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Vapor−Liquid Equilibria in Quaternary Mixtures of Dimethyl Ether + *n*-Butane + Ethanol + Water

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The vapor−liquid equilibria, liquid densities, and liquid−liquid phase separation of the quaternary system dimethyl ether (DME) + *n*-butane + ethanol + water were determined at 293.15 K. The vapor−liquid equilibria were measured for mixtures with 0−70 wt % dimethyl ether, 0−40 wt % *n*-butane, 0−70 wt % ethanol, and 0−35 wt % water, depending on the presence of a second liquid phase. The experiments were carried out in a static vapor pressure apparatus. The UNIQUAC model was used to perform the necessary corrections of the measured vapor−liquid equilibrium data. On the basis of the Gibbs−Duhem equation and experimental data, a set of parameters for this model was calculated. Using the parameters in the UNIQUAC model, it was possible to describe the quaternary as well as some of the ternary and all six binary subsystems.

Introduction

Dimethyl ether (DME) has become a well-established propellant in the aerosol industry, because of its excellent solvent properties and its high solubility in both polar and nonpolar solvents. Due to possible increasing legal regulations concerning emissions of volatile organic compounds (VOCs), there is a general interest for formulators of hair spray (the largest single product group of the aerosol industry) in replacing some of the usual VOC load by non-VOC ingredients. The cheapest of these non-VOC compounds, water, forms two liquid phases with *n*-butane, which is one of the biggest fractions of an average propellant gas. However, experiments have shown that large fractions of water have a negative influence on the spray performance.

The aim of this work is to examine formulations using DME and water in addition to the usual ethanol and *n*-butane mixtures because these formulations can contain up to 20 wt % water without significant changes in the spray performance. The reason for partially replacing one VOC (*n*-butane) by another (DME) is that dimethyl ether has a short decomposition time in the atmosphere (7.7 days) compared to that of CFC 11, which has a decomposition time of over 170 years.[1] Additionally, water has a good solubility in DME, and because of its mediating effects, DME prevents the formation of a second liquid phase.

For optimizing an aerosol hair spray, some important factors need to be evaluated, for example, vapor pressure, liquid density, spray characteristics, solvent properties for the hair fixing polymer, prevention of phase separation, flammability, and efficacy.

Reliable literature data of this kind for the six binary systems bordering the quaternary mixture (except for water−ethanol[2]) were not available, so all data presented in this paper for these systems were determined experimentally.

Experimental Section

Materials. Dimethyl ether was supplied by DEA Mineralöl AG, Wesseling, with a purity of >99.999%. It was used without further purification. *n*-Butane was supplied by WESTFALENGAS in special carrier bottles used only for this substance. A purity of 99.99% was stated by the producer. The butane was used without further purification. Ethanol (pro analysi) was supplied by MERCK, Darmstadt. Water used in the experiments was triply distilled by the DEA laboratory.

Experimental Apparatus. The requirements which the experimental apparatus had to fulfill were precise vapor pressure measurements, clear detection of the phase envelope between complete miscibility and the two-phase area, rapid achievement of equilibrium, and short distances between the pressure sensor and the actual test cell. All this had to be achieved with a leak-free system so that measurements could be performed for several hours without any leakage. These prerequisites were met by the use of the BUECHI glass equipment shown in Figure 1. The glass autoclave used in the experiments was supplied by BUECHI Laboratoriumstechnik Göppingen. The maximum volume was 1 L, and the maximum pressure was 0.6 MPa. The autoclave was equipped with a special magnetic stirrer driven by an appropriate motor. The pressure indicator used was supplied by MÄTTIG M&R Technik, Unna, with a measuring range of 0−0.7 MPa (accuracy: ±2.4 kPa at maximum readout). It was calibrated at a defined vacuum and atmospheric pressure measured by a calibrated barometer. The voltage generated by the pressure indicator was displayed by a multimeter (2015 THD, Keithley). The temperature was measured by a platinum resistance thermometer (PT 100, LAUDA, Königshofen). The PT 100 was calibrated with the help of melting ice and boiling water. In combination with a digital display (6 digits) the accuracy of temperature was ±0.02 °C. The liquid density was determined by an vibrating u-tube density analyzer

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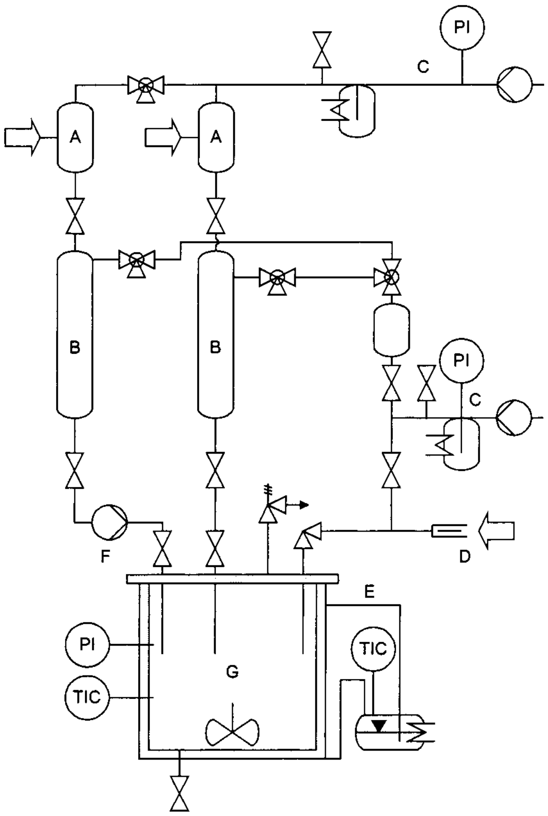

Figure 1. Experimental apparatus: A, degassing container (left: water/right: EtOH); B, glass buret (left: water/right: EtOH); C, vacuum pumps combined with cooling traps and pressure indicator; D, docking station for *n*-butane/DME; E, glass autoclave with cooling system; F, HPLC water pump; G, temperature-controlled interior of the autoclave stirred by a magnetic stirrer.

Table 1. Vapor Pressures (vp) and Densities of the Pure Substances (293.15 K) Compared with Literature

system	experiment	literature
vp water	0.0023 MPa	0.002 33 MPa[a]
vp ethanol	0.0059 MPa	0.005 85 MPa[a]
vp *n*-butane	0.2075 MPa	0.207 54 MPa[a]
vp DME	0.5125 MPa	0.507 39 MPa[a]
density water	998.2 kg·m^{-3}	998.3 kg·m^{-3} [b]
density ethanol	789.4 kg·m^{-3}	789.36 kg·m^{-3} [b]
density *n*-butane	579.0 kg·m^{-3}	579.0 kg·m^{-3} [b]
density DME	668.4 kg·m^{-3}	

[a] Boublik et al.[4] [b] Daubert and Danner.[5]

DMA 45 (Heraeus-Paar, Graz). To prepare the samples for the measurements, special pressure resistant glass bottles (PAMASOL) were used.

Preparation of VLE Samples. The degassing of water and ethanol was carried out in special glass containers, which could be evacuated by a vacuum pump (Figure 1; A and C). By keeping the substances at their pure-component vapor pressure until a decrease in temperature of >3 °C was achieved, a sufficient degassing was reached, which can be proven by a simple equilibrium calculation for the dissolved gases.[3] The quality of the degassing was proven by subsequent measurements of the pure substance vapor pressures, which were compared to values taken from the literature given in Table 1. The difference for the DME measurements results from the higher purity of the DME produced by DEA.

The preparation of a vapor−liquid equilibrium (VLE) experiment started with the evacuation of the autoclave to a pressure < 10^{-5} MPa with an EDWARDS E2M-12 vacuum pump. The second step was to fill the autoclave with the appropriate volume of ethanol from the glass buret (Figure 1; B) under the suction of the vacuum. The two liquified gases were then added, driven by their own vapor pressure. The amount of substance added could be calculated by the loss of weight of the carrier determined by a scale. The fourth component, water, was pumped in steps of 5 wt % from the glass buret against the pressure inside the autoclave by a HPLC-pump (P402, Latek). As in the case of ethanol, the administered volume could be determined by a scale on the buret. After each concentration step of water, the temperature of the autoclave was brought back to 293.15 K. During the experiments the stirring rate was adjusted to 700 rpm. This stirring was chosen to prevent the re-entering of gas into the liquid phase in the form of very small bubbles which hindered the detection of a liquid−liquid phase separation.

Evaluation of Data. The G^E model for the calculations in this work is UNIQUAC.[3,6] This model was selected from various other G^E models because of the special characteristics of the present mixture. With butane and water in the mixture a strong deviation from the mixture's ideal behavior was to be expected, and thus the G^E model had to be adjustable to cope with this problem. The model equations are

$$\frac{G^E}{RT} = \left(\frac{G^E}{RT}\right)^C + \left(\frac{G^E}{RT}\right)^R \tag{1}$$

$$\left(\frac{G^E}{RT}\right)^C = \sum_i x_i \ln\left(\frac{\Phi_i}{x_i}\right) + \frac{z}{2}\sum_i q_i x_i \ln \frac{\Psi_i}{\Phi_i} \tag{2}$$

$$\left(\frac{G^E}{RT}\right)^R = -\sum_i q_i x_i \ln \sum_j \Psi_i \tau_{ji} \tag{3}$$

$$\tau_{ji} = \exp\left(\frac{-\Delta u_{ij}}{T}\right) \tag{4}$$

where Φ_i is the volume fraction and Ψ_i is the surface fraction of component i.[7] The coordination number z was set to 10. These equations can be used to calculate the activity coefficient.

Because of an incomplete filling of the autoclave, a fraction of the substance evaporated and remained in the vapor phase. To correct the composition of the vapor phase, the full set of UNIQUAC parameters was necessary. Thus, both the determination of the UNIQUAC parameter and the correction of the liquid phase had to be done in one program, as shown in the flow sheet in Figure 2. As initial values for the UNIQUAC equation, the parameters determined by the binary systems and the parameters taken from the LLE of water−butane were used. These parameters and the necessary pure component and experimental data were read into the program from an input file in the first step (segment I). The second step was the calculation of activities, fugacities, and the molar composition of the vapor phase at the experimental pressure, until calculated and measured pressure converged (segment II). In the third step, the administered amounts of every substance were corrected by the calculated evaporated volume. Finally, the newly calculated molar composition was compared to the old molar composition (segment III). If the changes were below a certain limit (ϵ), the results were written to an output file (segment IV). For the calculation of the second virial coefficient, the method of Tsonopoulos[7] was employed.

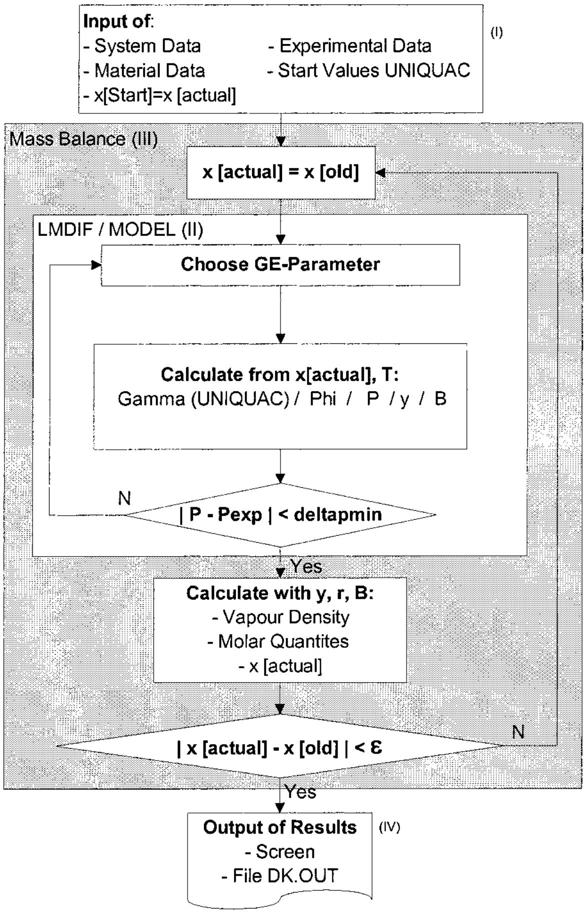

Figure 2. Flow sheet of data evaluation and liquid-phase correction.

In addition to the activities and the fugacities, the Poynting correction was used for the determination of the system pressure.

Liquid Density. The densities of liquified gases were measured in a u-tube sensor in the same way as it was done for liquids, except one side of the u-tube was sealed by a valve to hold the pressure during the measurements. The second side was used to feed the liquified gases from a PAMASOL bottle, which was kept at a higher temperature and pressure. To fill the u-tube, the valve was opened a little so the liquified gas flowed into the sensor driven by its own vapor pressure. Evaporation in the u-tube was avoided by the limited valve opening and the PAMASOL pressure. Thus, phase separation and cooling were prevented.

Detection of the Phase Envelope. The phase envelope was determined with the aid of a lamp mounted behind the glass autoclave. It was possible to estimate the onset of the phase separation through the strength of the turbidity at the injection point of the water. The feed rate was then reduced, and the crossing of the boundary into the two-phase region could be determined with a maximum error of 0.1 mL of water.

Results and Discussion

Measurements. The results of the present work are experimental data points for the six binary systems mentioned above and for the ternary system ethanol + *n*-butane + DME and quaternary data points measured for mixtures with 0−70 wt % dimethyl ether, 0−40 wt % *n*-butane, 0−70 wt % ethanol, and 0−35 wt % water, depending on the presence of a second liquid phase (Table 19), in 267 experiments. To get a complete basis for the modeling, 140 experiments were performed to determine the liquid density for the binary, ternary, and quaternary systems (Tables 3−7). On the basis of experimental data points and the UNIQUAC G^E model, a set of parameters (Table 2) was developed which describe the experimental VLE data for the quaternary (Tables 8−14) and all border systems (Tables 15−18, Figure 3) at 293.15 K in a very satisfactory manner (±1.5%). Furthermore, a model that describes the liquid densities of these systems was developed. These results were computed with a number of self-developed FORTRAN routines. The complete program code including the UNIQUAC and density model has been presented.[3]

Table 2. UNIQUAC Parameters Computed from Experimental Quaternary Data (293.15 K)

system	u_{ij}	u_{ji}
water + DME	−7.260	501.659
water + *n*-butane	587.784	452.913
ethanol + water	131.108	−16.228
ethanol + DME	−41.050	217.472
ethanol + *n*-butane	−35.113	466.662
n-butane−DME	7.162	77.335

Table 3. Liquid Densities for *n*-Butane (2)−DME (3) (293.15 K)

ρ/kg·m^{-3}	x(*n*-butane)	ρ/kg·m^{-3}	x(*n*-butane)
668.4	0.000	605.1	0.529
654.4	0.083	598.8	0.612
647.2	0.135	590.6	0.731
631.0	0.260	586.3	0.818
621.6	0.343	579.0	1.000
613.8	0.427		

Table 4. Liquid Densities for EtOH (1)−*n*-Butane (2) (293.15 K)

ρ/kg·m^{-3}	x(EtOH)	ρ/kg·m^{-3}	x(EtOH)
579.0	0.000	690.1	0.652
593.5	0.119	711.5	0.739
610.6	0.240	735.9	0.829
626.2	0.337	760.9	0.913
650.1	0.467	789.4	1.000
668.1	0.554		

Table 5. Liquid Densities for Ethanol (1)−DME (3) (293.15 K)

ρ/kg·m^{-3}	x(ethanol)	ρ/kg·m^{-3}	x(ethanol)
668.4	0.000	746.2	0.605
681.9	0.091	762.4	0.745
696.0	0.198	767.3	0.792
707.9	0.294	777.0	0.885
720.8	0.398	789.4	1.000
734.4	0.507		

Table 6. Liquid Densities for Water (4)−DME (3) (293.15 K)

ρ/kg·m^{-3}	x(water)	ρ/kg·m^{-3}	x(water)
668.4	0.000	921.5	0.838
677.4	0.049	934.7	0.863
686.5	0.094	959.3	0.924
694.0	0.129	981.4	0.971
916.1	0.833	998.2	1.000

Modeling. Modeling the quaternary system using the parameters determined from the binary data led to unsatisfactory results. The question whether UNIQUAC was able to describe quaternary systems with physically very different components had to be investigated. According to Walas et al.[8] and others, modeling based on binary data usually yields a bad description for multicomponent mixtures containing more than three components. It seems

Table 7. Liquid Densities for Ternary and Quaternary Mixtures

ρ/kg·m^{-3}	x(EtOH)	x(n-butane)	x(DME)	x(water)	ρ/kg·m^{-3}	x(EtOH)	x(n-butane)	x(DME)	x(water)
664.3	0.10	0.11	0.78	0.00	767.1	0.21	0.00	0.48	0.31
652.8	0.21	0.33	0.47	0.00	733.1	0.21	0.11	0.36	0.32
682.4	0.21	0.08	0.71	0.00	762.5	0.29	0.04	0.35	0.32
684.0	0.31	0.14	0.56	0.00	752.6	0.35	0.12	0.21	0.32
672.8	0.44	0.35	0.21	0.00	785.7	0.35	0.00	0.34	0.31
708.8	0.56	0.17	0.28	0.00	778.4	0.41	0.05	0.22	0.31
729.9	0.73	0.16	0.11	0.00	772.2	0.49	0.11	0.09	0.31
676.2	0.09	0.14	0.64	0.12	802.5	0.48	0.00	0.21	0.31
707.3	0.09	0.00	0.78	0.14	821.0	0.62	0.00	0.07	0.31
663.5	0.18	0.29	0.41	0.12	806.7	0.63	0.06	0.00	0.31
701.2	0.18	0.07	0.63	0.12	765.0	0.06	0.00	0.53	0.41
727.8	0.27	0.00	0.61	0.12	782.8	0.19	0.00	0.42	0.39
700.2	0.28	0.15	0.46	0.12	772.3	0.24	0.05	0.31	0.39
692.5	0.37	0.25	0.25	0.13	800.1	0.30	0.00	0.31	0.39
720.4	0.44	0.14	0.30	0.12	792.1	0.38	0.05	0.16	0.41
758.6	0.48	0.00	0.39	0.13	814.6	0.42	0.00	0.20	0.38
720.4	0.61	0.25	0.00	0.14	833.7	0.54	0.00	0.07	0.39
768.4	0.58	0.00	0.30	0.12	819.4	0.56	0.05	0.00	0.39
742.6	0.63	0.14	0.11	0.12	773.0	0.06	0.00	0.50	0.45
794.0	0.79	0.00	0.09	0.12	795.3	0.16	0.00	0.39	0.45
782.6	0.82	0.06	0.00	0.12	788.7	0.21	0.04	0.28	0.46
724.5	0.08	0.00	0.69	0.22	815.9	0.27	0.00	0.27	0.46
719.6	0.16	0.07	0.55	0.22	810.5	0.33	0.04	0.16	0.47
747.0	0.23	0.00	0.54	0.22	830.6	0.37	0.00	0.17	0.46
714.6	0.24	0.13	0.41	0.22	848.7	0.49	0.00	0.05	0.46
703.4	0.26	0.21	0.28	0.25	838.4	0.49	0.04	0.00	0.47
741.8	0.32	0.06	0.39	0.23	793.5	0.05	0.00	0.44	0.52
765.8	0.38	0.00	0.40	0.22	815.4	0.14	0.00	0.34	0.52
738.3	0.40	0.13	0.24	0.23	834.0	0.24	0.00	0.23	0.53
770.0	0.48	0.04	0.25	0.23	843.3	0.33	0.00	0.15	0.52
739.4	0.50	0.18	0.09	0.24	851.6	0.41	0.00	0.09	0.50
756.5	0.54	0.12	0.12	0.22	861.1	0.44	0.02	0.00	0.54
791.1	0.54	0.00	0.24	0.22	819.0	0.04	0.00	0.37	0.59
808.8	0.71	0.00	0.07	0.22	825.2	0.12	0.00	0.31	0.56
741.8	0.08	0.00	0.62	0.30	848.9	0.21	0.00	0.21	0.58
744.5	0.15	0.05	0.48	0.33	858.8	0.29	0.00	0.13	0.58

Table 8. Vapor Pressures of the Quaternary Mixture (≈5 wt % (∼12%) of VOC Content Replaced by Water) (293.15 K)

P/MPa	x(EtOH)	x(n-butane)	x(DME)	x(water)
0.3947	0.266	0.000	0.615	0.119
0.3553	0.357	0.000	0.523	0.120
0.3273	0.426	0.000	0.455	0.119
0.2763	0.525	0.000	0.356	0.119
0.2275	0.606	0.000	0.274	0.120
0.4116	0.179	0.071	0.629	0.121
0.3827	0.269	0.075	0.534	0.122
0.3533	0.357	0.073	0.449	0.121
0.3184	0.434	0.066	0.357	0.142
0.2713	0.552	0.065	0.262	0.121
0.2325	0.622	0.075	0.181	0.121
0.4250	0.091	0.148	0.637	0.124
0.3957	0.184	0.148	0.545	0.124
0.3695	0.271	0.143	0.462	0.124
0.3404	0.359	0.140	0.377	0.123
0.3024	0.459	0.142	0.275	0.123
0.2674	0.540	0.142	0.194	0.124
0.2187	0.637	0.139	0.100	0.123
0.3809	0.187	0.210	0.477	0.126
0.3474	0.283	0.217	0.374	0.126
0.3117	0.382	0.218	0.274	0.126
0.2800	0.464	0.217	0.192	0.126
0.2399	0.553	0.220	0.101	0.126
0.3563	0.188	0.298	0.385	0.129
0.3235	0.282	0.304	0.290	0.124
0.2879	0.377	0.297	0.197	0.129
0.2569	0.457	0.290	0.125	0.128
0.2036	0.560	0.312	0.000	0.129

Table 9. Vapor Pressures of the Quaternary Mixture (≈10 wt % (∼22.5%) of VOC Content Replaced by Water) (293.15 K)

P/MPa	x(EtOH)	x(n-butane)	x(DME)	x(water)
0.3895	0.235	0.000	0.543	0.223
0.3487	0.315	0.000	0.462	0.223
0.3190	0.376	0.000	0.402	0.222
0.2656	0.463	0.000	0.314	0.222
0.2156	0.535	0.000	0.243	0.222
0.4121	0.157	0.063	0.554	0.226
0.3842	0.237	0.066	0.471	0.226
0.3550	0.314	0.064	0.396	0.226
0.3203	0.392	0.060	0.323	0.226
0.2748	0.486	0.057	0.231	0.225
0.2398	0.548	0.066	0.160	0.226
0.3988	0.161	0.130	0.479	0.230
0.3734	0.238	0.126	0.407	0.230
0.3453	0.316	0.123	0.332	0.229
0.3094	0.403	0.125	0.242	0.229
0.2770	0.475	0.125	0.170	0.229
0.2334	0.561	0.122	0.088	0.229
0.3523	0.248	0.190	0.328	0.234
0.3179	0.335	0.191	0.241	0.234
0.2879	0.407	0.191	0.169	0.233
0.2509	0.485	0.193	0.089	0.233
0.2083	0.568	0.199	0.000	0.233

that sufficient binary parameters which presuppose an unchangeable reciprocal action between each two molecules in a binary system may not be able to describe effects appearing in the multicomponent mixture. As a result of this work, it can be stated that the use of the UNIQUAC equation to derive ternary or quaternary data from the binary systems involved will yield incorrect results. Deviations up to 0.02 MPa at average pressures of 0.3 MPa may occur. Therefore, it is desirable to compute the UNIQUAC parameters for multicomponent mixtures on the basis of experimental data.

However, there are several proposals in the literature to overcome the insufficient flexibility of models such as

Table 10. Vapor Pressures of the Quaternary Mixture (≈15 wt % (~31.5%) of VOC Content Replaced by Water) (293.15 K)

P/MPa	x(EtOH)	x(n-butane)	x(DME)	x(water)
0.3870	0.207	0.000	0.480	0.313
0.3433	0.279	0.000	0.409	0.313
0.3123	0.332	0.000	0.356	0.312
0.2569	0.410	0.000	0.278	0.312
0.2063	0.462	0.000	0.210	0.328
0.4167	0.139	0.055	0.489	0.317
0.3891	0.209	0.058	0.416	0.317
0.3605	0.277	0.056	0.350	0.317
0.3263	0.348	0.053	0.285	0.316
0.2828	0.429	0.050	0.204	0.316
0.2515	0.484	0.058	0.141	0.317

Table 11. Vapor Pressures of the Quaternary Mixture (≈20 wt % (~39%) of VOC Content Replaced by Water) (293.15 K)

P/MPa	x(EtOH)	x(n-butane)	x(DME)	x(water)
0.3859	0.183	0.000	0.425	0.392
0.3395	0.246	0.000	0.362	0.392
0.3071	0.294	0.000	0.315	0.391
0.2501	0.363	0.000	0.246	0.391
0.1995	0.418	0.000	0.190	0.391
0.4215	0.123	0.049	0.432	0.396
0.3961	0.185	0.051	0.367	0.397
0.3686	0.246	0.050	0.309	0.396
0.3358	0.306	0.046	0.252	0.396
0.2945	0.379	0.044	0.181	0.396
0.2663	0.427	0.051	0.125	0.369

Table 12. Vapor Pressures of the Quaternary Mixture (≈25 wt % (~46%) of VOC Content Replaced by Water) (293.15 K)

P/MPa	x(EtOH)	x(n-butane)	x(DME)	x(water)
0.3853	0.162	0.000	0.376	0.462
0.3365	0.218	0.000	0.320	0.462
0.3030	0.260	0.000	0.279	0.461
0.2446	0.321	0.000	0.218	0.461
0.1941	0.370	0.000	0.169	0.461
0.4022	0.163	0.045	0.325	0.467
0.3777	0.216	0.044	0.273	0.467
0.3473	0.270	0.041	0.223	0.466
0.3088	0.335	0.039	0.160	0.466
0.2812	0.378	0.045	0.111	0.467

Table 13. Vapor Pressures of the Quaternary Mixture (≈30 wt % (~52.5%) of VOC Content Replaced by Water) (293.15 K)

P/MPa	x(EtOH)	x(n-butane)	x(DME)	x(water)
0.3849	0.143	0.000	0.332	0.525
0.3339	0.192	0.000	0.283	0.524
0.2994	0.229	0.000	0.246	0.525
0.2401	0.283	0.000	0.193	0.524
0.1893	0.322	0.000	0.147	0.531

Table 14. Vapor Pressures of the Quaternary Mixture (≈35 wt % (~58%) of VOC Content Replaced by Water) (293.15 K)

P/MPa	x(EtOH)	x(n-butane)	x(DME)	x(water)
0.3844	0.126	0.000	0.293	0.581
0.3313	0.170	0.000	0.250	0.580
0.2965	0.202	0.000	0.218	0.580
0.2361	0.250	0.000	0.170	0.580
0.1860	0.288	0.000	0.132	0.580

UNIQUAC or NRTL by the help of adequate extensions. One example can be found in Connemann et al.,[9] where the NRTL equation is modified in two different ways to describe VLE and LLE data simultaneously.

Table 15. Binary Data for *n*-Butane (2)−DME (3) (293.15 K)

P/MPa	x_1	y_1	γ_1	γ_2
0.5125	0.000	0.000	2.069	1.000
0.5062	0.081	0.064	1.739	1.007
0.4957	0.165	0.117	1.509	1.027
0.4825	0.253	0.164	1.346	1.058
0.4625	0.345	0.210	1.229	1.100
0.4382	0.442	0.262	1.145	1.152
0.4085	0.542	0.322	1.086	1.212
0.3745	0.648	0.401	1.045	1.283
0.3302	0.758	0.510	1.019	1.362
0.2752	0.876	0.681	1.004	1.451
0.2075	1.000	1.000	1.000	1.551

Table 16. Binary Data for Ethanol (1)−*n*-Butane (2) (293.15 K)

P/MPa	x_1	y_1	γ_1	γ_2
0.2075	0.000	0.000	17.030	1.000
0.2057	0.123	0.025	6.163	1.064
0.2055	0.124	0.025	6.117	1.065
0.2037	0.241	0.026	3.314	1.220
0.2015	0.352	0.025	2.205	1.446
0.2012	0.355	0.025	2.186	1.453
0.1982	0.458	0.025	1.669	1.747
0.1927	0.561	0.025	1.369	2.145
0.1845	0.656	0.026	1.200	2.631
0.1700	0.747	0.030	1.099	3.237
0.1402	0.836	0.039	1.038	4.011
0.1352	0.848	0.042	1.032	4.137
0.1257	0.868	0.046	1.024	4.342
0.0850	0.919	0.067	1.008	4.950
0.0058	1.000	1.000	1.000	6.120

Table 17. Binary Data for Ethanol (1)−DME (3) (293.15K)

P/MPa	x_1	y_1	γ_1	γ_2
0.5125	0.000	0.000	3.211	1.000
0.4675	0.101	0.003	2.307	1.017
0.4317	0.201	0.006	1.807	1.062
0.4042	0.285	0.007	1.548	1.116
0.4002	0.302	0.008	1.506	1.128
0.3707	0.389	0.010	1.335	1.200
0.3660	0.401	0.010	1.316	1.214
0.3396	0.464	0.011	1.231	1.277
0.3210	0.506	0.012	1.185	1.323
0.2977	0.562	0.014	1.136	1.389
0.2785	0.604	0.016	1.106	1.443
0.2285	0.702	0.021	1.054	1.579
0.1700	0.804	0.031	1.021	1.740
0.1596	0.820	0.034	1.017	1.766
0.1155	0.878	0.048	1.007	1.867
0.0058	1.000	1.000	1.000	2.102

Table 18. Binary Data for Water (4)−DME (3) (293.15 K)

P/MPa	x_1	y_1	γ_1	γ_2
0.5125	0.000	0.000	29.764	1.000
0.4985	0.025	0.002	20.694	1.004
0.4902	0.049	0.004	15.423	1.016
0.4837	0.073	0.004	12.079	1.032
0.4802	0.096	0.005	9.819	1.052
0.4785	0.119	0.005	8.215	1.075
0.4777	0.132	0.005	7.465	1.090
0.4777	0.815	0.005	1.089	5.067
0.4775	0.821	0.005	1.083	5.198
0.4740	0.288	0.005	1.077	5.332
0.4685	0.834	0.005	1.072	5.469
0.4620	0.840	0.005	1.066	5.608
0.4417	0.853	0.005	1.056	5.917
0.3285	0.906	0.006	1.023	7.457
0.2222	0.945	0.009	1.008	9.035
0.0023	1.000	1.000	1.000	12.201

Error Estimation. For an assessment of the method of measurement, two possible kinds of errors have to be considered. Systematic errors would have become visible through deviations between the experimental data and control data determined with a different measurement

Table 19. Border of the Miscibility Area for Different Formulations (293.15 K)

P/MPa	*x*(EtOH)	*x*(*n*-butane)	*x*(DME)	*x*(water)
4.220	0.121	0.048	0.425	0.407
4.027	0.161	0.045	0.322	0.472
3.833	0.198	0.040	0.251	0.510
3.568	0.241	0.037	0.199	0.523
4.249	0.088	0.143	0.618	0.150
3.809	0.201	0.106	0.343	0.351
3.570	0.252	0.096	0.266	0.384
3.245	0.322	0.100	0.194	0.384
2.944	0.385	0.101	0.138	0.375
2.546	0.465	0.101	0.073	0.361
4.673	0.000	0.251	0.744	0.005
4.082	0.095	0.224	0.573	0.106
3.840	0.169	0.190	0.433	0.206
3.543	0.236	0.181	0.313	0.270
3.215	0.308	0.176	0.222	0.294
2.919	0.377	0.176	0.157	0.290
2.542	0.460	0.183	0.084	0.273
2.091	0.568	0.199	0.000	0.233
4.355	0.000	0.345	0.655	0.000
3.884	0.099	0.321	0.502	0.077
3.573	0.182	0.288	0.372	0.158
3.268	0.259	0.280	0.267	0.195
2.929	0.336	0.265	0.176	0.222
2.644	0.408	0.259	0.111	0.222
2.110	0.526	0.293	0.000	0.182

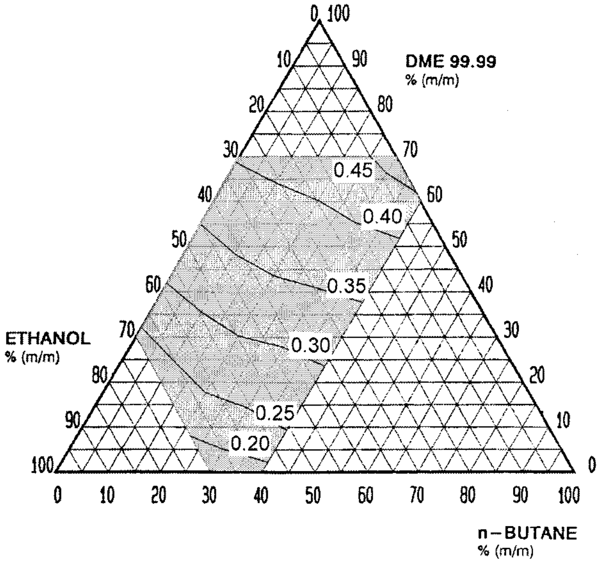

Figure 3. Vapor pressure (in MPa) of ternary mixtures of DME + *n*-butane + ethanol at 293.15 K. The gray area represents the area of interest for propellants with the possible compositions of the water-free mixtures (in wt %).

method showing a perceptible tendency. However, with the vapor pressures of the four components distributed over the full range of the possible pressures, the comparison of these pure substance vapor pressures with the literature data can hint at the quality of the measurements. Except for the case of DME, all vapor pressures determined with the system match the literature. The deviation of the data for DME can be explained by the high purity of the DME produced at DEA. Measurement errors occur because of inaccuracies of the apparatus. An exact error computation for every measured data point yielded an average uncertainty of about 1.3 kPa and a maximum possible deviation of 2.2 kPa at average pressures of 0.3 MPa. These errors are caused by uncertainties in the dosage of the components and the pressure and temperature readings. Other deviations, such as the gas-phase volume in the pipe layout between the test cell and the gas containers, can be neglected, since these uncertainties are small (ca. 6×10^{-3} kPa) compared to the other stated uncertainties. A complete summary of the deviations caused by the apparatus and the fitting of the data has been presented.[3]

Temperature Dependence. Concerning the extrapolation in temperature of the UNIQUAC parameters given in this article, it should be stated that deviations between measurements and the extrapolated model of <7% in total pressure were calculated for a temperature of 278.15 K.

Consistency. Assessment of experimental thermodynamic data is usually done by a consistency test based on the Gibbs−Duhem equation, which requires redundant VLE data, for example the liquid and the gaseous molar fractions. In this work, thermodynamic consistency was the basis for the computation of the molar fractions in the vapor and was therefore not further verified.

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