	≥ 0.999	GC ^a
water	H ₂ O	7732-18-5	TU Berlin		

^aGas chromatography

Experimental method

The density ρ was measured at 298.15 K and 0.1 MPa for all six binary and four ternary subsystems as well as the quaternary mixture itself with an Anton Paar DMA 5000 M vibrating-tube densimeter with a precision of 0.001 kg·m⁻³ and a reproducibility of 0.005 kg·m⁻³. The temperature was controlled internally by two integrated platinum thermometers with a precision of 0.001 K. Sample mixtures of about 5 cm³ were prepared by weight using an analytical balance (Kern ABJ 220) with a sensitivity of 0.1 mg. Before use, all pure substances were degassed by stirring under reduced pressure. The densimeter was calibrated with water and air at 293.15 K following the procedure given by the manufacturer.

Initially, the density of the pure components was successfully compared with data from the literature, cf. Table 2. An average absolute relative deviation (AARD) of 0.013% was found for all substances. Subsequently, the density of the six binary subsystems at selected compositions was measured and compared with correlations of experimental literature data^{7–16}. Again, a very good agreement between the present binary data and the literature was found with an AARD of 0.07% for the aqueous mixtures and of 0.03% for the alcoholic mixtures. A graphical comparison is provided in Fig. S1 of the supporting information. Further, the calculated excess molar volume was compared with other experimental literature data. A very good agreement was found for the aqueous alcoholic mixtures, cf. Fig. 1. In the case of the binary mixtures containing two alcohols, literature values exhibit strong scattering of the excess molar volume, which can be explained by the extremely low values. Density and excess molar volumes of the binary mixtures are listed in Table 3. The density of the ternary and quaternary mixtures was measured subsequently. The density values of the ternary mixtures compare well with literature data, cf. Fig. S3 to S6 of the supporting information. To cover the entire composition range of the quaternary mixture, the mass fraction of the four components were varied sequentially in steps of 0.1 g/g. Further, the state points studied in previous simulation work⁶ were also measured. The alcohol/water mass ratio varied between 0.053 and 2.33 and a total of 94 quaternary and 48 ternary composition points were measured.

Uncertainties

The combined uncertainties of the density measurements were obtained with the error propagation law by considering the individual uncertainties from the employed densimeter and possible temperature and pressure drifts. These uncertainties were estimated based on the temperature and pressure dependence of the density of the pure components^{21–23}. The expanded uncertainty of the density was estimated to be $U(\rho) = 0.014 \text{ kg}\cdot\text{m}^{-3}$. The combined uncertainty of the mole fractions, excess and partial molar volumes was calculated with the error propagation law. In case of the partial molar volumes, the largest part of the uncertainty originates from the fit, while the un-

certainty due to the mole fraction represents typically only 0.05% of the combined uncertainty. All reported expanded uncertainties are based on the estimated combined uncertainty and a coverage factor $k = 2$, providing a level of confidence of approximately 95%.

Table 2: Comparison of the measured density ρ with experimental data from the literature for the pure components at 298.15 K and 0.101 MPa^a.

Substance	$\rho / \text{kg}\cdot\text{m}^{-3}$ ^b		ARD %	Reference
	this work	literature		
Water	997.06	997.07	0.001	10
		997.05	0.001	13
		997.048	0.001	24
		997.04	0.002	25
		997.02	0.004	26
Methanol	786.87	786.57	0.038	10
		786.9	0.004	14
		786.62	0.031	26
		786.33	0.068	27
		786.64	0.023	28
Ethanol	785.14	786.58	0.036	29
		785.18	0.005	10
		785.08	0.008	26
		785.13	0.001	30,31
		785.1	0.005	15,32,33
propan-2-ol	780.92	781.1	0.023	16,34
		780.95	0.003	35
		780.8	0.016	36
		780.9	0.003	37
		780.7	0.029	38
		780.82	0.013	39

^aThe expanded uncertainty of the temperature and pressure are $U(T) = 0.01$ K and $U(p) = 0.006$ MPa

^bThe expanded uncertainty of the measured density is $0.014 \text{ kg}\cdot\text{m}^{-3}$

Coverage factor $k = 2$ for a level of confidence of 95%

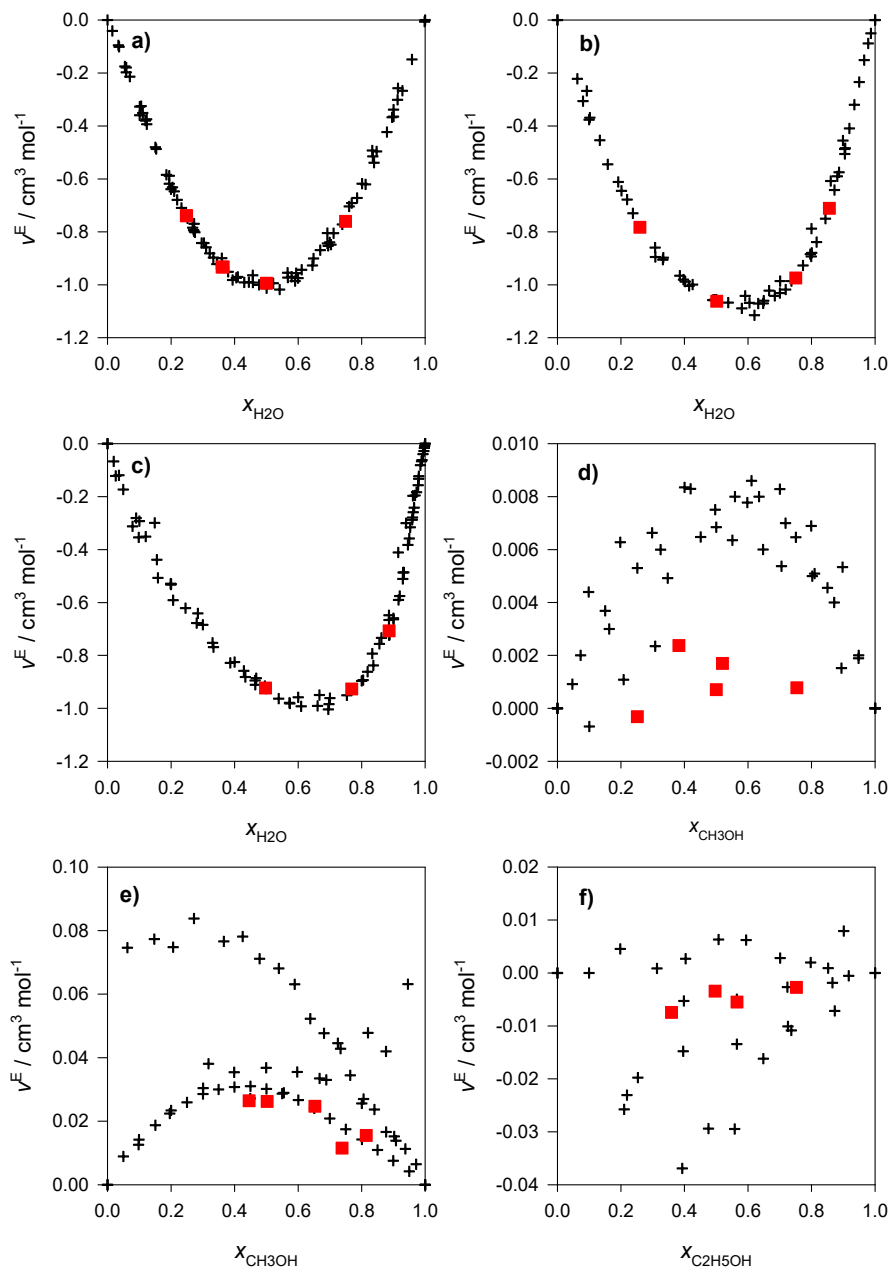


Figure 1: Excess molar volume of the binary mixtures: a) water + methanol, b) water + ethanol, c) water + propan-2-ol, d) methanol + ethanol, e) methanol + propan-2-ol and f) ethanol + propan-2-ol as a function of mole fraction at 298.15 K and 0.101 MPa. Measured data (red squares) are compared with other experimental literature values (black crosses)^{7–11,13–16,26,31,40–46}.

Table 3: Density ρ and excess molar volume v^E of the binary mixtures at 298.15 K and 0.101 MPa^a. x_i is the mole fraction of component i .

water (1) + methanol (2)		
x_1^b	$\rho/\text{kg}\cdot\text{m}^{-3}^c$	$v^E/\text{cm}^3\cdot\text{mol}^{-1}^d$
0.7512	936.44	-0.739
0.6394	911.84	-0.933
0.4997	881.21	-0.994
0.2507	832.09	-0.761
water (1) + ethanol (2)		
x_1^b	$\rho/\text{kg}\cdot\text{m}^{-3}^c$	$v^E/\text{cm}^3\cdot\text{mol}^{-1}^e$
0.2598	819.13	-0.783
0.5017	859.11	-1.062
0.7504	918.76	-0.974
0.8564	950.63	-0.711
water (1) + propan-2-ol (2)		
x_1^b	$\rho/\text{kg}\cdot\text{m}^{-3}^c$	$v^E/\text{cm}^3\cdot\text{mol}^{-1}^e$
0.4974	837.92	-0.924
0.7688	902.08	-0.927
0.8863	947.73	-0.7076
methanol (1) + ethanol (2)		
x_1^b	$\rho/\text{kg}\cdot\text{m}^{-3}^c$	$v^E/\text{cm}^3\cdot\text{mol}^{-1}^e$
0.2518	785.47	-0.000
0.5196	785.86	0.001
0.7540	786.31	0.000
0.3825	785.63	0.002
0.5002	785.84	0.000
methanol (1) + propan-2-ol (2)		
x_1^b	$\rho/\text{kg}\cdot\text{m}^{-3}^c$	$v^E/\text{cm}^3\cdot\text{mol}^{-1}^f$
0.7382	784.30	0.012
0.5023	782.64	0.026
0.6525	783.52	0.025
0.8142	784.82	0.016
0.4457	782.36	0.027
ethanol (1) + propan-2-ol (2)		
x_1^b	$\rho/\text{kg}\cdot\text{m}^{-3}^c$	$v^E/\text{cm}^3\cdot\text{mol}^{-1}^f$
0.7523	783.90	-0.002
0.4965	782.77	-0.003
0.5654	783.09	-0.006
0.3592	782.27	-0.008

^aThe expanded uncertainty of the temperature and pressure are $U(T) = 0.01$ K and $U(p) = 0.006$ MPa

^bThe expanded uncertainty of both mole fractions was estimated to be 0.0001 mol·mol⁻¹

^cThe expanded uncertainty of the density was estimated to be 0.014 kg·m⁻³

^dThe expanded uncertainty of the excess molar volume was estimated to be 0.007 cm³·mol⁻¹

^e 0.008 cm³·mol⁻¹, ^f 0.009 cm³·mol⁻¹

Coverage factor $k = 2$ for a level of confidence of 95%

Molecular simulation

Molecular dynamics simulations performed in this work were based on rigid and non-polarizable molecular models of united-atom type. These molecular models account for the intermolecular interactions, including hydrogen bonding, by a set of Lennard-Jones sites and superimposed point charges which may or may not coincide with respect to their site position. The molecular models for the alcohols were developed by our group based on quantum chemical calculations, parameter optimization to experimental VLE data and, in the case of propan-2-ol, also to experimental data on the self-diffusion coefficient^{5,47–49}. For water, the TIP4P/2005 force field by Abascal and Vega⁴⁷ was employed. The parameters of these molecular models are given in Table 4, for more detailed information the interested reader is directed to the original publications^{5,47–49}. Lorentz-Berthelot combining rules were chosen here to define the unlike interactions, i.e. $\sigma_{ab} = (\sigma_{aa} + \sigma_{bb})/2$ and $\epsilon_{ab} = \sqrt{\epsilon_{aa}\epsilon_{bb}}$, so that the present mixture data are strictly predictive.

To calculate the density, molecular dynamics simulations were performed with the program *ms2*⁵⁰ in the isobaric-isothermal (NpT) ensemble at the desired temperature, pressure and composition. The simulations in the NpT ensemble were equilibrated over 4×10^5 time steps, followed by a production run over 3×10^6 time steps. Newton’s equations of motion were solved with a fifth-order Gear predictor-corrector numerical integrator and the temperature was controlled by velocity scaling. Throughout, the integration time step was 0.93 fs. The simulations contained 6000 molecules and were carried out in a cubic volume with periodic boundary conditions, where the cut-off radius was set to $r_c = 24.5$ Å. Lennard-Jones long range interactions were considered using angle averaging⁵¹. Electrostatic long-range corrections were approximated by the reaction field technique with conducting boundary conditions ($\epsilon_{RF} = \infty$). The statistical uncertainties of the predicted values were estimated with a block averaging method⁵².

Table 4: Lennard-Jones and point charge parameters of the employed molecular models, Boltzmann’s constant is k_B and the electronic charge is e .

site	$\epsilon/k_B \cdot K^{-1}$	$\sigma/\text{\AA}$	q/e	site	$\epsilon/k_B \cdot K^{-1}$	$\sigma/\text{\AA}$	q/e
methanol ⁴⁸				ethanol ⁴⁹			
S _{CH3}	3.7543	120.592	+0.24746	S _{CH3}	3.6072	120.15	—
S _{OH}	3.0300	87.879	−0.67874	S _{CH2}	3.4612	86.291	+0.25560
S _H	—	—	+0.43128	S _{OH}	3.1496	85.053	−0.69711
				S _H	—	—	+0.44151
propan-2-ol ⁵				water ⁴⁷			
S _{CH3}	103.59	3.866	0	S _O	93.2	3.1589	−1.1128
S _{CH3}	103.59	3.866	0	S _H	—	—	+0.5564
S _{CH}	20.20	3.238	0.310	S _H	—	—	+0.5564
S _{OH}	85.90	3.154	−0.747				
S _H	—	—	0.437				

Results

The measured densities and calculated excess molar volumes v^E are listed in Tables 3, 5 and 6 as a function of composition. Partial molar volumes of the ternary and quaternary mixtures are also given. The excess molar volume was obtained from the measured density data by

$$v^E = \sum_{i=1}^n \rho^{-1} x_i M_i - \sum_{i=1}^n \rho_i^{-1} x_i M_i, \quad (1)$$

where ρ is the mass density of the mixture and ρ_i that of the pure component i . x_i and M_i are the mole fraction and molar mass of component i , respectively. n is the number of components in the mixture. The excess molar volume of the quaternary mixture is throughout negative, indicating the expected prevalence of molecular association over dissociation¹⁰. Its highest values of around $-1.1 \text{ cm}^3 \cdot \text{mol}^{-1}$ were found for mixtures with a water mole fraction near 0.5, regardless of the concentration of the individual alcohols, cf. Fig. 2. Here, the most pronounced molecular association can be expected in the studied mixtures. In fact, there is a clear dependence of the excess molar volume and water mole fraction, similar to the one typically observed for binary aqueous alcoholic mixtures, cf. Fig. 1. Likewise, the studied aqueous ternary mixtures show a negative excess molar volume. To gain a better insight into the excess molar volume of the aqueous ternary

mixtures, equation (4) was employed to calculate its value when the concentration of one component was kept constant as shown in Fig. 3. The calculated minimum of the excess molar volume for the mixtures water + methanol + ethanol and water + ethanol + propan-2-ol shifts from higher to lower water mole fractions from around $x_{\text{H}_2\text{O}} = 0.55$ down to 0.45 when the mole fraction of the second component was increased. In case of the mixture water + methanol + propan-2-ol, the location of the excess molar volume at approximately $x_{\text{H}_2\text{O}} = 0.55$ does not show any significant dependence on the methanol mole fraction. In the case of the solely alcoholic ternary mixture methanol + ethanol + propan-2-ol, the excess molar volume is in general smaller by one order of magnitude than the one found for the aqueous mixtures, sometimes exhibiting even positive values.

Table 5: Density ρ , excess molar volume v^E and partial molar volumes v_i of the quaternary mixture water (1) + methanol (2) + ethanol (3) + propan-2-ol (4) at 298.15 K and 0.101 MPa ^a. x_i is the mole fraction of component i .

x_1	x_2	x_3	$\rho/\text{kg}\cdot\text{m}^{-3}$	$v^E/\text{cm}^3\cdot\text{mol}^{-1}$	$v_1/\text{cm}^3\cdot\text{mol}^{-1}$	$v_2/\text{cm}^3\cdot\text{mol}^{-1}$	$v_3/\text{cm}^3\cdot\text{mol}^{-1}$
0.1263	0.1254	0.4901	798.81	-0.447	15.63	39.86	58.64
0.1204	0.2528	0.3786	798.93	-0.430	15.46	40.25	58.643
0.1328	0.4950	0.1267	802.20	-0.462	15.34	40.63	58.26
0.2483	0.1272	0.3729	814.27	-0.743	16.14	39.61	58.51
0.2569	0.2533	0.2524	817.42	-0.766	16.12	40.04	58.43
0.2500	0.3724	0.1216	818.12	-0.767	16.00	40.33	58.18
0.3725	0.1283	0.2506	831.68	-0.933	16.60	39.42	58.32
0.3747	0.2452	0.1317	834.87	-0.954	16.56	39.87	58.12
0.5005	0.1279	0.1250	854.07	-1.113	16.89	39.20	57.94
0.4434	0.2500	0.1740	851.37	-1.039	16.84	39.57	57.96
0.4867	0.2735	0.1908	865.18	-1.071	17.01	39.43	57.81
0.3499	0.3932	0.2046	841.12	-0.947	16.51	40.07	58.04
0.6055	0.1708	0.1779	887.91	-1.079	17.27	38.73	57.58
0.7100	0.0803	0.1666	909.52	-1.012	17.38	38.01	57.35
0.1910	0.5310	0.2213	814.83	-0.625	15.66	40.59	58.24
0.5909	0.2485	0.1159	888.91	-1.074	17.25	39.13	57.44
0.4734	0.3558	0.1233	865.77	-1.057	16.93	39.73	57.62
0.6945	0.1557	0.1082	910.76	-1.006	17.43	38.53	57.28
0.3386	0.4769	0.1331	841.28	-0.928	16.39	40.25	57.81
0.7853	0.0736	0.1023	931.14	-0.884	17.52	37.93	57.14
0.1857	0.6174	0.1425	815.40	-0.619	15.55	40.65	57.99
0.5770	0.3236	0.0567	889.95	-1.066	17.18	39.42	57.22
0.4613	0.4324	0.0606	866.50	-1.044	16.82	39.91	57.36
0.6786	0.2284	0.0528	911.57	-0.996	17.42	38.92	57.12

Table 5: continues on next page

Table 5: continued from previous page

x_1	x_2	x_3	$\rho/\text{kg}\cdot\text{m}^{-3}$	$v^E/\text{cm}^3\cdot\text{mol}^{-1}$	$v_1/\text{cm}^3\cdot\text{mol}^{-1}$	$v_2/\text{cm}^3\cdot\text{mol}^{-1}$	$v_3/\text{cm}^3\cdot\text{mol}^{-1}$
0.3310	0.5545	0.0648	841.94	-0.909	16.27	40.33	57.52
0.7691	0.1434	0.0495	931.94	-0.870	17.57	38.42	57.05
0.8492	0.0677	0.0472	950.34	-0.695	17.67	37.94	57.01
0.6233	0.0873	0.2427	886.02	-1.034	17.28	38.20	57.66
0.1973	0.4389	0.3047	814.48	-0.638	15.78	40.46	58.44
0.3607	0.3035	0.2817	840.49	-0.957	16.61	39.79	58.21
0.5007	0.1883	0.2612	864.50	-1.079	17.05	39.00	57.92
0.5149	0.0967	0.3363	863.52	-1.085	17.01	38.41	57.92
0.2026	0.3405	0.3960	814.70	-0.691	15.85	40.18	58.53
0.3837	0.1080	0.4508	839.24	-0.983	16.68	38.78	58.24
0.2089	0.2360	0.4921	814.02	-0.693	15.98	39.84	58.59
0.2172	0.1223	0.5948	813.61	-0.703	16.10	39.33	58.54
0.3658	0.3095	0.2145	840.08	-0.984	16.57	39.85	58.10
0.5089	0.1900	0.1992	863.79	-1.087	17.03	39.13	57.86
0.6327	0.0883	0.1845	886.29	-1.075	17.25	38.35	57.61
0.4945	0.2781	0.1291	864.90	-1.089	16.98	39.51	57.70
0.3559	0.3992	0.1386	840.44	-0.952	16.49	40.11	57.91
0.1938	0.5389	0.1517	814.34	-0.639	15.65	40.58	58.11
0.6149	0.1728	0.1202	887.13	-1.078	17.26	38.87	57.52
0.7195	0.0818	0.1123	908.39	-1.004	17.40	38.21	57.35
0.7949	0.0745	0.0514	930.32	-0.888	17.53	38.13	57.13
0.1873	0.6271	0.0733	814.47	-0.618	15.55	40.63	57.84
0.3776	0.2133	0.2956	839.01	-0.973	16.66	39.50	58.24
0.5242	0.0975	0.2732	862.55	-1.075	17.04	38.60	57.93
0.2078	0.3472	0.3219	813.92	-0.677	15.88	40.26	58.48
0.3912	0.1094	0.3826	838.35	-0.976	16.70	38.95	58.25
0.2141	0.2404	0.4177	812.83	-0.657	16.02	39.96	58.60
0.2218	0.1250	0.5204	812.83	-0.700	16.10	39.45	58.55
0.5026	0.2823	0.0646	863.74	-1.077	16.95	39.61	57.60
0.3613	0.4066	0.0698	839.73	-0.960	16.44	40.15	57.76
0.6240	0.1752	0.0601	886.08	-1.074	17.25	39.03	57.47
0.7301	0.0812	0.0573	907.20	-0.992	17.41	38.42	57.35
0.1963	0.5512	0.0768	813.71	-0.644	15.64	40.58	57.96
0.3721	0.3146	0.1455	838.96	-0.969	16.56	39.95	58.02
0.5174	0.1933	0.1344	862.70	-1.075	17.03	39.28	57.82
0.6410	0.0900	0.1251	884.74	-1.061	17.27	38.57	57.62
0.2018	0.4572	0.1582	813.25	-0.660	15.74	40.49	58.21
0.3848	0.2173	0.2252	838.34	-0.976	16.65	39.62	58.19
0.2102	0.3550	0.2461	813.06	-0.676	15.86	40.32	58.41
0.5318	0.1006	0.2081	861.31	-1.065	17.05	38.80	57.93
0.3985	0.1116	0.3113	837.49	-0.973	16.70	39.12	58.26
0.2187	0.2449	0.3404	812.82	-0.695	15.97	40.02	58.53

Table 5: continues on next page

Table 5: continued from previous page

x_1	x_2	x_3	$\rho/\text{kg}\cdot\text{m}^{-3}$	$v^E/\text{cm}^3\cdot\text{mol}^{-1}$	$v_1/\text{cm}^3\cdot\text{mol}^{-1}$	$v_2/\text{cm}^3\cdot\text{mol}^{-1}$	$v_3/\text{cm}^3\cdot\text{mol}^{-1}$
0.2260	0.1267	0.4437	812.17	-0.700	16.08	39.57	58.55
0.3786	0.3198	0.0742	838.12	-0.970	16.53	40.02	57.91
0.5255	0.1966	0.0679	861.63	-1.097	17.02	39.43	57.76
0.6499	0.0919	0.0632	883.30	-1.047	17.28	38.79	57.62
0.2066	0.4649	0.0810	812.80	-0.666	15.73	40.50	58.08
0.3915	0.2199	0.1531	837.47	-0.979	16.63	39.73	58.13
0.2149	0.3615	0.1673	812.61	-0.686	15.84	40.35	58.31
0.5415	0.1016	0.1407	860.43	-1.060	17.06	39.00	57.93
0.2233	0.2495	0.2605	812.18	-0.697	15.96	40.10	58.48
0.4043	0.1150	0.2378	836.39	-0.969	16.70	39.30	58.26
0.2326	0.1293	0.3613	811.76	-0.707	16.07	39.69	58.54
0.2364	0.1338	0.2764	810.87	-0.700	16.04	39.83	58.53
0.4139	0.1164	0.1609	835.73	-0.936	16.70	39.47	58.25
0.2267	0.2554	0.1774	811.35	-0.695	15.93	40.19	58.41
0.2165	0.3683	0.0873	811.58	-0.683	15.81	40.40	58.21
0.2199	0.3686	0.0848	812.07	-0.690	15.83	40.40	58.20
0.5506	0.1034	0.0715	859.18	-1.044	17.07	39.21	57.93
0.2412	0.1353	0.1890	810.18	-0.704	16.00	39.94	58.50
0.2310	0.2603	0.0908	810.59	-0.695	15.90	40.26	58.34
0.4201	0.1181	0.0828	834.42	-0.951	16.69	39.67	58.24
0.2476	0.1384	0.0958	809.46	-0.696	15.97	40.08	58.47
0.1263	0.3742	0.1246	799.21	-0.458	15.32	40.50	58.37
0.2504	0.2494	0.2499	816.74	-0.782	16.06	40.02	58.41
0.4493	0.1254	0.1754	843.89	-1.023	16.81	39.30	58.13
0.3752	0.1247	0.2500	832.28	-0.955	16.59	39.38	58.29
0.5001	0.1258	0.1248	852.50	-1.051	16.95	39.26	58.00
0.2450	0.1756	0.3242	815.41	-0.764	16.11	39.78	58.49
0.2499	0.3246	0.1754	817.57	-0.778	16.01	40.22	58.28

^aThe expanded uncertainty of the temperature and pressure are $U(T) = 0.01$ K and $U(p) = 0.006$ MPa

The expanded uncertainty of all mole fractions was estimated to be 0.00013 mol·mol⁻¹

The expanded uncertainty of the density was estimated to be 0.014 kg·m⁻³

The expanded uncertainty of the excess molar volume was estimated to be 0.009 cm³·mol⁻¹

The expanded uncertainty of the partial molar volume was estimated to be 0.14 cm³·mol⁻¹

Coverage factor $k = 2$ for a level of confidence of 95%

Table 6: Density ρ , excess molar volume v^E and partial molar volumes v_i of the ternary mixtures at 298.15 K and 0.101 MPa ^a. x_i is the mole fraction of component i .

x_1	x_2	$\rho/\text{kg}\cdot\text{m}^{-3}$	$v^E/\text{cm}^3\cdot\text{mol}^{-1}$	$v_1/\text{cm}^3\cdot\text{mol}^{-1}$	$v_2/\text{cm}^3\cdot\text{mol}^{-1}$
water (1) + methanol (2) + ethanol (3)					
0.5826	0.2462	889.57	-1.065	17.32	39.07
0.3451	0.3859	841.96	-0.945	16.46	39.95
0.8929	0.0629	965.20	-0.424	17.72	37.73
0.6708	0.2253	911.96	-0.975	17.48	38.83
0.5040	0.2485	870.58	-1.075	17.13	39.22
0.5051	0.2478	870.74	-1.073	17.13	39.21
0.2496	0.4997	826.10	-0.763	15.89	40.33
0.2495	0.5002	825.99	-0.757	15.89	40.33
0.2543	0.2539	822.44	-0.780	16.18	39.71
0.2583	0.2532	823.05	-0.787	16.20	39.70
0.6257	0.2493	901.39	-1.036	17.39	39.01
0.3742	0.2501	843.52	-0.979	16.70	39.46
0.1314	0.2494	803.48	-0.468	15.52	39.94
0.6228	0.1253	892.79	-1.073	17.45	38.42
0.3755	0.3751	847.58	-0.976	16.60	39.87
0.1306	0.6206	806.76	-0.458	15.05	40.60
water (1) + methanol (2) + propan-2-ol (3)					
0.2574	0.4992	821.27	-0.776	15.92	40.44
0.3759	0.3780	838.50	-0.964	16.46	40.16
0.4985	0.2501	856.48	-1.056	16.92	39.76
0.6244	0.1230	875.72	-1.049	17.28	39.25
0.1252	0.6269	802.27	-0.448	15.20	40.64
0.2577	0.2504	812.29	-0.722	15.94	40.28
0.3739	0.2502	830.97	-0.933	16.46	40.08
0.1437	0.1857	796.49	-0.446	15.32	40.32
0.6248	0.2506	895.39	-1.181	17.28	39.33
0.1359	0.2448	797.22	-0.488	15.29	40.38
0.2585	0.2493	812.48	-0.730	15.94	40.27
0.5698	0.2498	875.60	-1.104	17.14	39.53
0.6903	0.2494	915.30	-0.992	17.42	39.07
water (1) + ethanol (2) + propan-2-ol (3)					
0.1298	0.6177	798.39	-0.443	15.95	58.67
0.2601	0.4944	814.11	-0.747	16.42	58.60
0.3707	0.3736	828.37	-0.907	16.75	58.49
0.4945	0.2480	846.43	-0.997	17.07	58.31
0.6232	0.1255	869.30	-1.024	17.33	58.05
0.3838	0.2462	826.60	-0.868	16.69	58.50
0.1262	0.2495	794.37	-0.401	15.49	58.63
0.6245	0.2500	877.67	-1.077	17.40	57.98

Table 6: continues on next page

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x_1	x_2	$\rho^c/\text{kg}\cdot\text{m}^{-3}$	$v^E/\text{cm}^3\cdot\text{mol}^{-1}$	$v_1/\text{cm}^3\cdot\text{mol}^{-1}$	$v_2/\text{cm}^3\cdot\text{mol}^{-1}$
0.6899	0.2500	897.10	-1.041	17.53	57.77
methanol (1) + ethanol (2) + propan-2-ol (3)					
0.1210	0.6244	783.78	0.012	40.12	58.63
0.2445	0.5004	783.78	0.019	40.30	58.57
0.3739	0.3753	783.85	0.023	40.45	58.48
0.5033	0.2485	783.92	0.027	40.57	58.35
0.6230	0.1325	784.04	0.028	40.66	58.20
0.2492	0.2473	782.49	0.028	40.36	58.48
0.1164	0.2538	783.14	-0.077	40.22	58.52
0.3746	0.2496	784.50	-0.074	40.48	58.43
0.6246	0.2500	785.60	-0.025	40.64	58.25
0.6901	0.2500	786.20	-0.027	40.67	58.20

^aThe expanded uncertainty of the temperature and pressure are $U(T) = 0.01 \text{ K}$ and $U(p) = 0.006 \text{ MPa}$

The expanded uncertainty of both all mole fractions was estimated to be $0.00012 \text{ mol}\cdot\text{mol}^{-1}$

The expanded uncertainty of the density was estimated to be $0.014 \text{ kg}\cdot\text{m}^{-3}$

The expanded uncertainty of the excess molar volume was estimated to be $0.009 \text{ cm}^3\cdot\text{mol}^{-1}$

The expanded uncertainty of the partial molar volume was estimated to be $0.14 \text{ cm}^3\cdot\text{mol}^{-1}$

Coverage factor $k = 2$ for a level of confidence of 95%

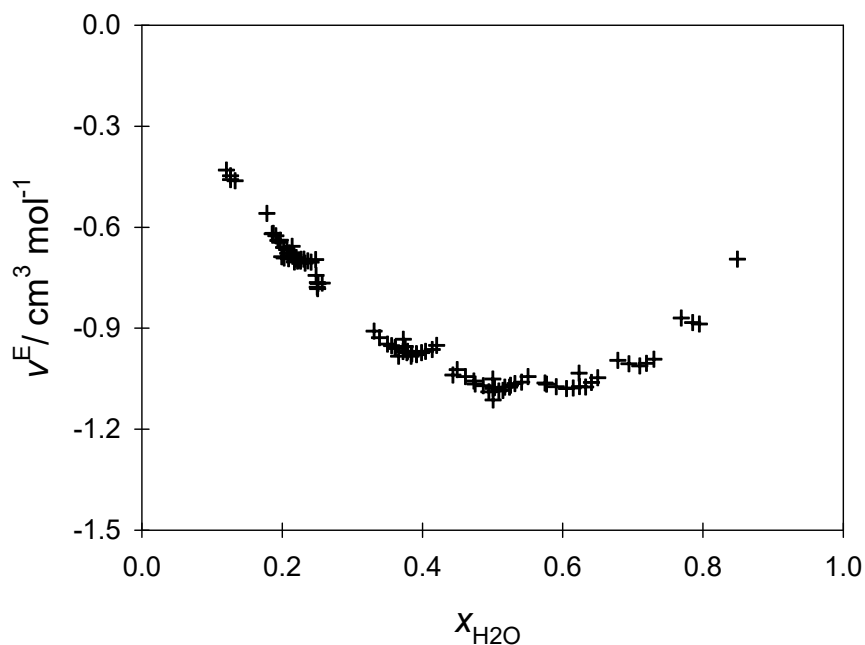


Figure 2: Excess molar volume of the quaternary mixture water + methanol + ethanol + propan-2-ol as a function of water mole fraction at 298.15 K and 0.101 MPa.

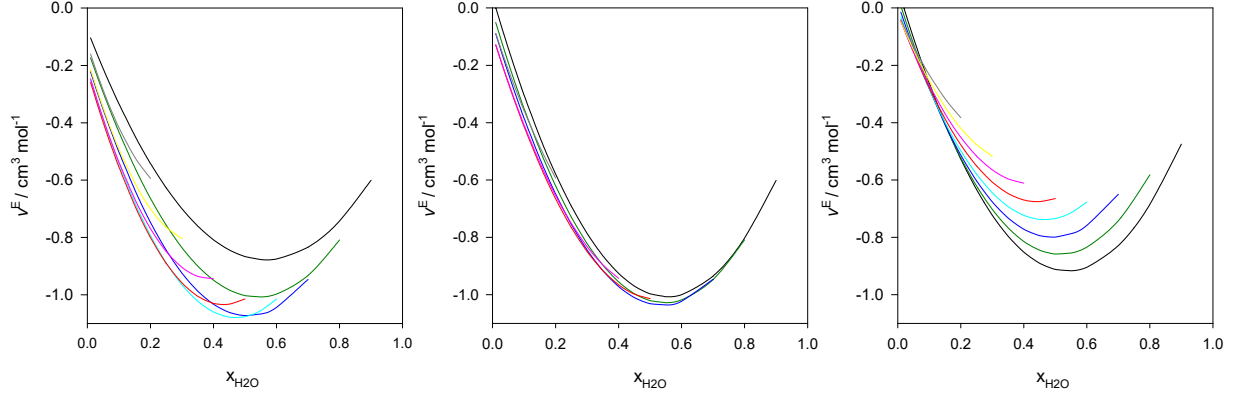


Figure 3: Excess molar volume of the ternary mixtures: (left) water(1)+methanol(2)+ethanol(3), (center) water(1)+methanol(2)+propan-2-ol(3) and (right) water(1)+ethanol(2)+propan-2-ol(3) as a function of water mole fraction evaluated with equation (4) at 298.15 K and 0.101 MPa. The lines represent a constant mole fraction of the second component $x_2 = 0.1$ (black), 0.2 (green), 0.3 (blue), 0.4 (cyan), 0.5 (red), 0.6 (pink), 0.7 (yellow) and 0.8 (gray).

A response surface model for the molar volume v consisting of linear, quadratic, bilinear and trilinear interaction terms given by

$$v = \alpha_0 + \sum_{i=1}^{n-1} \alpha_i x_i + \sum_{i=1}^{n-1} \alpha_{ii} x_i^2 + \sum_{i \neq j}^{n-1} \alpha_{ij} x_i x_j + \sum_{i \neq j \neq k}^{n-1} \alpha_{ijk} x_i x_j x_k, \quad (2)$$

was fitted to the calculated multicomponent molar volume $v = \rho^{-1} \cdot M$ in $\text{cm}^3 \cdot \text{mol}^{-1}$ of the studied ternary and quaternary mixtures. Note that the composition space is linearly constrained by

$$\sum_{i=1}^n x_i = 1. \quad (3)$$

For a quaternary mixture, i.e. $n = 4$, equation (2) can be written as

$$v(x_1, x_2, x_3) = \alpha_0 + \alpha_1 x_1 + \alpha_2 x_2 + \alpha_3 x_3 + \alpha_{11} x_1^2 + \alpha_{22} x_2^2 + \alpha_{33} x_3^2 + \alpha_{12} x_1 x_2 + \alpha_{13} x_1 x_3 + \alpha_{23} x_2 x_3 + \alpha_{123} x_1 x_2 x_3. \quad (4)$$

Thus, 11 coefficients of the response surface model were regressed, i.e. α_0 , α_1 , α_2 , α_3 , α_{11} , α_{22} , α_{33} , α_{12} , α_{13} , α_{23} and α_{123} , which are listed in Table 7. Equation (4) can also be employed for mixtures containing three components by setting one of the mole fractions to zero. The standard error of regression (SER) for the entire experimental data set is $0.11 \text{ cm}^3 \cdot \text{mol}^{-1}$. Further, the molar volume calculated with equation (4) was successfully compared with the experimental literature data and molecular simulation results for the ternary and quaternary mixtures with an AARD of 0.57%. Numerical molecular simulation results are given in Tables S1 and S2 of the supporting information. The highest deviations for the ternary mixtures occur for solutions near the infinite dilution limit, which can be partially explained by the lack of measurements for strongly diluted mixtures. Additionally, simulation results are in excellent agreement with the regressed correlation, underlining the accuracy of present measurements and the quality of the employed force fields. Numerical values for the observed AARD are listed in Table 8. Molecular simulation results are listed in the supporting information material. The molar volumes of the pure substances calculated with equation (4) are $17.74 \text{ cm}^3 \cdot \text{mol}^{-1}$, $40.76 \text{ cm}^3 \cdot \text{mol}^{-1}$, $58.68 \text{ cm}^3 \cdot \text{mol}^{-1}$ and $77.06 \text{ cm}^3 \cdot \text{mol}^{-1}$ for water, methanol, ethanol and propan-2-ol, respectively. Although equation (4) was not fitted to the molar volume of the pure substances or their binary mixtures, relative deviations of the molar volume from the measured values for the pure substances are below 0.14% for the alcohols. In case of water, the molar volume is underestimated by 1.8%. Note that equation (4) is only intended for use with the studied quaternary mixture and its ternary subsystems.

Table 7: Coefficients of equation (4) for the molar volume v in $\text{cm}^3 \cdot \text{mol}^{-1}$ of the studied ternary and quaternary mixtures at 298.15 K and 0.101 MPa.

α_0	α_i	α_{ii}	α_{ij}	α_{123}
77.06	$\alpha_1 = -62.71700$	$\alpha_{11} = 3.40057$	$\alpha_{12} = 0.58011$	-4.68173
	$\alpha_2 = -36.95818$	$\alpha_{22} = 0.65434$	$\alpha_{13} = 1.65257$	
	$\alpha_3 = -18.65280$	$\alpha_{33} = 0.27704$	$\alpha_{23} = -0.042509$	

The resulting expression for the molar volume v was subsequently employed to determine the partial molar volumes v_i , which are defined by

$$v_i \equiv \left(\frac{\partial V}{\partial n_i} \right)_{T,p,n_{j \neq i}}, \quad (5)$$

where the subscript $n_{j \neq i}$ means that all mole numbers except n_i are held constant. Employing $V = nv$, the volume change of a mixture under isothermal and isobaric conditions can be expressed by the total differential

$$d(nv) = \sum_{i=1}^N \left(\frac{\partial nv}{\partial n_i} \right)_{T,p,n_{j \neq i}} dn_i. \quad (6)$$

Since $dn_i = x_i dn + n dx_i$ and $d(nv) \equiv ndv + vdn$, it follows that

Table 8: Comparison of the molar volume calculated by equation (4) with experimental literature data and molecular simulation results for the ternary and quaternary mixtures at 298.15 K and 0.101 MPa.

Mixture	No. data points	ARD %	Source
water + methanol + ethanol	14	0.24	experiment ¹¹
	8	0.65	experiment ¹⁸
	36	0.25	experiment ¹⁰
	13	1.20	experiment ¹⁹
	5	0.80	experiment ²⁰
	3	0.29	simulation, this work
	27	0.43	simulation ⁴
water + methanol + propan-2-ol	23	1.4	experiment ¹⁷
	33	0.44	simulation, this work
water + ethanol + propan-2-ol	21	0.73	experiment ¹⁷
	33	0.41	simulation, this work
methanol + ethanol + propan-2-ol	12	0.24	experiment ⁵³
	33	0.12	simulation, this work
water + methanol + ethanol + propan-2-ol	32	0.94	experiment ¹⁷
	10	0.31	simulation ⁶

$$dv = \sum_{i=1}^N v_i dx_i, \quad (7)$$

where the definition of partial molar volume (5) has been taken into account. However, the mole fractions are constrained by equation (3), i.e. $n - 2$ mole fractions are kept constant and the condition $\sum_{i=1}^n dx_i = 0$ has to hold. Thus, equation (7) can be written as⁵⁴

$$dv = v_j dx_j + \sum_{i \neq j}^n v_i dx_i. \quad (8)$$

Since T , p and all mole fractions x_k except x_i and x_j are held constant,

$$dv = (v_i - v_j) dx_i, \quad (9)$$

holds. Thus, the constrained derivative of the molar volume v is given by⁵⁴

$$\left(\frac{\partial v}{\partial x_i} \right)_{T, p, x_{k \neq i, j}} = v_i - v_j, \quad (10)$$

or

$$\left(\frac{\partial v}{\partial x_i} \right)_{T, p, x_{k \neq i, j}} = \left(\frac{\partial nv}{\partial n_i} \right)_{T, p, n_{k \neq i}} - \left(\frac{\partial nv}{\partial n_j} \right)_{T, p, n_{k \neq j}}. \quad (11)$$

For the quaternary mixture, employing $x_i = 1 - \sum_{j \neq i}^4 x_j$ and $v = \sum_{j=1 \dots 4} v_j x_j$, the molar volume is

given by

$$v = x_1(v_1 - v_4) + x_2(v_2 - v_4) + x_3(v_3 - v_4) + v_4, \quad (12)$$

Rearranging equation (12) and employing equation (10), the partial molar volumes v_i can be written as

$$v_1 = v + (1 - x_1) \left(\frac{\partial v}{\partial x_1} \right)_{T,p,x_{2,3}} - x_2 \left(\frac{\partial v}{\partial x_2} \right)_{T,p,x_{1,3}} - x_3 \left(\frac{\partial v}{\partial x_3} \right)_{T,p,x_{1,2}}, \quad (13)$$

$$v_2 = v + (1 - x_2) \left(\frac{\partial v}{\partial x_2} \right)_{T,p,x_{1,3}} - x_1 \left(\frac{\partial v}{\partial x_1} \right)_{T,p,x_{2,3}} - x_3 \left(\frac{\partial v}{\partial x_3} \right)_{T,p,x_{1,2}}, \quad (14)$$

$$v_3 = v + (1 - x_3) \left(\frac{\partial v}{\partial x_3} \right)_{T,p,x_{1,2}} - x_1 \left(\frac{\partial v}{\partial x_1} \right)_{T,p,x_{2,3}} - x_2 \left(\frac{\partial v}{\partial x_2} \right)_{T,p,x_{1,3}}, \quad (15)$$

$$v_4 = v - x_1 \left(\frac{\partial v}{\partial x_1} \right)_{T,p,x_{2,3}} - x_2 \left(\frac{\partial v}{\partial x_2} \right)_{T,p,x_{1,3}} - x_3 \left(\frac{\partial v}{\partial x_3} \right)_{T,p,x_{1,2}}. \quad (16)$$

Consequently, to obtain the partial molar volumes of the quaternary mixture, the partial derivatives of equation (4) are needed

$$\left(\frac{\partial v}{\partial x_1} \right)_{x_{2,3}} = \alpha_1 + 2\alpha_{11}x_1 + \alpha_{12}x_2 + \alpha_{13}x_3 + \alpha_{123}x_2x_3, \quad (17)$$

$$\left(\frac{\partial v}{\partial x_2} \right)_{x_{1,3}} = \alpha_2 + 2\alpha_{22}x_2 + \alpha_{12}x_1 + \alpha_{23}x_3 + \alpha_{123}x_1x_3, \quad (18)$$

$$\left(\frac{\partial v}{\partial x_3} \right)_{x_{1,2}} = \alpha_3 + 2\alpha_{33}x_3 + \alpha_{13}x_1 + \alpha_{23}x_2 + \alpha_{123}x_1x_2, \quad (19)$$

and the corresponding partial molar volumes can be calculated with equations (13) to (19).

In analogy to the quaternary mixture, the partial molar volumes of a ternary mixture are given by

$$v_1 = v + (1 - x_1) \left(\frac{\partial v}{\partial x_1} \right)_{T,p,x_2} - x_2 \left(\frac{\partial v}{\partial x_2} \right)_{T,p,x_1}, \quad (20)$$

$$v_2 = v + (1 - x_2) \left(\frac{\partial v}{\partial x_2} \right)_{T,p,x_1} - x_1 \left(\frac{\partial v}{\partial x_1} \right)_{T,p,x_2}, \quad (21)$$

$$v_3 = v - x_1 \left(\frac{\partial v}{\partial x_1} \right)_{T,p,x_2} - x_2 \left(\frac{\partial v}{\partial x_2} \right)_{T,p,x_1}. \quad (22)$$

The partial molar volumes obtained in this way are listed in Tables 5 and 6. Throughout, negative deviations of the partial molar volume from the molar volume of the pure substance were found, which is explained by the ordering effect of solvation due to the presence of strong inter-

molecular interactions. As expected, the partial molar volume of water shows relative deviations up to -17% from its pure substance value given by hydrogen-bond formation between water and alcohol molecules. Methanol, ethanol and propan-2-ol show smaller deviations of up to -7% , -4% and -3% from the molar volume of their pure substance state, respectively.

Conclusion

The density of the quaternary mixture water + methanol + ethanol + propan-2-ol and its four ternary subsystems was measured at ambient temperature and pressure. The corresponding molar volume data were correlated employing a response function model with 11 adjustable parameters. An excellent agreement was found between the proposed correlation and experimental literature as well as molecular simulation data. Excess and partial molar volumes of the ternary and quaternary mixtures were also determined. The excess molar volumes of the quaternary mixture and the aqueous ternary mixtures were found to have throughout negative values as a result of the presence of strongly attractive intermolecular interactions, such as hydrogen bonding between unlike molecules. Moreover, it was found that the excess molar volume of the quaternary mixture exhibits a clear dependence on water mole fraction, showing a similar behavior as the aqueous binary and ternary mixtures.

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Supporting Information Available

Supporting information includes a graphical comparison of the measured density for the six studied binary mixtures with other experimental data as well as the tabulated numerical results of the performed molecular dynamics simulations.

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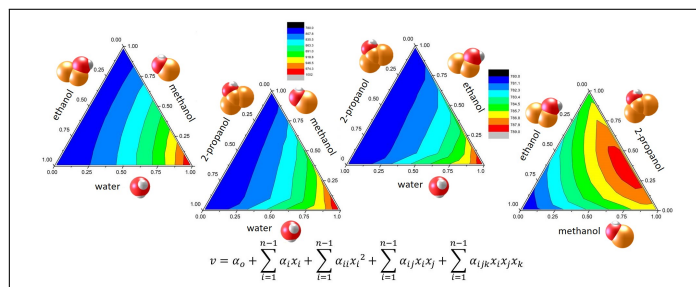
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Graphical TOC Entry



Supporting Information to:**Density and partial molar volumes of the liquid mixture water + methanol + ethanol + 2-propanol at 298.15 K and 0.1 MPa**

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DENSITY OF THE BINARY SUBSYSTEMS

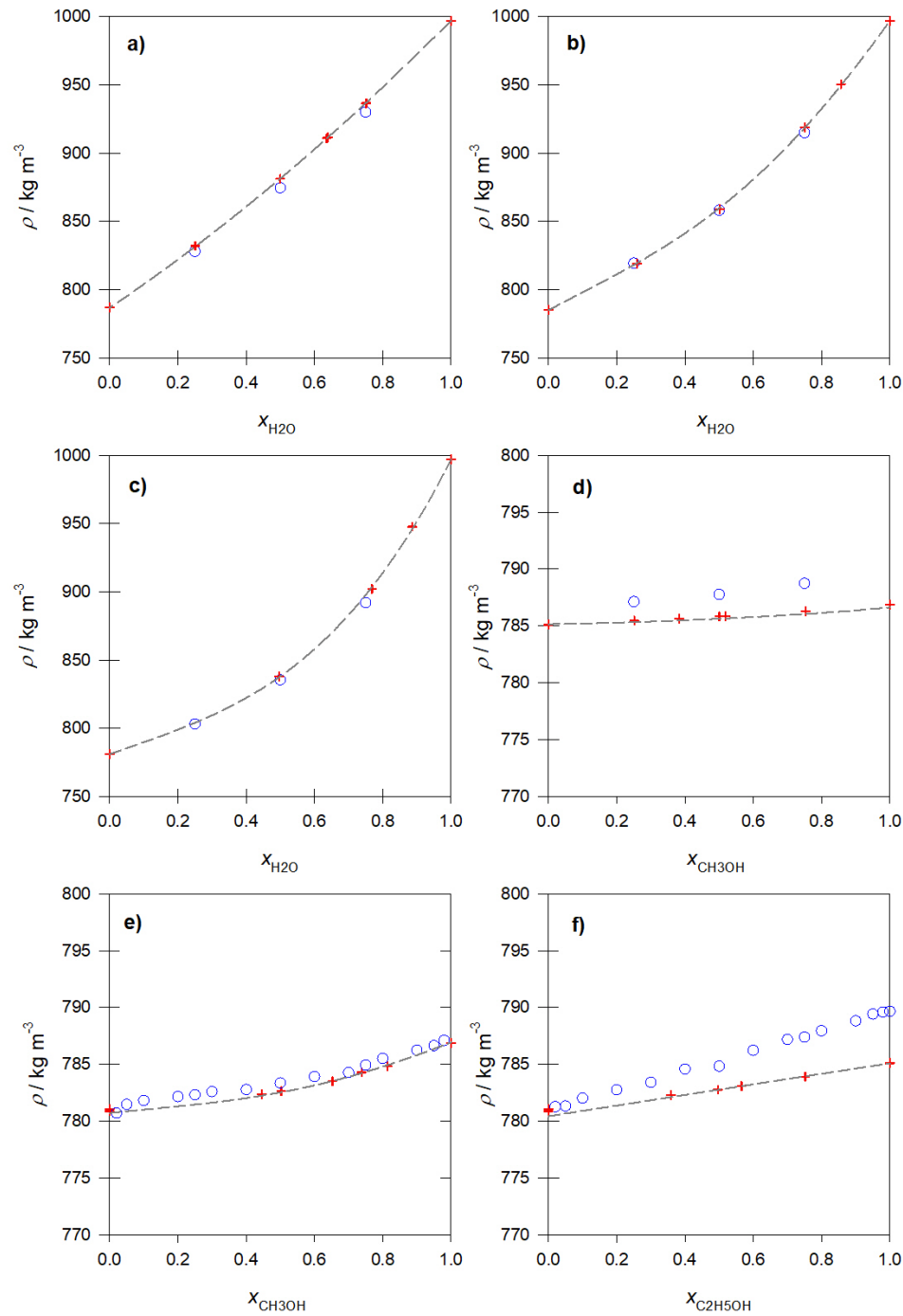


FIG. S1. Density of the binary mixtures: a) water + methanol, b) water + ethanol, c) water + propan-2-ol, d) methanol + ethanol, e) methanol + propan-2-ol and f) ethanol + propan-2-ol as a function of mole fraction at 298.15 K and 0.101 MPa. Measured data (red squares) are compared with a fourth order polynomial fit of other experimental values from the literature (gray line) [1–10] and to present simulation results (blue circles).

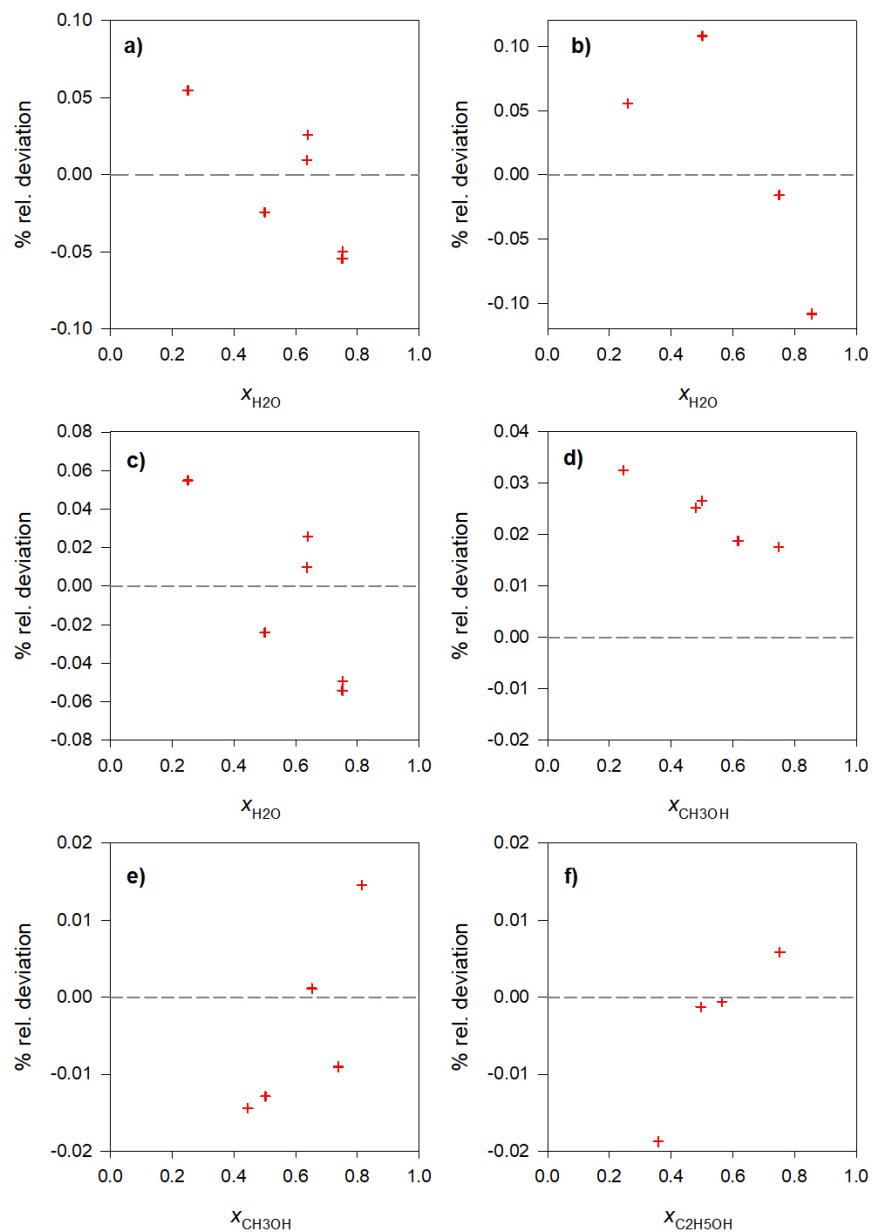


FIG. S2. Deviation plot of the density of the binary mixtures: a) water + methanol, b) water + ethanol, c) water + propan-2-ol, d) methanol + ethanol, e) methanol + propan-2-ol and f) ethanol + propan-2-ol as a function of mole fraction at 298.15 K and 0.101 MPa.

DENSITY OF THE TERNARY SUBSYSTEMS

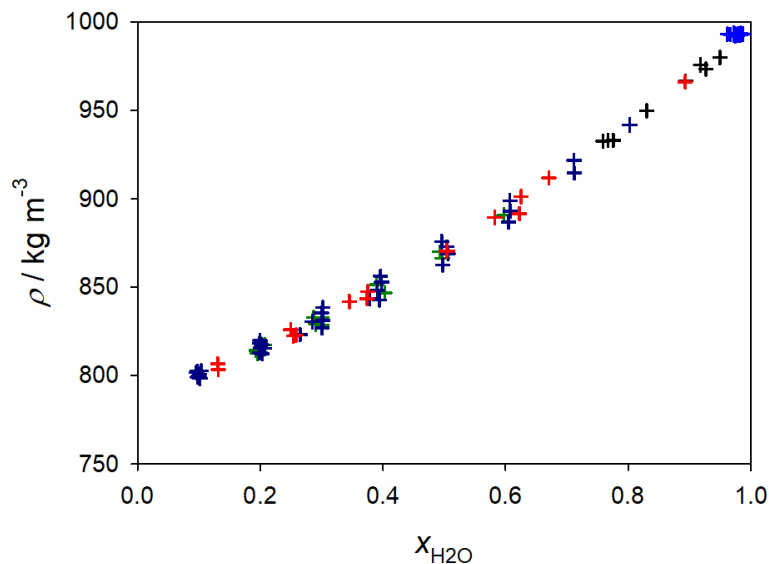


FIG. S3. Density of the ternary mixture water + methanol + ethanol as a function of water mole fraction at 298.15 K and 0.101 MPa. Measured data (red crosses) are compared with experimental data by Hernandez et al. [11] (black crosses), Zarei et al. [4] (dark blue crosses), Mori et al. [5] (green crosses) and by Perron and Desnoyers [12] (light blue crosses). Note that the mole fractions of methanol and propan-2-ol do not necessarily match.

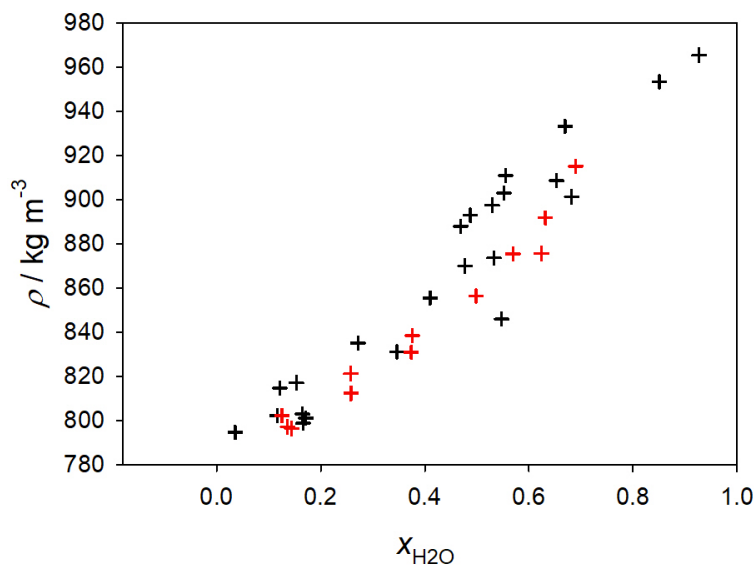


FIG. S4. Density of the ternary mixture water + methanol + propan-2-ol as a function of water mole fraction at 298.15 K and 0.101 MPa. Measured data (red crosses) are compared with experimental data by Chen and Hou [13] (black crosses). Note that the mole fractions of methanol and propan-2-ol do not necessarily match.

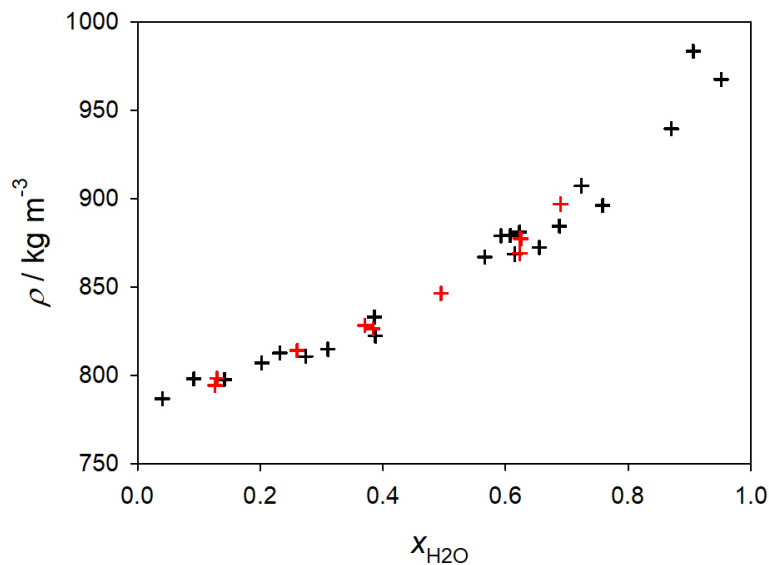


FIG. S5. Density of the ternary mixture water + ethanol + propan-2-ol as a function of water mole fraction at 298.15 K and 0.101 MPa. Measured data (red crosses) are compared with experimental data by Chen and Hou [13] (black crosses). Note that the mole fractions of ethanol and propan-2-ol do not necessarily match.

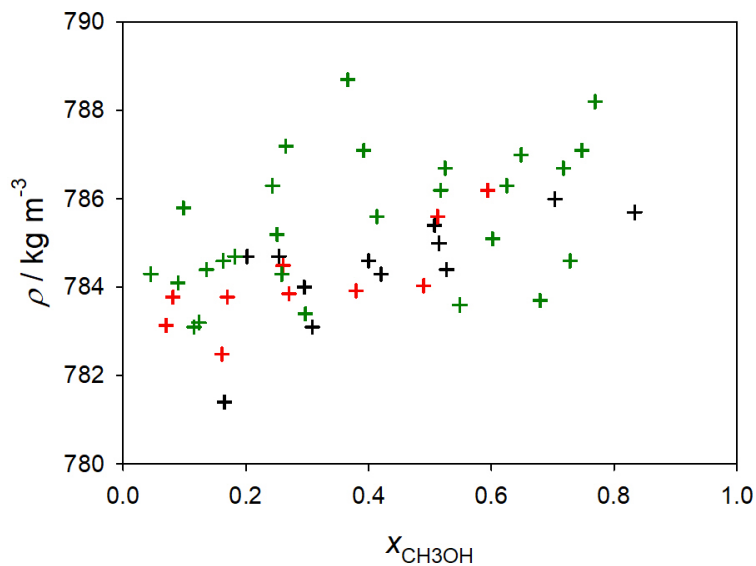


FIG. S6. Density of the ternary mixture methanol + ethanol + propan-2-ol as a function of methanol mole fraction at 298.15 K and 0.101 MPa. Measured data (red crosses) are compared with experimental data by Wei and Rowley [1] (black crosses) as well as by Chen and Hou [13] (black crosses). Note that the mole fractions of ethanol and propan-2-ol do not necessarily match.

MOLECULAR SIMULATION RESULTS

TABLE S1. Molecular simulation results for the density of the ternary mixtures water + methanol + propan-2-ol, water + ethanol + 2-propanol and methanol + ethanol + propan-2-ol at 298.15 K and 0.101 MPa ^a. The mole fraction of component *i* is x_i .

H ₂ O (1) + CH ₄ O (2) + C ₃ H ₈ O (3)			H ₂ O (1) + C ₂ H ₆ O (2) + C ₃ H ₈ O (3)			CH ₄ O (1) + C ₂ H ₆ O (2) + C ₃ H ₈ O (3)		
x_1	x_2	$\rho/\text{kg}\cdot\text{m}^{-3}$	x_1	x_2	$\rho/\text{kg}\cdot\text{m}^{-3}$	x_1	x_2	$\rho/\text{kg}\cdot\text{m}^{-3}$
0.202	0.284	805.10	0.202	0.284	802.98	0.202	0.284	784.76
0.194	0.404	807.16	0.194	0.404	804.45	0.194	0.404	785.73
0.186	0.523	809.05	0.186	0.523	805.62	0.186	0.523	786.66
0.180	0.608	810.28	0.180	0.608	806.61	0.180	0.608	787.36
0.175	0.688	811.62	0.175	0.688	807.15	0.175	0.688	787.99
0.170	0.764	812.68	0.170	0.764	807.86	0.170	0.764	788.59
0.400	0.100	825.58	0.400	0.100	824.14	0.400	0.100	784.27
0.400	0.250	833.20	0.400	0.250	828.59	0.400	0.250	785.58
0.400	0.500	848.71	0.400	0.500	837.26	0.400	0.500	787.46
0.600	0.100	863.37	0.600	0.100	860.03	0.600	0.100	785.09
0.062	0.510	791.62	0.062	0.510	791.42	0.062	0.510	785.80
0.600	0.250	878.98	0.600	0.250	868.96	0.600	0.250	786.30
0.800	0.100	926.93	0.800	0.100	919.96	0.800	0.100	786.28
0.100	0.200	792.05	0.100	0.200	791.65	0.100	0.200	783.40
0.100	0.400	794.92	0.100	0.400	794.22	0.100	0.400	785.04
0.100	0.600	797.81	0.100	0.600	797.01	0.100	0.600	786.90
0.300	0.200	815.42	0.300	0.200	813.00	0.300	0.200	784.61
0.300	0.300	819.00	0.300	0.300	815.54	0.300	0.300	785.44
0.300	0.500	827.56	0.300	0.500	820.72	0.300	0.500	786.96
0.190	0.469	808.12	0.190	0.469	805.19	0.190	0.469	786.26
0.340	0.421	831.32	0.340	0.421	824.54	0.340	0.421	786.58
0.404	0.400	842.96	0.404	0.400	834.28	0.404	0.400	786.76
0.462	0.381	854.86	0.462	0.381	844.37	0.462	0.381	786.76
0.564	0.348	878.94	0.564	0.348	865.09	0.564	0.348	786.98
0.649	0.321	903.02	0.649	0.321	887.00	0.649	0.321	787.21
0.213	0.120	802.22	0.213	0.120	801.69	0.213	0.120	783.47
0.208	0.199	803.59	0.208	0.199	802.43	0.208	0.199	784.17
0.125	0.625	802.00	0.125	0.625	800.00	0.125	0.625	800.00
0.250	0.500	818.61	0.250	0.500	813.53	0.250	0.500	813.53
0.375	0.375	833.88	0.375	0.375	828.49	0.375	0.375	828.49
0.500	0.250	853.07	0.500	0.250	846.26	0.500	0.250	846.26
0.625	0.125	872.13	0.625	0.125	867.29	0.625	0.125	867.29
0.250	0.250	809.61	0.250	0.250	807.43	0.250	0.250	807.43

^aThe statistical uncertainties of the temperature and pressure are $U_s(T) = 0.001$ K and $U_s(p) = 0.1$ MPa

The statistical uncertainties of the density is 0.005 $\text{kg}\cdot\text{m}^{-3}$

TABLE S2. Molecular simulation results for density of the ternary mixture water + methanol + ethanol at 298.15 K and 0.101 MPa ^a. The mole fraction of component i is x_i .

H ₂ O (1) + CH ₄ O (2) + C ₃ H ₈ O (3)		
x_1	x_2	$\rho/\text{kg}\cdot\text{m}^{-3}$
0.25	0.25	822.02
0.25	0.50	824.78
0.50	0.25	865.97

^aThe statistical uncertainties of the temperature and pressure are $U_s(T) = 0.001$ K and $U_s(p) = 0.1$ MPa
The statistical uncertainties of the density is 0.005 kg·m⁻³

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