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Vapor−Liquid Equilibrium for the *cis*-2-Butene + Methanol, + 2-Propanol, + 2-Butanol, + 2-Methyl-2-propanol Systems at 364.5 K

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Vapor−liquid equilibrium (VLE) data for *cis*-2-butene + methanol, + 2-propanol, + 2-butanol, and + 2-methyl-2-propanol were measured at 364.5 K with a static total pressure apparatus. Measured *pTz* (pressure−temperature−total composition) data were reduced to liquid- and vapor-phase compositions using Barker's method. An azeotropic point was found for *cis*-2-butene + methanol ($x_1 = 0.847$; $T = 364.52$ K; $p = 1303.8$ kPa). Wilson parameters were calculated; the results were compared with predictive UNIFAC and UNIFAC−Dortmund models; and an error analysis was made.

1. Introduction

Vapor−liquid equilibrium (VLE) data are necessary for modeling of separation processes in many stages of development, design, and optimization of chemical plants. UNIFAC[1] or UNIFAC−Dortmund[2] models can be used to predict VLE data, although the accuracy of these models is often not sufficient for later stages of the process design and modeling or in the case of a separation process that is sensitive to VLE.

Systems of hydrocarbons in alcohols and alcohols in hydrocarbons have strong temperature dependence in their fluid-phase behavior. This is especially the case in the dilute alcohol area (see, e.g., Pokki et al.[3]). Activity coefficients at infinite dilution of *cis*-2-butene in alcohols have been measured by Miyano et al.[4] In this work, the infinite dilution activity coefficients of alcohols in *cis*-2-butene were determined as well. Insight into the fluid phase behavior of hydrocarbons and alcohols is important in the design and operation of distillation processes used in gasoline production. For instance, 2-methyl-2-propanol is present, and 2-butanol can be present in the iso-octene production process.[5,6]

Henry's law constants and infinite dilution activity coefficients have been reported for *cis*-2-butene in methanol, 2-propanol, 2-butanol, and 2-methyl-2-propanol at (250 to 330) K.[4] We have previously published VLE data for *cis*-2-butene + methanol, + 2-propanol, + 2-butanol, and + 2-methyl-2-propanol at 337 K.[3] These same systems are investigated in this work, at a slightly higher temperature of 364.5 K. The effect of this temperature increase on the fluid-phase behavior is significant.

2. Experimental

2.1. Materials. The quality and suppliers of materials used, as well as the critical properties and the acentric factors for these materials, are presented in Table 1. The alcohols were dried over Merck 3A molecular sieves for at least 24 h before degassing. Degassing of the alcohols was performed by the method of vacuum rectification[7] with modifications.[8] *cis*-2-Butene was degassed by evacuation in a syringe pump where the vacuum line was opened ten times for a period of 10 s. In Table 2, a comparison between measured vapor pressure and correlations from the literature is shown. In this work, *cis*-2-butene is designated component (1) and the alcohols component (2).

2.2. Apparatus. The experiments have been conducted using a static total pressure apparatus, which is described in detail by Uusi-Kyyny et al.[9] The pressure transducer was replaced by a Digiquartz 2300A-101 model with a pressure range of (0 to 2) MPa. The total uncertainty in the pressure measurements was 0.4 kPa The pressure cell volume was $112.68 \cdot 10^{-6}$ m^3, and the temperature stability of the water bath was ± 0.02 K, measured by a Frontek Thermolyzer S2541 equipped with Pt-100 probes.

2.3. Procedure. The temperatures of the cell and the syringe pumps, the cell pressure, and the total volume of components fed to the cell were recorded at each equilibrium point. From the injected volumes of components, the total number of moles and the total composition were calculated. Then, the liquid and vapor mole fractions were calculated from the total pressure measurements by means of Barker data reduction.[10] A detailed description of the method can be found in Uusi-Kyyny et al.[9]

The composition range was covered by approaching the equimolar point from both sides. Each measurement series was started by first injecting component 1 into the cell and measuring the vapor pressure. Then, a small amount of component 2 was injected, and again the vapor pressure in the cell was measured after the pressure stabilized. Then, another volume of component 2 was injected, the system left to stabilize, and the pressure measured. This procedure was repeated until the equimolar point was reached. After emptying the cell, the same procedure was performed from the other side of the composition scale until the equimolar point was reached.

2.4. Data Reduction. The Barker method[10] was used to convert the moles of each component injected into the cell

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Table 1. Material Purities and Suppliers and Pure Component Critical Properties:[16] Critical Temperature T_c, Critical Pressure P_c, and Acentric Factor ω[a]

component	supplier	purity (wt %)	T_c/K	p_c/MPa	ω
cis-2-butene	Messer Finland Oy	99.4	435.58 ± 4.36	4.2058 ± 0.1262	0.2030
methanol	Merck	99.8	512.58 ± 5.13	8.0959 ± 0.2429	0.5656
2-propanol	Riedel-de-Haën	99.8	508.31 ± 5.08	4.7643 ± 0.1429	0.6689
2-butanol	Fluka	>99.8	536.01 ± 5.36	4.1938 ± 0.1258	0.5711
2-methyl-2-propanol	Fluka	>99.8	506.20 ± 5.06	3.9719 ± 0.1192	0.6158

[a] The errors are calculated from the maximum error percent estimated by the authors of the database.

Table 2. Measured Pure Component Vapor Pressure (p_i) vs Literature Correlations[a]

		(p_i)/kPa			
component	T/K	this work	ref 24	ref 25	ref 15
cis-2-butene	364.52	1190.5	1187.7	1179.6	1195.4
	364.52	1190.5	1187.7	1179.6	1195.4
	364.52	1189.6	1187.7	1179.6	1195.4
	364.53	1190.7	1187.9	1179.9	1194.9
methanol	364.52	267.3	267.7	266.9	267.5
2-propanol	364.52	143.9	144.8	142.1	142.7
2-butanol	364.52	74.0	73.7	75.0	74.9
2-methyl-2-propanol	364.52	143.0	142.3	141.7	143.1

[a] The vapor pressure values for *cis*-2-butene were obtained from four different experiments.

to mole fraction of the vapor and liquid phase with the VLEFIT-software.[11] In the method of Barker[10] data reduction, it is assumed that there is an activity coefficient model that can predict the bubble point pressure, p_{calcd}, with a smaller modeling error than the experimental error for the pressure measurements. The scheme for data reduction used in this work has been reported by Uusi-Kyyny et al.[9] The data were reduced with a Legendre polynomial[12] as the activity coefficient model. The fugacities were calculated using the Soave−Redlich−Kwong equation of state[13] with binary interaction parameters set to zero. From the total pressure measurements, the activity coefficients were calculated using the least-squares-based Barker method. By equating fugacities in the vapor and liquid phases, the following relation is found

$$\frac{y_i}{x_i} = \frac{\gamma_i \varphi_i^{\text{s}} p_i^{\text{s}}}{\varphi_i p} \exp \int_{p_i^{\text{s}}}^{p} \frac{V_i^{\text{L}}}{RT} \mathrm{d}p \tag{1}$$

where x_i and y_i are the liquid and vapor phase mole fractions for component i, respectively; γ_i is the activity coefficient for component i; φ_i^{s} is the saturated liquid fugacity coefficient for pure component i at system temperature; φ_i is the fugacity coefficient of the vapor phase for component i; p_i^{s} is the vapor pressure of pure component i at system temperature; p is the total pressure; V_i^{L} is the molar volume of pure component i in the liquid phase at system temperature and pressure; R is the universal gas constant; and T is the system temperature.

The liquid molar volume in the Poynting correction was calculated with the Rackett equation.[14] The liquid phase activity coefficients were obtained by optimizing the parameters of Legendre polynomials.[12] To prevent overfitting, the number of parameters was chosen separately for each system.

2.5. Error Analysis. The overall uncertainty in the temperature measurements was ± 0.03 K in the water bath and

Table 3. VLE Data for *cis*-2-Butene (1) + Methanol (2) at 364.5 K[a]

n_1/mol	n_2/mol	z_1	T/K	p_{exptl}/kPa	p_{leg}/kPa	x_1	y_1	γ_1	γ_2
0.6817 ± 0.0072	0	1.0 ± 0.0	364.52	1190.5	1190.5 ± 0.4	1.0 ± 0.0	1.0 ± 0.0	1.00 ± 0.00	10.02 ± 0.17
0.6817 ± 0.0072	0.0075 ± 0.0006	0.9892 ± 0.0009	364.52	1215.5	1214.7 ± 1.5	0.9896 ± 0.0009	0.9752 ± 0.0018	1.00 ± 0.00	9.25 ± 0.18
0.6817 ± 0.0072	0.0125 ± 0.0006	0.9821 ± 0.0011	364.52	1229.7	1228.3 ± 1.4	0.9827 ± 0.0010	0.9612 ± 0.0017	1.00 ± 0.00	8.79 ± 0.16
0.6817 ± 0.0072	0.0217 ± 0.0007	0.9692 ± 0.0013	364.52	1251.9	1249.0 ± 1.1	0.9701 ± 0.0013	0.9394 ± 0.0017	1.00 ± 0.00	8.04 ± 0.14
0.6817 ± 0.0072	0.0366 ± 0.0009	0.9490 ± 0.0016	364.52	1275.4	1272.1 ± 0.9	0.9501 ± 0.0016	0.9127 ± 0.0016	1.01 ± 0.00	7.03 ± 0.11
0.6817 ± 0.0072	0.0760 ± 0.0013	0.8997 ± 0.0024	364.51	1297.4	1297.9 ± 0.8	0.9005 ± 0.0025	0.8716 ± 0.0017	1.03 ± 0.00	5.27 ± 0.07
0.6817 ± 0.0072	0.1218 ± 0.0017	0.8484 ± 0.0032	364.51	1300.3	1303.1 ± 0.8	0.8484 ± 0.0033	0.8482 ± 0.0019	1.07 ± 0.00	4.10 ± 0.04
0.6817 ± 0.0072	0.1717 ± 0.0022	0.7988 ± 0.0038	364.51	1297.5	1300.2 ± 0.9	0.7980 ± 0.0039	0.8346 ± 0.0021	1.12 ± 0.00	3.35 ± 0.03
0.6817 ± 0.0072	0.2285 ± 0.0028	0.7490 ± 0.0043	364.52	1292.2	1294.0 ± 1.0	0.7475 ± 0.0044	0.8253 ± 0.0022	1.18 ± 0.00	2.82 ± 0.02
0.6817 ± 0.0072	0.2928 ± 0.0035	0.6996 ± 0.0047	364.53	1285.5	1286.4 ± 1.1	0.6976 ± 0.0048	0.8185 ± 0.0021	1.24 ± 0.01	2.43 ± 0.01
0.6817 ± 0.0072	0.3680 ± 0.0042	0.6494 ± 0.0050	364.53	1277.6	1277.7 ± 0.9	0.6473 ± 0.0051	0.8130 ± 0.0020	1.32 ± 0.01	2.14 ± 0.01
0.6817 ± 0.0072	0.4542 ± 0.0051	0.6001 ± 0.0052	364.52	1268.8	1268.3 ± 0.8	0.5981 ± 0.0053	0.8083 ± 0.0018	1.42 ± 0.01	1.91 ± 0.01
0.6817 ± 0.0072	0.5587 ± 0.0062	0.5496 ± 0.0053	364.52	1258.2	1257.4 ± 0.7	0.5479 ± 0.0054	0.8040 ± 0.0016	1.53 ± 0.01	1.73 ± 0.01
0.6817 ± 0.0072	0.6812 ± 0.0074	0.5002 ± 0.0054	364.52	1246.2	1245.3 ± 0.7	0.4990 ± 0.0054	0.7998 ± 0.0014	1.66 ± 0.02	1.58 ± 0.01
0.6845 ± 0.0072	0.6910 ± 0.0075	0.4976 ± 0.0054	364.52	1245.9	1244.8 ± 0.7	0.4965 ± 0.0054	0.7995 ± 0.0014	1.66 ± 0.02	1.57 ± 0.01
0.5601 ± 0.0060	0.6910 ± 0.0075	0.4477 ± 0.0053	364.53	1229.4	1228.8 ± 0.9	0.4443 ± 0.0054	0.7947 ± 0.0013	1.83 ± 0.02	1.45 ± 0.01
0.4565 ± 0.0049	0.6910 ± 0.0075	0.3978 ± 0.0052	364.52	1208.1	1208.1 ± 0.9	0.3918 ± 0.0053	0.7891 ± 0.0013	2.04 ± 0.03	1.34 ± 0.00
0.3691 ± 0.0004	0.6910 ± 0.0075	0.3481 ± 0.0049	364.53	1179.8	1180.2 ± 0.8	0.3391 ± 0.0050	0.7819 ± 0.0013	2.29 ± 0.03	1.25 ± 0.00
0.2940 ± 0.0032	0.6910 ± 0.0075	0.2984 ± 0.0046	364.53	1140.5	1141.1 ± 0.6	0.2864 ± 0.0046	0.7720 ± 0.0014	2.61 ± 0.04	1.18 ± 0.00
0.2293 ± 0.0026	0.6910 ± 0.0075	0.2492 ± 0.0042	364.52	1085.4	1085.8 ± 0.9	0.2343 ± 0.0041	0.7580 ± 0.0015	3.01 ± 0.05	1.12 ± 0.00
0.1729 ± 0.0020	0.6910 ± 0.0075	0.2001 ± 0.0036	364.52	1007.6	1007.5 ± 0.9	0.1834 ± 0.0035	0.7367 ± 0.0015	3.53 ± 0.06	1.08 ± 0.00
0.1238 ± 0.0015	0.6910 ± 0.0075	0.1519 ± 0.0030	364.52	899.9	899.5 ± 0.7	0.1348 ± 0.0029	0.7029 ± 0.0013	4.17 ± 0.08	1.04 ± 0.00
0.0815 ± 0.0011	0.6910 ± 0.0075	0.1055 ± 0.0023	364.52	758.8	758.5 ± 0.9	0.0902 ± 0.0021	0.6461 ± 0.0010	4.97 ± 0.12	1.02 ± 0.00
0.0425 ± 0.0007	0.6910 ± 0.0075	0.0579 ± 0.0015	364.52	568.4	568.5 ± 0.9	0.0474 ± 0.0013	0.5274 ± 0.0006	6.00 ± 0.18	1.01 ± 0.00
0.0275 ± 0.0005	0.6910 ± 0.0075	0.0383 ± 0.0011	364.51	475.6	475.4 ± 0.6	0.0307 ± 0.0010	0.4354 ± 0.0008	6.49 ± 0.21	1.00 ± 0.00
0.0141 ± 0.0004	0.6910 ± 0.0075	0.0199 ± 0.0007	364.52	379.6	379.9 ± 1.1	0.0157 ± 0.0007	0.2946 ± 0.002	7.00 ± 0.25	1.00 ± 0.00
0	0.6910 ± 0.0075	0.0 ± 0.0	364.52	267.3	267.3 ± 0.4	0.0 ± 0.0	0.0 ± 0.0	7.61 ± 0.28	1.00 ± 0.00

[a] T is the experimental temperature; n_1 and n_2 are the moles of components injected into the equilibrium cell; z_1 is the total mol fraction; x_1 and y_1 are the calculated mole fractions in the liquid and vapor phases, respectively; the experimental pressure is p_{exptl}; and the pressure calculated from the Legendre polynomial fit is p_{leg}; γ_1 and γ_2 are the calculated activity coefficients.

Table 4. VLE Data for *cis*-2-Butene (1) + 2-Propanol (2) at 364.5 K[a]

n_1/mol	n_2/mol	z_1	T/K	p_{exptl}/kPa	p_{leg}/kPa	x_1	y_1	γ_1	γ_2
0.5411 ± 0.0058	0	1.0 ± 0.0	364.52	1190.5	1190.5 ± 0.4	1.0 ± 0.0	1.0 ± 0.0	1.00 ± 0.00	5.03 ± 0.06
0.5411 ± 0.0058	0.0059 ± 0.0003	0.9892 ± 0.0007	364.52	1186.5	1186.9 ± 0.5	0.9891 ± 0.0007	0.9915 ± 0.0006	1.00 ± 0.00	4.74 ± 0.04
0.5411 ± 0.0058	0.0113 ± 0.0004	0.9795 ± 0.0009	364.52	1182.8	1183.4 ± 0.5	0.9793 ± 0.0009	0.9847 ± 0.0008	1.00 ± 0.00	4.51 ± 0.04
0.5411 ± 0.0058	0.0171 ± 0.0004	0.9694 ± 0.0011	364.52	1178.5	1179.3 ± 0.5	0.9689 ± 0.0011	0.9782 ± 0.0009	1.00 ± 0.00	4.28 ± 0.03
0.5411 ± 0.0058	0.0288 ± 0.0006	0.9495 ± 0.0014	364.52	1169.7	1170.6 ± 0.5	0.9486 ± 0.0015	0.9671 ± 0.0012	1.01 ± 0.00	3.88 ± 0.03
0.5411 ± 0.0058	0.0606 ± 0.0009	0.8993 ± 0.0023	364.52	1146.4	1146.7 ± 0.7	0.8972 ± 0.0024	0.9463 ± 0.0015	1.03 ± 0.00	3.13 ± 0.01
0.5411 ± 0.0058	0.0964 ± 0.0012	0.8488 ± 0.0030	364.52	1122.8	1122.1 ± 0.7	0.8457 ± 0.0032	0.9320 ± 0.0017	1.05 ± 0.00	2.60 ± 0.01
0.5411 ± 0.0058	0.1360 ± 0.0016	0.7992 ± 0.0036	364.52	1099.1	1098.2 ± 0.7	0.7954 ± 0.0038	0.9214 ± 0.0018	1.09 ± 0.00	2.23 ± 0.01
0.5411 ± 0.0058	0.1806 ± 0.0021	0.7498 ± 0.0042	364.51	1074.9	1074.2 ± 0.7	0.7456 ± 0.0043	0.9127 ± 0.0017	1.13 ± 0.00	1.97 ± 0.01
0.5411 ± 0.0058	0.2328 ± 0.0026	0.6992 ± 0.0046	364.52	1049.4	1049.0 ± 0.5	0.6950 ± 0.0048	0.9048 ± 0.0017	1.18 ± 0.01	1.76 ± 0.00
0.5411 ± 0.0058	0.2918 ± 0.0032	0.6497 ± 0.0049	364.52	1022.6	1022.8 ± 0.4	0.6457 ± 0.0051	0.8974 ± 0.0016	1.23 ± 0.01	1.60 ± 0.00
0.5411 ± 0.0058	0.3606 ± 0.0039	0.6001 ± 0.0052	364.52	994.1	994.5 ± 0.6	0.5968 ± 0.0053	0.8900 ± 0.0016	1.30 ± 0.01	1.48 ± 0.00
0.5411 ± 0.0058	0.4428 ± 0.0048	0.5500 ± 0.0053	364.52	962.6	963.3 ± 0.6	0.5476 ± 0.0054	0.8822 ± 0.0016	1.36 ± 0.01	1.38 ± 0.00
0.5411 ± 0.0058	0.5404 ± 0.0058	0.5004 ± 0.0053	364.52	928.7	929.2 ± 0.7	0.4991 ± 0.0054	0.8739 ± 0.0015	1.44 ± 0.01	1.30 ± 0.00
0.5402 ± 0.0058	0.5423 ± 0.0058	0.4990 ± 0.0053	364.53	928.2	928.3 ± 0.7	0.4978 ± 0.0054	0.8736 ± 0.0015	1.44 ± 0.01	1.30 ± 0.00
0.4450 ± 0.0048	0.5423 ± 0.0058	0.4507 ± 0.0053	364.52	888.9	888.9 ± 0.6	0.4478 ± 0.0053	0.8640 ± 0.0016	1.53 ± 0.02	1.24 ± 0.00
0.3636 ± 0.0039	0.5423 ± 0.0058	0.4014 ± 0.0052	364.52	843.6	843.4 ± 0.4	0.3966 ± 0.0052	0.8526 ± 0.0016	1.63 ± 0.02	1.18 ± 0.00
0.2951 ± 0.0032	0.5423 ± 0.0058	0.3524 ± 0.0050	364.52	792.6	792.2 ± 0.6	0.3459 ± 0.0050	0.8390 ± 0.0016	1.75 ± 0.02	1.13 ± 0.00
0.2361 ± 0.0026	0.5423 ± 0.0058	0.3033 ± 0.0046	364.52	734.0	733.6 ± 0.7	0.2952 ± 0.0046	0.8220 ± 0.0017	1.88 ± 0.03	1.09 ± 0.00
0.1849 ± 0.0021	0.5423 ± 0.0058	0.2543 ± 0.0042	364.52	667.1	666.9 ± 0.7	0.2451 ± 0.0042	0.8000 ± 0.0017	2.03 ± 0.03	1.06 ± 0.00
0.1409 ± 0.0017	0.5423 ± 0.0058	0.2062 ± 0.0037	364.52	592.0	592.1 ± 0.6	0.1964 ± 0.0036	0.7705 ± 0.0017	2.19 ± 0.04	1.04 ± 0.00
0.1014 ± 0.0013	0.5423 ± 0.0058	0.1575 ± 0.0031	364.52	505.5	505.8 ± 0.5	0.1481 ± 0.0030	0.7267 ± 0.0016	2.38 ± 0.05	1.02 ± 0.00
0.0665 ± 0.0009	0.5423 ± 0.0058	0.1093 ± 0.0024	364.52	408.5	408.7 ± 0.7	0.1012 ± 0.0023	0.6567 ± 0.0014	2.59 ± 0.06	1.01 ± 0.00
0.0354 ± 0.0006	0.5423 ± 0.0058	0.0613 ± 0.0016	364.52	300.1	300.0 ± 0.7	0.0558 ± 0.0015	0.5263 ± 0.0011	2.82 ± 0.08	1.00 ± 0.00
0.0241 ± 0.0005	0.5423 ± 0.0058	0.0425 ± 0.0012	364.52	254.1	254.2 ± 0.4	0.0384 ± 0.0012	0.4384 ± 0.0014	2.91 ± 0.09	1.00 ± 0.00
0.0125 ± 0.0004	0.5423 ± 0.0058	0.0225 ± 0.0009	364.53	203.6	203.4 ± 0.8	0.0202 ± 0.0008	0.2954 ± 0.0025	3.02 ± 0.10	1.00 ± 0.00
0	0.5423 ± 0.0058	0.0 ± 0.0	364.52	143.9	143.9 ± 0.4	0.0 ± 0.0	0.0 ± 0.0	3.14 ± 0.11	1.00 ± 0.00

[a] T is the experimental temperature; n_1 and n_2 are the moles of components injected into the equilibrium cell; z_1 is the total mol fraction; x_1 and y_1 are the calculated mole fractions in the liquid and vapor phases, respectively; the experimental pressure is p_{exptl}; and the pressure calculated from the Legendre polynomial fit is p_{leg}; γ_1 and γ_2 are the calculated activity coefficients.

Table 5. VLE Data for *cis*-2-Butene (1) + 2-Butanol (2) at 364.5 K[a]

n_1/mol	n_2/mol	z_1	T/K	p_{exptl}/kPa	p_{leg}/kPa	x_1	y_1	γ_1	γ_2
0.4962 ± 0.0053	0	1.0 ± 0.0	364.52	1189.6	1189.6 ± 0.4	1.0 ± 0.0	1.0 ± 0.0	1.00 ± 0.00	4.17 ± 0.17
0.4962 ± 0.0053	0.0053 ± 0.0003	0.9895 ± 0.0006	364.52	1178.8	1179.0 ± 0.8	0.9890 ± 0.0007	0.9960 ± 0.0004	1.00 ± 0.00	3.94 ± 0.13
0.4962 ± 0.0053	0.0101 ± 0.0003	0.9800 ± 0.0008	364.53	1169.4	1169.9 ± 0.8	0.9793 ± 0.0009	0.9928 ± 0.0005	1.00 ± 0.00	3.75 ± 0.11
0.4962 ± 0.0053	0.0154 ± 0.0004	0.9699 ± 0.0010	364.52	1159.2	1160.1 ± 0.8	0.9687 ± 0.0011	0.9896 ± 0.0006	1.00 ± 0.00	3.57 ± 0.09
0.4962 ± 0.0053	0.0264 ± 0.0005	0.9495 ± 0.0014	364.52	1140.6	1141.7 ± 0.8	0.9475 ± 0.0015	0.9840 ± 0.0008	1.01 ± 0.00	3.25 ± 0.06
0.4962 ± 0.0053	0.0556 ± 0.0008	0.8992 ± 0.0022	364.52	1099.8	1100.6 ± 0.8	0.8957 ± 0.0024	0.9734 ± 0.0009	1.02 ± 0.00	2.66 ± 0.02
0.4962 ± 0.0053	0.0882 ± 0.0011	0.8491 ± 0.0030	364.51	1064.3	1064.3 ± 0.7	0.8443 ± 0.0032	0.9657 ± 0.0010	1.05 ± 0.00	2.25 ± 0.01
0.4962 ± 0.0053	0.1248 ± 0.0015	0.7990 ± 0.0036	364.51	1030.9	1030.6 ± 0.6	0.7936 ± 0.0038	0.9595 ± 0.0010	1.08 ± 0.00	1.96 ± 0.00
0.4962 ± 0.0053	0.1654 ± 0.0019	0.7500 ± 0.0041	364.51	998.9	998.5 ± 0.5	0.7443 ± 0.0044	0.9542 ± 0.0011	1.12 ± 0.01	1.76 ± 0.00
0.4962 ± 0.0053	0.2133 ± 0.0024	0.6993 ± 0.0046	364.52	965.7	965.3 ± 0.6	0.6939 ± 0.0048	0.9491 ± 0.0011	1.16 ± 0.01	1.60 ± 0.00
0.4962 ± 0.0053	0.2677 ± 0.0029	0.6496 ± 0.0049	364.52	931.5	931.5 ± 0.7	0.6447 ± 0.0051	0.9442 ± 0.0012	1.21 ± 0.01	1.47 ± 0.00
0.4962 ± 0.0053	0.3309 ± 0.0036	0.5999 ± 0.0051	364.52	895.9	896.0 ± 0.6	0.5960 ± 0.0053	0.9392 ± 0.0012	1.26 ± 0.01	1.38 ± 0.00
0.4962 ± 0.0053	0.4054 ± 0.0043	0.5504 ± 0.0053	364.52	858.3	858.4 ± 0.6	0.5476 ± 0.0054	0.9338 ± 0.0012	1.31 ± 0.01	1.30 ± 0.00
0.4962 ± 0.0053	0.4960 ± 0.0053	0.5001 ± 0.0053	364.52	817.1	817.4 ± 0.5	0.4987 ± 0.0053	0.9279 ± 0.0012	1.38 ± 0.01	1.24 ± 0.00
0.4997 ± 0.0053	0.4982 ± 0.0053	0.5008 ± 0.0053	364.53	818.2	818.1 ± 0.5	0.4995 ± 0.0053	0.9280 ± 0.0012	1.37 ± 0.01	1.24 ± 0.00
0.4103 ± 0.0044	0.4982 ± 0.0053	0.4517 ± 0.0053	364.53	771.8	771.7 ± 0.6	0.4487 ± 0.0053	0.9209 ± 0.0012	1.45 ± 0.02	1.18 ± 0.00
0.3353 ± 0.0037	0.4982 ± 0.0053	0.4023 ± 0.0052	364.53	720.5	720.5 ± 0.6	0.3977 ± 0.0052	0.9126 ± 0.0012	1.52 ± 0.02	1.14 ± 0.00
0.2730 ± 0.0030	0.4982 ± 0.0053	0.3540 ± 0.0050	364.52	665.5	665.6 ± 0.6	0.3479 ± 0.0050	0.9027 ± 0.0012	1.61 ± 0.02	1.10 ± 0.00
0.2186 ± 0.0025	0.4982 ± 0.0053	0.3050 ± 0.0046	364.52	604.2	604.3 ± 0.5	0.2976 ± 0.0046	0.8900 ± 0.0013	1.70 ± 0.03	1.07 ± 0.00
0.1720 ± 0.0020	0.4982 ± 0.0053	0.2567 ± 0.0042	364.52	538.0	537.9 ± 0.6	0.2484 ± 0.0042	0.8736 ± 0.0014	1.80 ± 0.03	1.05 ± 0.00
0.1310 ± 0.0016	0.4982 ± 0.0053	0.2082 ± 0.0037	364.52	465.2	465.0 ± 0.6	0.1997 ± 0.0037	0.8507 ± 0.0016	1.92 ± 0.03	1.03 ± 0.00
0.0947 ± 0.0012	0.4982 ± 0.0053	0.1597 ± 0.0031	364.52	385.5	385.4 ± 0.6	0.1516 ± 0.0030	0.8165 ± 0.0017	2.04 ± 0.04	1.02 ± .00
0.0629 ± 0.0009	0.4982 ± 0.0053	0.1120 ± 0.0024	364.52	300.4	300.5 ± 0.5	0.1052 ± 0.0024	0.7608 ± 0.0017	2.17 ± 0.05	1.01 ± 0.00
0.0332 ± 0.0006	0.4982 ± 0.0053	0.0624 ± 0.0016	364.52	204.7	204.9 ± 0.6	0.0579 ± 0.0016	0.6439 ± 0.0016	2.31 ± 0.07	1.00 ± 0.00
0.0223 ± 0.0005	0.4982 ± 0.0053	0.0428 ± 0.0013	364.52	165.1	165.0 ± 0.5	0.0395 ± 0.0012	0.5556 ± 0.0018	2.37 ± 0.07	1.00 ± 0.00
0.0132 ± 0.0004	0.4982 ± 0.0053	0.0257 ± 0.0010	364.52	129.5	129.5 ± 0.6	0.0237 ± 0.0009	0.4314 ± 0.0027	2.43 ± 0.08	1.00 ± 0.00
0	0.4982 ± 0.0053	0.0 ± 0.0	364.52	74.0	74.0 ± 0.4	0.0 ± 0.0	0.0 ± 0.0	2.51 ± 0.10	1.00 ± 0.00

[a] T is the experimental temperature; n_1 and n_2 are the moles of components injected into the equilibrium cell; z_1 is the total mol fraction; x_1 and y_1 are the calculated mole fractions in the liquid and vapor phases, respectively; the experimental pressure is p_{exptl}; and the pressure calculated from the Legendre polynomial fit is p_{leg}; γ_1 and γ_2 are the calculated activity coefficients.

0.1 K in the syringe pumps. The uncertainty in the cell pressure measurements was ± 0.4 kPa and in the pressure measurements in the syringe pumps ± 20 kPa. The uncertainty in the injected volumes was obtained from calibration tests with distilled water and was $\pm\ 0.02 \cdot 10^{-6}$ m^3. For calculation of the pure component liquid densities, a density correlation was used.[15] In the density correlation, the uncertainty was assumed to be less than 1.0 %.[15,16] Because of the small excess volume of the solutions, the volume change due to mixing was assumed negligible.[17]

The maximum error for the number of injected moles n_i and the total composition z_i was calculated by a method proposed by Laakkonen et al.[18] and improved by Hynynen et al.[19]

3. Results and Discussion

The results of the four binary systems are presented in Tables 3 to 6. The injected amount of moles is given with a higher accuracy than the error estimates to allow for recalculation. Figure 1 shows the measured vapor pressure

Table 6. VLE Data for *cis*-2-Butene (1) + 2-Methyl-2-propanol (2) at 364.5 K[a]

n_1/mol	n_2/mol	z_1	T/K	p_{exptl}/kPa	p_{leg}/kPa	x_1	y_1	γ_1	γ_2
0.4878 ± 0.0052	0	1.0 ± 0.0	364.53	1190.7	1190.7 ± 0.4	1.0 ± 0.0	1.0 ± 0.0	1.00 ± 0.00	3.30 ± 0.07
0.4878 ± 0.0052	0.0052 ± 0.0003	0.9895 ± 0.0006	364.52	1182.6	1183.1 ± 0.6	0.9892 ± 0.0007	0.9942 ± 0.0005	1.00 ± 0.00	3.16 ± 0.05
0.4878 ± 0.0052	0.0095 ± 0.0003	0.9809 ± 0.0008	364.52	1176.2	1176.8 ± 0.6	0.9803 ± 0.0008	0.9898 ± 0.0006	1.00 ± 0.00	3.05 ± 0.05
0.4878 ± 0.0052	0.0154 ± 0.0004	0.9693 ± 0.0010	364.52	1167.7	1168.4 ± 0.6	0.9684 ± 0.0011	0.9842 ± 0.0008	1.00 ± 0.00	2.92 ± 0.05
0.4878 ± 0.0052	0.0259 ± 0.0005	0.9496 ± 0.0014	364.52	1153.4	1154.1 ± 0.7	0.9480 ± 0.0015	0.9757 ± 0.0010	1.01 ± 0.00	2.72 ± 0.04
0.4878 ± 0.0052	0.0547 ± 0.0008	0.8992 ± 0.0022	364.52	1118.4	1118.7 ± 0.7	0.8962 ± 0.0024	0.9581 ± 0.0015	1.02 ± 0.00	2.30 ± 0.02
0.4878 ± 0.0052	0.0866 ± 0.0011	0.8492 ± 0.0030	364.52	1085.3	1085.0 ± 0.7	0.8451 ± 0.0031	0.9444 ± 0.0017	1.04 ± 0.00	2.01 ± 0.02
0.4878 ± 0.0052	0.1224 ± 0.0015	0.7994 ± 0.0036	364.52	1052.7	1052.1 ± 0.7	0.7945 ± 0.0038	0.9330 ± 0.0018	1.07 ± 0.00	1.79 ± 0.01
0.4878 ± 0.0052	0.1629 ± 0.0019	0.7496 ± 0.0041	364.52	1019.9	1019.4 ± 0.6	0.7445 ± 0.0043	0.9228 ± 0.0018	1.10 ± 0.00	1.62 ± 0.01
0.4878 ± 0.0052	0.2088 ± 0.0023	0.7002 ± 0.0046	364.52	986.4	986.3 ± 0.5	0.6953 ± 0.0047	0.9133 ± 0.0018	1.13 ± 0.01	1.50 ± 0.00
0.4878 ± 0.0052	0.2625 ± 0.0029	0.6501 ± 0.0049	364.52	951.1	951.3 ± 0.5	0.6457 ± 0.0051	0.9037 ± 0.0018	1.17 ± 0.01	1.39 ± 0.00
0.4878 ± 0.0052	0.3247 ± 0.0035	0.6004 ± 0.0052	364.52	914.3	914.7 ± 0.6	0.5968 ± 0.0053	0.8939 ± 0.0018	1.22 ± 0.01	1.31 ± 0.00
0.4878 ± 0.0052	0.3985 ± 0.0043	0.5504 ± 0.0053	364.52	875.2	875.7 ± 0.6	0.5479 ± 0.0053	0.8834 ± 0.0018	1.26 ± 0.01	1.25 ± 0.00
0.4878 ± 0.0052	0.4862 ± 0.0052	0.5008 ± 0.0053	364.52	833.9	834.3 ± 0.6	0.4996 ± 0.0053	0.8720 ± 0.0018	1.31 ± 0.01	1.20 ± 0.00
0.4884 ± 0.0052	0.4867 ± 0.0052	0.5009 ± 0.0053	364.51	834.4	834.4 ± 0.6	0.4997 ± 0.0053	0.8720 ± 0.0018	1.31 ± 0.01	1.20 ± 0.00
0.4012 ± 0.0043	0.4867 ± 0.0052	0.4518 ± 0.0053	364.52	787.7	787.7 ± 0.5	0.4492 ± 0.0053	0.8585 ± 0.0018	1.37 ± 0.01	1.15 ± 0.00
0.3279 ± 0.0036	0.4867 ± 0.0052	0.4025 ± 0.0052	364.53	737.0	736.8 ± 0.5	0.3984 ± 0.0052	0.8428 ± 0.0019	1.43 ± 0.02	1.12 ± 0.00
0.2665 ± 0.0030	0.4867 ± 0.0052	0.3538 ± 0.0050	364.53	682.6	682.4 ± 0.6	0.3483 ± 0.0050	0.8243 ± 0.0020	1.50 ± 0.02	1.09 ± 0.00
0.2136 ± 0.0024	0.4867 ± 0.0052	0.3050 ± 0.0047	364.52	623.8	623.7 ± 0.6	0.2984 ± 0.0046	0.8015 ± 0.0021	1.57 ± 0.02	1.06 ± 0.00
0.1678 ± 0.0019	0.4867 ± 0.0052	0.2563 ± 0.0042	364.52	560.4	560.4 ± 0.6	0.2490 ± 0.0042	0.7726 ± 0.0021	1.65 ± 0.02	1.04 ± 0.00
0.1280 ± 0.0015	0.4867 ± 0.0052	0.2082 ± 0.0037	364.52	493.2	493.2 ± 0.5	0.2006 ± 0.0037	0.7346 ± 0.0021	1.74 ± 0.03	1.03 ± 0.00
0.0919 ± 0.0012	0.4867 ± 0.0052	0.1589 ± 0.0031	364.52	418.9	419.2 ± 0.5	0.1517 ± 0.0030	0.6800 ± 0.0019	1.83 ± 0.03	1.01 ± 0.00
0.0606 ± 0.0008	0.4867 ± 0.0052	0.1107 ± 0.0024	364.52	341.4	341.5 ± 0.7	0.1046 ± 0.0023	0.5984 ± 0.0016	1.93 ± 0.04	1.01 ± 0.00
0.0328 ± 0.0006	0.4867 ± 0.0052	0.0632 ± 0.0016	364.52	259.8	259.8 ± 0.6	0.0591 ± 0.0016	0.4615 ± 0.0014	2.04 ± 0.05	1.00 ± 0.00
0.0214 ± 0.0004	0.4867 ± 0.0052	0.0422 ± 0.0013	364.51	221.9	222.0 ± 0.4	0.0392 ± 0.0012	0.3649 ± 0.0016	2.09 ± 0.06	1.00 ± 0.00
0.0124 ± 0.0003	0.4867 ± 0.0052	0.0248 ± 0.0009	364.52	190.0	190.0 ± 0.7	0.0230 ± 0.0009	0.2530 ± 0.0024	2.13 ± 0.07	1.00 ± 0.00
0	0.4867 ± 0.0052	0.0 ± 0.0	364.52	143.0	143.0 ± 0.4	0.0 ± 0.0	0.0 ± 0.0	2.19 ± 0.07	1.00 ± 0.00

[a] T is the experimental temperature; n_1 and n_2 are the moles of components injected into the equilibrium cell; z_1 is the total mole fraction; x_1 and y_1 are the calculated mole fractions in the liquid and vapor phases, respectively; the experimental pressure is p_{exptl}; and the pressure calculated from the Legendre polynomial fit is p_{leg}; γ_1 and γ_2 are the calculated activity coefficients.

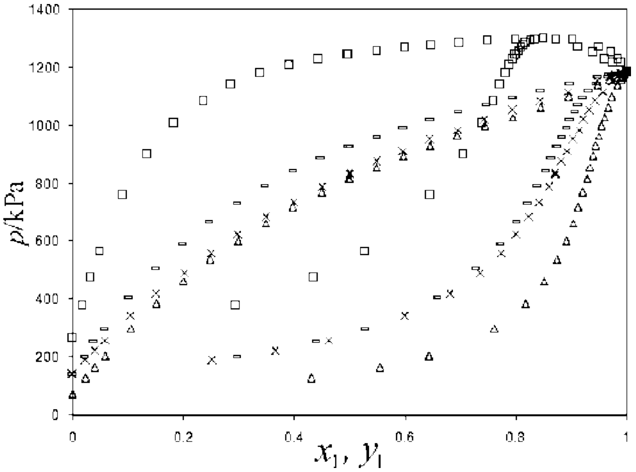

Figure 1. Pressure−composition diagram for *cis*-2-butene (1) + alcohols (2) at 364.5 K: □, *cis*-2-butene + methanol; −, + 2-propanol; Δ, + 2-butanol; ×, + 2-methyl-2-propanol.

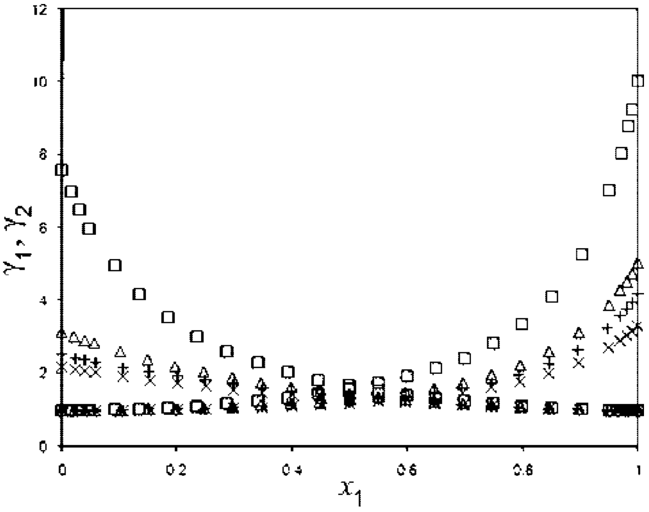

Figure 2. Activity coefficient−composition diagram for *cis*-2-butene (1) + alcohols (2) at 364.5 K: □, *cis*-2-butene + methanol; Δ, + 2-propanol; +, + 2-butanol; ×, + 2-methyl-2-propanol.

as a function of liquid and vapor composition. The activity coefficients presented in Tables 3 to 6 are graphically shown as a function of liquid composition in Figure 2. For the system *cis*-2-butene + methanol, an azeotropic point was found for $x(cis\text{-2-butene}) = 0.847$ and $p_{\text{leg}} = 1303.8$ kPa at $T = 364.52$ K, calculated with the Legendre polynomial (experimental pressure maximum of 1303.3 kPa at 364.52 K). The parameters of the Legendre polynomial and the Wilson[20] activity coefficient model with pressure residuals are presented in Table 7.

The total pressure and infinite dilution activity coefficients were also calculated using the UNIFAC and UNIFAC−Dortmund models. Comparison of these results with results calculated by Legendre polynomials are presented in Table 8. The parameters used in the UNIFAC and UNIFAC−Dortmund models include those reported by Gmehling et al.[21] and Wittig et al.[22] In the UNIFAC models, a predetermined methanol group can be chosen, or the molecule can be assembled from a CH_3 group and a primary hydroxyl group. Roininen et al.[23] have reported VLE data for *trans*-2-butene with the same system of alcohols as in this work at 364.5 K. It was found by Roininen et al.[23] that the model predictions were more accurate when the assembled methanol molecule was used. The same conclusion can be drawn from this work. In Table 8, the calculated values for Δp, $|\Delta p|$, γ^{∞}_1, and γ^{∞}_2 are presented for the default setting for methanol. When using the assembled methanol molecule, the pressure residuals and the infinite dilution coefficients were $\Delta p = 75.8$ kPa, $|\Delta p| = 76.2$ kPa, $\gamma^{\infty}_1 = 7.20$, and $\gamma^{\infty}_2 = 14.57$ for UNIFAC and $\Delta p = 22.8$ kPa, $|\Delta p| = 24.5$ kPa, $\gamma^{\infty}_1 = 7.43$, and $\gamma^{\infty}_2 = 14.56$ for UNIFAC−Dortmund.

Table 7. Parameters of the Legendre and Wilson Activity Coefficient Models[a]

cis-2-butene (1)	+ methanol	+ 2-propanol	+ 2-butanol	+ 2-methyl-2-propanol
Legendre, $a_{1,0}$	2.0003	1.3003	1.0976	0.93298
Legendre, $a_{2,0}$	0.11801	0.21879	0.23539	0.19574
Legendre, $a_{3,0}$	0.15604	0.079245	0.073619	0.056262
Legendre, $a_{4,0}$	0.019604	0.016842	0.017383	0.0093530
Legendre, $a_{5,0}$	0.010222	-	0.0029860	-
Δp/kPa	0.1	−0.1	−0.1	23 > 0.1
$\lvert\Delta p\rvert$/kPa	0.9	0.4	0.2	0.3
Wilson $\lambda_{1,2}$/K	168.4	90.30	76.64	53.11
Wilson $\lambda_{2,1}$/K	883.8	525.9	442.0	383.9
Wilson volume ratio[b]	2.149	1.139	0.949	0.922
Δp/kPa	−1.6	−0.0	−0.1	−0.2
$\lvert\Delta p\rvert$/kPa	4.0	1.5	1.1	1.2

[a] The Legendre model parameters were obtained with data reduction from measured values. Wilson parameters were regressed using the vapor and liquid phase compositions and experimental pressures from Tables 3 to 6; Wilson volume ratios, average pressure residuals Δ p, and absolute average pressure residual $\lvert\Delta p\rvert$ for *cis*-2-butene (1) + methanol, + 2-propanol, + 2-butanol, and + 2-methyl-2-propanol. [b] Defined as ν_1/ν_2, where υ_i is the liquid molar volume of component i at the normal boiling point for *cis*-2-butene and at 298.15 K for methanol, 2-propanol, and 2-butanol, and at 298.97 K for 2-methyl-2-propanol.[25]

Table 8. Comparison between VLE Data Predicted by the UNIFAC and UNIFAC−Dortmund Methods and the Fitted Legendre Polynomial for *cis*-2-Butene (1) + Alcohols (2)

cis-2-butene (1)	+ methanol	+ 2-propanol	+ 2-butanol	+ 2-methyl-2-propanol
		Legendre		
Δp/kPa	0.1	−0.1	−0.1	−0.1
$\lvert\Delta p\rvert$/kPa	0.9	0.4	0.2	0.3
γ^{∞}_1	7.61	3.14	2.51	2.19
γ^{∞}_2	10.02	5.03	4.17	3.30
		UNIFAC		
Δp/kPa	75.8	15.9	6.8	32.7
$\lvert\Delta p\rvert$/kPa	76.2	18.8	13.1	32.7
γ^{∞}_1	7.20	2.88	2.22	2.21
γ^{∞}_2	14.57	6.36	4.99	5.02
		UNIFAC−Dortmund		
Δp/kPa	22.8	9.0	17.1	5.0
$\lvert\Delta p\rvert$/kPa	24.5	14.3	18.3	11.6
γ^{∞}_1	7.43	2.84	2.35	1.96
γ^{∞}_2	14.56	6.36	5.63	4.20

The UNIFAC−Dortmund model performs in general better than the UNIFAC model. The values for Δp and $\lvert\Delta p\rvert$ in Table 8 are numerically smaller for the UNIFAC−Dortmund model than for the UNIFAC model, with the system *cis*-2-butene + 2-butanol being an exception. Both the UNIFAC and the UNIFAC−Dortmund model give an underestimate for the infinite dilution activity coefficients for *cis*-2-butene and an overestimate for the infinite dilution activity coefficients of the alcohols.

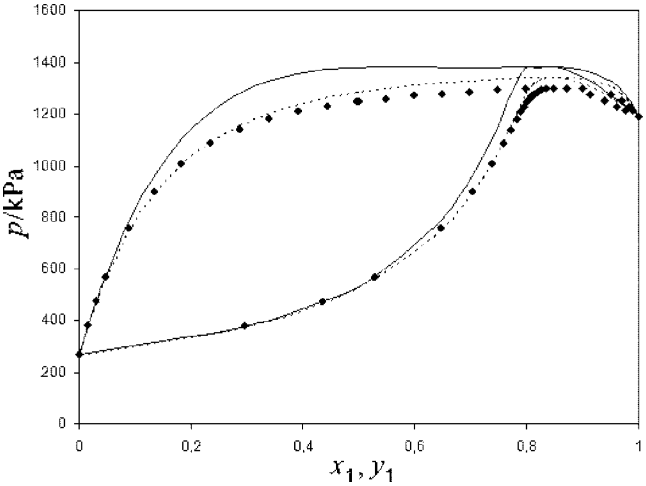

Figure 3. Pressure−composition diagram of the *cis*-2-butene (1) + methanol (2) system at 364.5 K: ♦, experimental values; —, UNIFAC results; - - -, UNIFAC−Dortmund results.

Table 9. Measured Azeotropic Composition of *cis*-2-Butene (1) + Methanol (2) Compared with UNIFAC and UNIFAC−Dortmund Model Predictions

	T/K	x_1	p/kPa
this work	364.52	0.847	1303.8
UNIFAC	364.52	0.798	1381.0
UNIFAC−Dortmund	364.52	0.845	1343.2
ref 3	337	0.89	683

In Figure 3, the measured vapor pressures are shown with the values predicted by the UNIFAC and UNIFAC−Dortmund models for the system of *cis*-2-butene + methanol. The UNIFAC and UNIFAC−Dortmund models both predict an azeotropic point. The UNIFAC−Dortmund model shows the most accurate prediction. The UNIFAC prediction for the azeotropic point is x(*cis*-2-butene) = 0.798 and p = 1382.2 kPa and for the UNIFAC−Dortmund model x(*cis*-2-butene) = 0.848 and p = 1342.8 kPa, both at T = 364.52 K. Pokki et al.[3] found with the Legendre polynomial fit an azeotropic point for the *cis*-2-butene + methanol system at x(*cis*-2-butene) = 0.89 and p = 683 kPa at T = 337 K. These values are compared in Table 9. The values for methanol were calculated with the predetermined methanol group.

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