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Vapor−Liquid Equilibrium for Methoxymethane + Methyl Formate, Methoxymethane + Hexane, and Methyl Formate + Methanol

Aarne T. Sundberg,* Petri Uusi-Kyyny, Minna Pakkanen, and Ville Alopaeus

Department of Biotechnology and Chemical Technology, School of Chemical Technology, Aalto University, P.O. Box 16100, FI-00076 Aalto, Finland

ABSTRACT: Isothermal vapor−liquid equilibrium (VLE) for three binary systems was measured with a static total pressure method. The methoxymethane + methyl formate equilibrium was measured at 308 K, methoxymethane + hexane at 308 K and 335 K, and methyl formate + methanol at 359 K. The measured data were reduced to phase equilibrium data with the Barker's method. Legendre, Wilson, nonrandom two-liquid (NRTL), and universal quasichemical (UNIQUAC) parameters and modified universal functional (UNIFAC, Dortmund) pressure residuals were calculated. All binaries exhibited a positive deviation from the Raoult's law. A maximum pressure azeotrope was observed for the methyl formate + methanol system.

INTRODUCTION

Methoxymethane is a colorless, almost odorless gas at normal temperature and pressure. It is used as a propellant and as a substitute for liquefied petroleum gas, especially in China. Methoxymethane is also viewed as a potential next generation fuel for transportation and fuel cells. Current worldwide methoxymethane production is approximately 5 million tons per year. Methoxymethane is produced mainly from syngas via a methanol dehydration step, but new single-step processes are also in use.[1] Methoxymethane is also obtained on a smaller scale as a byproduct from industrial processes.[2] The target of this work was to provide new phase equilibrium data for process modeling.

EXPERIMENTAL SECTION

Materials. The suppliers and the purities of the materials used are presented in Table 1.[15−17] Purity was analyzed with a gas chromatography (GC), equipped with a flame ionization detector, which does not detect the presence of water. The water content was analyzed with Karl Fischer titration after drying over molecule sieves (Merck, 3A); the mass fraction of water was less than 0.0003 for methanol and less than 0.0001 for methyl formate and hexane. The degassing of liquid components was performed in a round-bottomed flask. The flask was placed in an ultrasonic bath filled with water and ice and vacuumed for (1 to 2) hours. The purity of the components and the success of degassing was determined by comparing the measured vapor pressure and the refractive index with values obtained from literature.[15,18,19] The vapor pressures are shown in Table 2. Each reported pure component vapor pressure value was separately measured in separate vapor−liquid equilibrium (VLE) runs. Methoxymethane was degassed before use by opening the vacuum valve 10 times for a period of 10 s.

Apparatus. The static total pressure apparatus employed in the experiment has been explained in detail in Uusi-Kyyny et al.[3] Temperatures were measured with Pt-100 probes connected to a temperature meter (Termolyzer S2541, Frontek). Probes had been calibrated at the Centre for Metrology and Accreditation.

Table 1. Supplier and the Purity of the Material

component	supplier	mass fraction	$n_{D,\text{measured}}$	$n_{D,\text{literature}}$
methoxymethane	Linde Gas	0.999[a]	NA	NA
methyl formate	Sigma-Aldrich	0.9874	1.34359 at 20 °C	1.3428[16]
hexane	Sigma-Aldrich	0.9930	1.37514 at 25 °C	1.37226[15]
methanol	Sigma-Aldrich	0.9938	1.32853 at 20 °C	1.32840[17]

[a] Purity as reported by the supplier.

Table 2. Pure Component Vapor Pressures[a]

component	T/K	p/kPa			
		this work	18	19	15
methoxymethane	308.10	788.0	772.3	781.7	782.1
	308.13	785.2	772.9	782.3	782.7
	335.65	1539.6	1513.5	1546.5	1537.0
methyl formate	308.11	114.7	114.1	114.2	114.0
	358.92	550.4	544.1	545.3	542.9
hexane	308.12	30.8	30.6	30.8	30.7
	335.66	83.0	82.9	82.7	83.1
methanol	358.93	221.4	221.7	221.2	221.6

[a] Each line represent a different measurement.

The pressure of the cell was measured with a Digiquartz 2300A-101-CE pressure transducer connected to a Digiquartz 740 intelligent display unit (Paroscientific). The range of the pressure measurement was from 0 kPa to 2070 kPa with a temperature range from 219 K to 380 K. The equilibrium cell had a total volume of 103.3 cm^3. The cell volume had been determined by injecting degassed water in the cell at 298.15 K. Injections of the

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components were made with syringe pumps (ISCO 260D and 100D).

Procedure. After degassing, the first component was injected into the cell, and the pure component vapor pressure was measured and compared to the value obtained from literature. If the error was within the combined uncertainty of the equilibrium cell pressure measurement and the pressure correlation, taking into account the uncertainty of the temperature measurement, the second component was added into the cell. After the pressure had reached equilibrium, in about 30 min, the total pressure was measured. The addition of the second component was repeated until an approximately equimolar composition was reached. At this point the cell was drained and emptied with vacuum. Then the injection of the components was repeated in a reversed order to obtain the other half of the data set. The quality of the data was evaluated based on how well the vapor pressure of each half coincided at the equimolar composition and how well the measured pure component vapor pressure agreed with the values reported in literature.

Data Reduction. The data measured in the experiment consisted of total pressure, temperature, and the total composition inside the cell at equilibrium. To obtain the compositions of the vapor and liquid phases, the data were reduced by the Legendre polynomials as the liquid activity coefficient model[4] and the cubic Soave−Redlich−Kwong[5] equation of state; the binary interaction parameters were set to 0. The data reduction was performed according to the Barker method.[6] The amount of parameters for the Legendre polynomials was increased until the average deviation was below the uncertainty of the measured cell pressure or until the average deviation no longer decreased. The details of this data reduction have been reported in Uusi-Kyyny et al.[3] The data were reduced with the in-house software,

Table 3. Pure Component Physical Properties

component	methoxymethane	methyl formate	hexane	methanol
CAS number	115-10-6	107-31-3	110-54-3	67-56-1
$T_C{}^a$/K	400.1	487.2	507.6	512.58
$p_C{}^b$/MPa	5.37	6.00	3.03	7.95
ω^c	0.200221	0.255551	0.301261	0.565831
$v_i{}^d/\mathrm{cm^3 \cdot mol^{-1}}$	70.2314	62.1041	131.362	40.58
Q^e	1.9360	2.0360	3.8560	1.4320
R^f	2.0461	2.1430	4.4997	1.4311

[a] Critical temperature, T_C.[15] [b] Critical pressure, p_C.[15] [c] Acentric factor, ω.[15] [d] Liquid molar volume at 298 K, v_i.[15] [e] Relative van der Waals volume, R.[15] [f] Relative van der Waals surface area, Q.[15] Normalization factors for volume and surface parameters are given in Abrams et al.[13]

Table 4. VLE Data for Methoxymethane (1) + Methyl Formate (2)

T^a	$n_1{}^b$	$n_2{}^b$		$p_{\mathrm{exp}}{}^d$	$p_{\mathrm{Leg}}{}^e$				
K	mole	mole	$z_1{}^c$	kPa	kPa	$x_1{}^f$	$y_1{}^f$	$\gamma_1{}^g$	$\gamma_2{}^g$
308.10	0.6603 ± 0.0107	0.0000 ± 0.0000	1.0000 ± 0.0000	788.0	788.0	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	1.36 ± 0.06
308.10	0.6603 ± 0.0107	0.0064 ± 0.0002	0.9904 ± 0.0004	780.6	781.0	0.9902 ± 0.0004	0.9977 ± 0.0002	1.00 ± 0.00	1.36 ± 0.06
308.11	0.6603 ± 0.0107	0.0199 ± 0.0004	0.9707 ± 0.0010	767.1	767.0	0.9701 ± 0.0011	0.9928 ± 0.0006	1.00 ± 0.00	1.35 ± 0.05
308.11	0.6603 ± 0.0107	0.0345 ± 0.0005	0.9504 ± 0.0015	753.3	752.8	0.9494 ± 0.0015	0.9878 ± 0.0009	1.00 ± 0.00	1.34 ± 0.05
308.10	0.6603 ± 0.0107	0.0725 ± 0.0009	0.9011 ± 0.0026	720.0	719.1	0.8993 ± 0.0027	0.9754 ± 0.0014	1.00 ± 0.00	1.31 ± 0.04
308.11	0.6603 ± 0.0107	0.1174 ± 0.0014	0.8490 ± 0.0037	686.0	685.2	0.8468 ± 0.0038	0.9622 ± 0.0018	1.01 ± 0.00	1.28 ± 0.03
308.11	0.6603 ± 0.0107	0.1648 ± 0.0019	0.8003 ± 0.0045	655.1	654.7	0.7979 ± 0.0046	0.9497 ± 0.0021	1.01 ± 0.00	1.24 ± 0.02
308.11	0.6603 ± 0.0107	0.2206 ± 0.0025	0.7496 ± 0.0052	623.7	624.1	0.7471 ± 0.0053	0.9367 ± 0.0022	1.02 ± 0.01	1.20 ± 0.01
308.11	0.6603 ± 0.0107	0.2825 ± 0.0031	0.7004 ± 0.0058	593.9	595.0	0.6980 ± 0.0059	0.9237 ± 0.0023	1.04 ± 0.01	1.16 ± 0.01
308.10	0.6603 ± 0.0107	0.3559 ± 0.0039	0.6498 ± 0.0062	563.7	565.2	0.6476 ± 0.0063	0.9096 ± 0.0024	1.05 ± 0.01	1.13 ± 0.01
308.10	0.6603 ± 0.0107	0.4405 ± 0.0047	0.5998 ± 0.0065	534.4	535.8	0.5981 ± 0.0066	0.8946 ± 0.0025	1.06 ± 0.01	1.10 ± 0.01
308.10	0.6603 ± 0.0107	0.5235 ± 0.0056	0.5578 ± 0.0066	510.3	510.5	0.5564 ± 0.0067	0.8807 ± 0.0026	1.08 ± 0.01	1.08 ± 0.00
308.11	0.6603 ± 0.0107	0.6582 ± 0.0068	0.5008 ± 0.0066	478.7	475.5	0.5000 ± 0.0067	0.8596 ± 0.0027	1.10 ± 0.01	1.06 ± 0.00
308.10	0.6541 ± 0.0104	0.6595 ± 0.0070	0.4980 ± 0.0066	476.6	473.7	0.4971 ± 0.0067	0.8584 ± 0.0027	1.10 ± 0.01	1.06 ± 0.00
308.10	0.5349 ± 0.0087	0.6595 ± 0.0070	0.4479 ± 0.0066	440.1	440.4	0.4464 ± 0.0067	0.8361 ± 0.0029	1.11 ± 0.01	1.05 ± 0.00
308.10	0.4363 ± 0.0071	0.6595 ± 0.0070	0.3982 ± 0.0064	405.1	406.5	0.3962 ± 0.0065	0.8100 ± 0.0031	1.13 ± 0.01	1.04 ± 0.00
308.10	0.3528 ± 0.0058	0.6595 ± 0.0070	0.3485 ± 0.0061	370.6	372.0	0.3461 ± 0.0062	0.7789 ± 0.0032	1.15 ± 0.02	1.03 ± 0.00
308.11	0.2820 ± 0.0047	0.6595 ± 0.0070	0.2995 ± 0.0057	336.6	337.3	0.2968 ± 0.0057	0.7415 ± 0.0032	1.16 ± 0.02	1.02 ± 0.00
308.11	0.2189 ± 0.0037	0.6595 ± 0.0070	0.2492 ± 0.0051	301.4	301.3	0.2462 ± 0.0051	0.6942 ± 0.0031	1.18 ± 0.02	1.02 ± 0.00
308.11	0.1645 ± 0.0028	0.6595 ± 0.0070	0.1997 ± 0.0044	266.1	265.6	0.1967 ± 0.0044	0.6353 ± 0.0029	1.20 ± 0.02	1.01 ± 0.00
308.10	0.1158 ± 0.0020	0.6595 ± 0.0070	0.1494 ± 0.0036	229.6	229.2	0.1468 ± 0.0036	0.5570 ± 0.0026	1.22 ± 0.03	1.01 ± 0.00
308.10	0.0842 ± 0.0015	0.6595 ± 0.0070	0.1132 ± 0.0029	202.9	202.7	0.1109 ± 0.0029	0.4830 ± 0.0023	1.24 ± 0.03	1.01 ± 0.00
308.11	0.0401 ± 0.0008	0.6595 ± 0.0070	0.0573 ± 0.0016	160.5	160.7	0.0558 ± 0.0016	0.3170 ± 0.0016	1.29 ± 0.03	1.00 ± 0.00
308.11	0.0240 ± 0.0006	0.6595 ± 0.0070	0.0352 ± 0.0012	143.2	143.4	0.0342 ± 0.0011	0.2214 ± 0.0018	1.32 ± 0.04	1.00 ± 0.00
308.11	0.0140 ± 0.0004	0.6595 ± 0.0070	0.0208 ± 0.0008	131.8	131.9	0.0202 ± 0.0008	0.1438 ± 0.0018	1.34 ± 0.04	1.00 ± 0.00
308.11	0.0000 ± 0.0000	0.6595 ± 0.0070	0.0000 ± 0.0000	114.7	114.7	0.0000 ± 0.0000	0.0000 ± 0.0000	1.37 ± 0.04	1.00 ± 0.00

[a] Experimental temperature, T. [b] Amount of component in the equilibrium cell, n_i. [c] Total mole fraction, z_1. [d] Experimental pressure, p_{exp}. [e] Pressure calculated with Legendre model, p_{Leg}. [f] Liquid and vapor phase equilibrium mole fractions, x_1 and y_1. [g] Activity coefficients calculated with Legendre model, γ_i.

Table 5. VLE Data for Methoxymethane (1) + Hexane (2)

T[a] K	n_1[b] mole	n_2[b] mole	z_1[c]	p_{exp}[d] kPa	p_{Leg}[e] kPa	x_1[f]	y_1[f]	γ_1[g]	γ_2[g]
308.13	0.3541 ± 0.0059	0.0000 ± 0.0000	1.0000 ± 0.0000	785.2	785.2	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	1.74 ± 0.10
308.13	0.3541 ± 0.0059	0.0036 ± 0.0001	0.9899 ± 0.0004	775.4	776.1	0.9891 ± 0.0005	0.9989 ± 0.0001	1.00 ± 0.00	1.71 ± 0.09
308.13	0.3541 ± 0.0059	0.0109 ± 0.0002	0.9702 ± 0.0010	758.9	759.3	0.9681 ± 0.0011	0.9969 ± 0.0003	1.00 ± 0.00	1.67 ± 0.08
308.14	0.3541 ± 0.0059	0.0184 ± 0.0003	0.9505 ± 0.0015	743.1	743.1	0.9473 ± 0.0016	0.9950 ± 0.0004	1.00 ± 0.00	1.63 ± 0.07
308.14	0.3541 ± 0.0059	0.0391 ± 0.0005	0.9005 ± 0.0026	704.8	704.3	0.8950 ± 0.0029	0.9904 ± 0.0007	1.01 ± 0.00	1.52 ± 0.05
308.14	0.3541 ± 0.0059	0.0623 ± 0.0007	0.8505 ± 0.0037	669.1	668.3	0.8434 ± 0.0040	0.9860 ± 0.0009	1.02 ± 0.00	1.44 ± 0.03
308.13	0.3541 ± 0.0059	0.0879 ± 0.0010	0.8012 ± 0.0045	635.6	635.0	0.7933 ± 0.0048	0.9818 ± 0.0010	1.03 ± 0.00	1.36 ± 0.02
308.13	0.3541 ± 0.0059	0.1177 ± 0.0013	0.7506 ± 0.0052	602.6	602.2	0.7424 ± 0.0055	0.9776 ± 0.0010	1.04 ± 0.01	1.30 ± 0.02
308.13	0.3541 ± 0.0059	0.1512 ± 0.0017	0.7008 ± 0.0058	570.7	570.8	0.6928 ± 0.0061	0.9735 ± 0.0011	1.06 ± 0.01	1.24 ± 0.01
308.13	0.3541 ± 0.0059	0.1901 ± 0.0021	0.6507 ± 0.0063	538.9	539.5	0.6434 ± 0.0065	0.9691 ± 0.0011	1.08 ± 0.01	1.19 ± 0.01
308.14	0.3541 ± 0.0059	0.2342 ± 0.0025	0.6019 ± 0.0066	508.1	508.9	0.5955 ± 0.0067	0.9646 ± 0.0012	1.10 ± 0.01	1.16 ± 0.01
308.13	0.3541 ± 0.0059	0.2879 ± 0.0030	0.5516 ± 0.0067	476.1	476.7	0.5464 ± 0.0068	0.9594 ± 0.0013	1.13 ± 0.01	1.12 ± 0.00
308.13	0.3541 ± 0.0059	0.3510 ± 0.0036	0.5023 ± 0.0067	444.5	444.3	0.4985 ± 0.0068	0.9536 ± 0.0013	1.15 ± 0.02	1.10 ± 0.00
308.13	0.3473 ± 0.0055	0.3502 ± 0.0037	0.4979 ± 0.0067	442.4	441.3	0.4940 ± 0.0067	0.9530 ± 0.0013	1.15 ± 0.02	1.10 ± 0.00
308.14	0.2836 ± 0.0047	0.3502 ± 0.0037	0.4474 ± 0.0067	405.0	405.0	0.4425 ± 0.0068	0.9457 ± 0.0015	1.18 ± 0.02	1.07 ± 0.00
308.13	0.2320 ± 0.0039	0.3502 ± 0.0037	0.3985 ± 0.0066	368.2	368.5	0.3927 ± 0.0066	0.9371 ± 0.0016	1.21 ± 0.02	1.06 ± 0.00
308.14	0.1878 ± 0.0032	0.3502 ± 0.0037	0.3491 ± 0.0063	330.4	330.5	0.3426 ± 0.0063	0.9265 ± 0.0018	1.24 ± 0.02	1.04 ± 0.00
308.13	0.1501 ± 0.0026	0.3502 ± 0.0037	0.3000 ± 0.0059	291.7	291.7	0.2931 ± 0.0059	0.9130 ± 0.0020	1.26 ± 0.02	1.03 ± 0.00
308.13	0.1151 ± 0.0020	0.3502 ± 0.0037	0.2474 ± 0.0053	249.1	249.1	0.2405 ± 0.0053	0.8936 ± 0.0022	1.30 ± 0.03	1.02 ± 0.00
308.13	0.0864 ± 0.0016	0.3502 ± 0.0037	0.1979 ± 0.0046	208.1	208.0	0.1913 ± 0.0046	0.8679 ± 0.0024	1.33 ± 0.03	1.01 ± 0.00
308.13	0.0670 ± 0.0013	0.3502 ± 0.0037	0.1606 ± 0.0040	176.8	176.5	0.1545 ± 0.0040	0.8403 ± 0.0026	1.36 ± 0.04	1.01 ± 0.00
308.14	0.0454 ± 0.0009	0.3502 ± 0.0037	0.1149 ± 0.0031	136.8	136.9	0.1098 ± 0.0031	0.7882 ± 0.0027	1.40 ± 0.04	1.01 ± 0.00
308.14	0.0201 ± 0.0004	0.3502 ± 0.0037	0.0543 ± 0.0017	82.4	82.5	0.0514 ± 0.0017	0.6363 ± 0.0035	1.47 ± 0.05	1.00 ± 0.00
308.14	0.0151 ± 0.0005	0.3502 ± 0.0037	0.0415 ± 0.0016	70.3	70.6	0.0392 ± 0.0016	0.5721 ± 0.0046	1.49 ± 0.06	1.00 ± 0.00
308.13	0.0060 ± 0.0002	0.3502 ± 0.0037	0.0168 ± 0.0008	47.5	47.2	0.0158 ± 0.0007	0.3514 ± 0.0048	1.53 ± 0.06	1.00 ± 0.00
308.12	0.0000 ± 0.0000	0.3502 ± 0.0037	0.0000 ± 0.0000	30.8	30.8	0.0000 ± 0.0000	0.0000 ± 0.0000	1.56 ± 0.07	1.00 ± 0.00
335.65	0.3525 ± 0.0058	0.0000 ± 0.0000	1.0000 ± 0.0000	1539.6	1539.6	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	1.56 ± 0.09
335.66	0.3525 ± 0.0058	0.0052 ± 0.0001	0.9853 ± 0.0006	1510.8	1510.9	0.9832 ± 0.0007	0.9975 ± 0.0003	1.00 ± 0.00	1.53 ± 0.08
335.66	0.3525 ± 0.0058	0.0111 ± 0.0002	0.9694 ± 0.0010	1481.2	1481.1	0.9652 ± 0.0013	0.9949 ± 0.0005	1.00 ± 0.00	1.50 ± 0.07
335.66	0.3525 ± 0.0058	0.0190 ± 0.0003	0.9489 ± 0.0015	1443.7	1443.9	0.9424 ± 0.0018	0.9917 ± 0.0007	1.00 ± 0.00	1.46 ± 0.06
335.66	0.3525 ± 0.0058	0.0397 ± 0.0005	0.8989 ± 0.0027	1360.0	1360.2	0.8882 ± 0.0032	0.9843 ± 0.0010	1.01 ± 0.00	1.38 ± 0.04
335.67	0.3525 ± 0.0058	0.0627 ± 0.0007	0.8489 ± 0.0037	1284.0	1283.8	0.8357 ± 0.0042	0.9775 ± 0.0012	1.02 ± 0.00	1.32 ± 0.03
335.67	0.3525 ± 0.0058	0.0887 ± 0.0010	0.7990 ± 0.0045	1212.6	1212.4	0.7846 ± 0.0051	0.9709 ± 0.0013	1.03 ± 0.01	1.26 ± 0.02
335.67	0.3525 ± 0.0058	0.1181 ± 0.0013	0.7491 ± 0.0053	1144.4	1144.4	0.7345 ± 0.0058	0.9645 ± 0.0014	1.04 ± 0.01	1.21 ± 0.02
335.66	0.3525 ± 0.0058	0.1510 ± 0.0017	0.7001 ± 0.0058	1079.5	1079.8	0.6862 ± 0.0063	0.9580 ± 0.0014	1.05 ± 0.01	1.18 ± 0.01
335.65	0.3525 ± 0.0058	0.1904 ± 0.0021	0.6493 ± 0.0063	1013.9	1014.4	0.6369 ± 0.0066	0.9511 ± 0.0015	1.07 ± 0.01	1.14 ± 0.01
335.65	0.3525 ± 0.0058	0.2353 ± 0.0025	0.5997 ± 0.0066	950.7	951.0	0.5892 ± 0.0068	0.9439 ± 0.0015	1.08 ± 0.01	1.12 ± 0.01
335.66	0.3525 ± 0.0058	0.2883 ± 0.0030	0.5501 ± 0.0067	888.1	887.6	0.5419 ± 0.0069	0.9359 ± 0.0015	1.10 ± 0.01	1.09 ± 0.01
335.67	0.3525 ± 0.0058	0.3515 ± 0.0036	0.5007 ± 0.0067	826.1	824.1	0.4950 ± 0.0068	0.9270 ± 0.0016	1.12 ± 0.01	1.07 ± 0.00
335.66	0.3495 ± 0.0057	0.3506 ± 0.0037	0.4992 ± 0.0067	821.3	821.6	0.4935 ± 0.0068	0.9268 ± 0.0016	1.12 ± 0.01	1.07 ± 0.00
335.66	0.2883 ± 0.0048	0.3506 ± 0.0037	0.4513 ± 0.0067	752.4	753.1	0.4440 ± 0.0068	0.9160 ± 0.0017	1.14 ± 0.02	1.06 ± 0.00
335.66	0.2357 ± 0.0039	0.3506 ± 0.0037	0.4020 ± 0.0066	681.5	682.0	0.3933 ± 0.0066	0.9028 ± 0.0018	1.16 ± 0.02	1.04 ± 0.00
335.66	0.1910 ± 0.0032	0.3506 ± 0.0037	0.3526 ± 0.0063	609.7	610.0	0.3429 ± 0.0063	0.8867 ± 0.0020	1.18 ± 0.02	1.03 ± 0.00
335.65	0.1531 ± 0.0026	0.3506 ± 0.0037	0.3039 ± 0.0059	538.3	538.3	0.2936 ± 0.0059	0.8669 ± 0.0021	1.20 ± 0.02	1.02 ± 0.00
335.66	0.1193 ± 0.0021	0.3506 ± 0.0037	0.2538 ± 0.0054	464.5	464.3	0.2434 ± 0.0053	0.8405 ± 0.0022	1.22 ± 0.02	1.02 ± 0.00
335.66	0.0909 ± 0.0017	0.3506 ± 0.0037	0.2059 ± 0.0047	393.3	393.1	0.1958 ± 0.0046	0.8062 ± 0.0022	1.25 ± 0.03	1.01 ± 0.00
335.66	0.0655 ± 0.0012	0.3506 ± 0.0037	0.1575 ± 0.0039	321.4	321.2	0.1486 ± 0.0039	0.7567 ± 0.0021	1.28 ± 0.03	1.01 ± 0.00
335.66	0.0424 ± 0.0009	0.3506 ± 0.0037	0.1078 ± 0.0030	246.7	247.1	0.1008 ± 0.0029	0.6764 ± 0.0019	1.31 ± 0.04	1.00 ± 0.00
335.66	0.0210 ± 0.0005	0.3506 ± 0.0037	0.0564 ± 0.0018	169.7	169.6	0.0522 ± 0.0017	0.5187 ± 0.0015	1.34 ± 0.05	1.00 ± 0.00
335.66	0.0140 ± 0.0004	0.3506 ± 0.0037	0.0383 ± 0.0015	142.1	142.0	0.0353 ± 0.0014	0.4218 ± 0.0028	1.36 ± 0.05	1.00 ± 0.00
335.66	0.0064 ± 0.0002	0.3506 ± 0.0037	0.0179 ± 0.0008	110.7	110.8	0.0165 ± 0.0008	0.2539 ± 0.0031	1.38 ± 0.05	1.00 ± 0.00

Table 5. Continued

T^a	$n_1{}^b$	$n_2{}^b$		$p_{\mathrm{exp}}{}^d$	$p_{\mathrm{Leg}}{}^e$				
K	mole	mole	$z_1{}^c$	kPa	kPa	$x_1{}^f$	$y_1{}^f$	$\gamma_1{}^g$	$\gamma_2{}^g$
335.66	0.0000 ± 0.0000	0.3506 ± 0.0037	0.0000 ± 0.0000	83.0	83.0	0.0000 ± 0.0000	0.0000 ± 0.0000	1.39 ± 0.06	1.00 ± 0.00

[a] Experimental temperature, T. [b] Amount of component in the equilibrium cell, n_i. [c] Total mole fraction, z_1. [d] Experimental pressure, p_{exp}. [e] Pressure calculated with Legendre model, p_{Leg}. [f] Liquid and vapor phase equilibrium mole fractions, x_1 and y_1. [g] Activity coefficients calculated with Legendre model, γ_i.

Table 6. VLE Data for Methyl Formate (1) + Methanol (2)

T^a	$n_1{}^b$	$n_2{}^b$		$p_{\mathrm{exp}}{}^d$	$p_{\mathrm{Leg}}{}^e$				
K	mole	mole	$z_1{}^c$	kPa	kPa	$x_1{}^f$	$y_1{}^f$	$\gamma_1{}^g$	$\gamma_2{}^g$
358.92	0.7857 ± 0.0083	0.0000 ± 0.0000	1.0000 ± 0.0000	550.4	550.4	1.0000 ± 0.0000	1.0000 ± 0.0000	1.00 ± 0.00	2.59 ± 0.01
358.93	0.7857 ± 0.0083	0.0080 ± 0.0002	0.9900 ± 0.0004	551.0	551.0	0.9900 ± 0.0004	0.9892 ± 0.0004	1.00 ± 0.00	2.55 ± 0.01
358.93	0.7857 ± 0.0083	0.0252 ± 0.0005	0.9690 ± 0.0010	551.8	551.7	0.9690 ± 0.0010	0.9677 ± 0.0010	1.00 ± 0.00	2.46 ± 0.01
358.93	0.7857 ± 0.0083	0.0426 ± 0.0007	0.9486 ± 0.0013	551.9	552.0	0.9486 ± 0.0013	0.9482 ± 0.0013	1.00 ± 0.00	2.38 ± 0.00
358.94	0.7857 ± 0.0083	0.0884 ± 0.0012	0.8988 ± 0.0022	551.2	551.1	0.8988 ± 0.0022	0.9059 ± 0.0023	1.01 ± 0.00	2.19 ± 0.01
358.94	0.7857 ± 0.0083	0.1400 ± 0.0018	0.8488 ± 0.0030	548.3	548.2	0.8486 ± 0.0030	0.8698 ± 0.0029	1.02 ± 0.00	2.02 ± 0.01
358.94	0.7857 ± 0.0083	0.1990 ± 0.0024	0.7979 ± 0.0037	543.8	543.6	0.7976 ± 0.0037	0.8382 ± 0.0034	1.04 ± 0.00	1.86 ± 0.01
358.94	0.7857 ± 0.0083	0.2635 ± 0.0031	0.7488 ± 0.0042	537.9	537.9	0.7484 ± 0.0042	0.8115 ± 0.0036	1.06 ± 0.00	1.73 ± 0.00
358.94	0.7857 ± 0.0083	0.3388 ± 0.0038	0.6987 ± 0.0046	531.1	531.1	0.6982 ± 0.0046	0.7870 ± 0.0037	1.09 ± 0.00	1.61 ± 0.00
358.94	0.7857 ± 0.0083	0.4252 ± 0.0047	0.6489 ± 0.0049	523.4	523.4	0.6483 ± 0.0050	0.7645 ± 0.0036	1.13 ± 0.00	1.51 ± 0.00
358.94	0.7857 ± 0.0083	0.5263 ± 0.0057	0.5989 ± 0.0052	514.7	514.8	0.5983 ± 0.0052	0.7429 ± 0.0035	1.17 ± 0.01	1.42 ± 0.00
358.93	0.7857 ± 0.0083	0.6464 ± 0.0070	0.5487 ± 0.0053	504.8	505.0	0.5482 ± 0.0053	0.7215 ± 0.0034	1.22 ± 0.01	1.34 ± 0.00
358.94	0.7857 ± 0.0083	0.7884 ± 0.0082	0.4992 ± 0.0052	494.2	494.3	0.4988 ± 0.0052	0.6999 ± 0.0033	1.27 ± 0.01	1.28 ± 0.00
358.94	0.7856 ± 0.0082	0.7937 ± 0.0086	0.4974 ± 0.0053	494.2	493.9	0.4971 ± 0.0053	0.6992 ± 0.0033	1.28 ± 0.01	1.28 ± 0.00
358.93	0.6433 ± 0.0068	0.7937 ± 0.0086	0.4477 ± 0.0053	481.5	481.6	0.4470 ± 0.0053	0.6761 ± 0.0032	1.34 ± 0.01	1.22 ± 0.00
358.93	0.5229 ± 0.0056	0.7937 ± 0.0086	0.3972 ± 0.0051	467.1	467.3	0.3961 ± 0.0051	0.6507 ± 0.0031	1.42 ± 0.01	1.17 ± 0.00
358.93	0.4235 ± 0.0046	0.7937 ± 0.0086	0.3479 ± 0.0049	451.4	451.4	0.3465 ± 0.0049	0.6230 ± 0.0031	1.50 ± 0.02	1.13 ± 0.00
358.93	0.3364 ± 0.0037	0.7937 ± 0.0086	0.2977 ± 0.0046	432.9	432.8	0.2959 ± 0.0046	0.5905 ± 0.0029	1.60 ± 0.02	1.10 ± 0.00
358.93	0.2621 ± 0.0029	0.7937 ± 0.0086	0.2483 ± 0.0041	411.8	411.6	0.2461 ± 0.0041	0.5525 ± 0.0028	1.72 ± 0.02	1.07 ± 0.00
358.94	0.1966 ± 0.0022	0.7937 ± 0.0086	0.1986 ± 0.0035	386.9	386.6	0.1962 ± 0.0035	0.5055 ± 0.0026	1.86 ± 0.03	1.05 ± 0.00
358.94	0.1382 ± 0.0016	0.7937 ± 0.0086	0.1483 ± 0.0029	356.5	356.6	0.1459 ± 0.0029	0.4437 ± 0.0022	2.04 ± 0.03	1.03 ± 0.00
358.93	0.0879 ± 0.0011	0.7937 ± 0.0086	0.0997 ± 0.0021	321.2	321.6	0.0976 ± 0.0021	0.3608 ± 0.0017	2.25 ± 0.04	1.01 ± 0.00
358.94	0.0420 ± 0.0006	0.7937 ± 0.0086	0.0502 ± 0.0012	277.7	277.8	0.0488 ± 0.0012	0.2325 ± 0.0011	2.52 ± 0.05	1.00 ± 0.00
358.94	0.0253 ± 0.0005	0.7937 ± 0.0086	0.0309 ± 0.0009	257.9	257.8	0.0300 ± 0.0009	0.1608 ± 0.0012	2.65 ± 0.06	1.00 ± 0.00
358.94	0.0090 ± 0.0002	0.7937 ± 0.0086	0.0112 ± 0.0004	235.9	235.3	0.0108 ± 0.0004	0.0667 ± 0.0008	2.79 ± 0.07	1.00 ± 0.00
358.93	0.0000 ± 0.0000	0.7937 ± 0.0086	0.0000 ± 0.0000	221.4	221.4	0.0000 ± 0.0000	0.0000 ± 0.0000	2.88 ± 0.07	1.00 ± 0.00

[a] Experimental temperature, T. [b] Amount of component in the equilibrium cell, n_i. [c] Total mole fraction, z_1. [d] Experimental pressure, p_{exp}. [e] Pressure calculated with Legendre model, p_{Leg}. [f] Liquid and vapor phase equilibrium mole fractions, x_1 and y_1. [g] Activity coefficients calculated with Legendre model, γ_i.

VLEFIT.[7] The component properties used in the data reduction are shown in Table 3.[15]

Error Analysis. The uncertainty in the injected volume was ± 0.02 cm^3, obtained from calibration experiments with distilled water. The uncertainty in the temperature of the pump was ± 0.1 K. The uncertainty in the pressure of the pump was ± 20 kPa. The uncertainty in the cell temperature measurement was ± 0.02 K. The uncertainty in the cell pressure measurement was ± 0.4 kPa. The maximum theoretical error of the injected amount of substance was calculated as presented in Laakkonen et al.,[9] and the maximum theoretical error of the overall molar composition was calculated as presented in Hynynen et al.[8] Upper and lower boundary values for equilibrium cell temperature, pressure, and the injected amount of moles were used to perform the data reduction. The absolute maximum errors were rounded up and the highest value used as a representative scale of error.[8,9]

RESULTS AND DISCUSSION

The measured pure component vapor pressures agreed well with the pressures calculated using the literature correlations,[15,18,19] as shown in Table 2. The total pressure of each measured system coincided well at the equimolar composition. The experimental data were regressed separately for each experiment to obtain gas and liquid phase concentrations. The amount of parameters for the Legendre polynomials was increased until the pressure average deviation was below the uncertainty of the cell pressure measurement, or the pressure average deviation no longer decreased. Four parameters were found to be sufficient for each measurement. The measured data, equilibrium phase compositions, and component activity coefficients are shown in Tables 4 to 6. Equilibrium phase compositions are presented in Figures 1 and 2. All measured binaries showed a positive deviation from the Raoult's law. The binary system of methoxymethane + hexane showed a weak temperature dependency, as shown in the liquid activity coefficient graph in Figure 3. The measured pure component vapor pressures were acceptable; both sides of the measured binaries coincided, and the Legendre polynomials could describe the data with good accuracy. This verified that the data were of good quality.

Parameters for the local composition models were regressed for each system based on the data measured in this work in both temperatures. The calculated pressure agreed well with the experimental pressure. The local composition models could describe the data with roughly equal accuracy. The best accuracy in most cases was obtained with the Legendre polynomials,

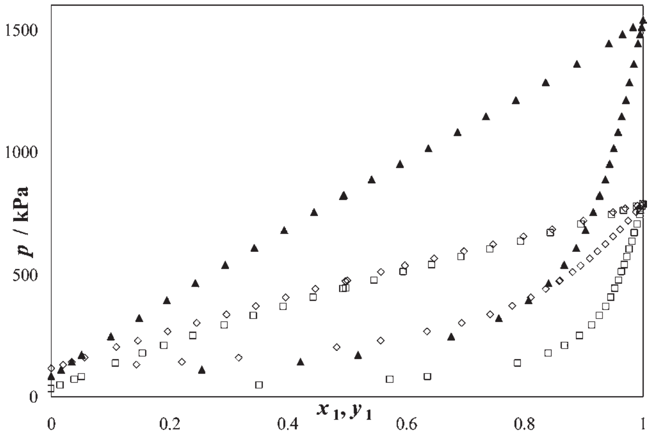

Figure 1. Liquid and vapor phase equilibrium composition in mole fractions of methoxymethane + hexane at 335.66 K, ▲; methoxymethane + methyl formate at 308.11 K, ◇; methoxymethane + hexane at 308.13 K, ☐.

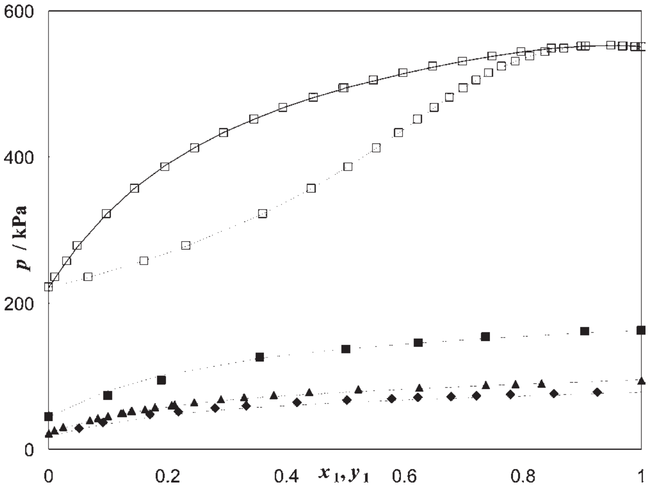

Figure 2. Liquid phase equilibrium composition in mole fractions of methyl formate + methanol. This work at 358.94 K, ☐; Zharov and Pervukhin[23] at 318.15 K, ■; Kozub et al.[20] at 303.15 K, ▲; Polak and Lu[21] at 298.15 K, ◆. Lines represent values calculated with the Wilson model.

Table 7. Liquid Activity Coefficient Model Parameters

	methoxymethane (1) + methyl formate	methoxymethane (1) + hexane		methylformate (1) + methanol
T/K	308.11	308.13	335.66	358.94
Legendre, $a_{1,0}$[a]	0.307667	0.478848	0.373008	0.983255
Legendre, $a_{2,0}$[a]	0.022309	0.069275	0.062405	−0.036607
Legendre, $a_{3,0}$[a]	0.003743	0.017712	0.015173	0.020771
Legendre, $a_{4,0}$[a]	−0.028618	−0.014347	−0.007085	−0.016476
Δp/kPa[b]	−0.03	−0.01	0.01	−0.02
$\lvert\Delta p\rvert$/kPa[c]	0.74	0.33	0.29	0.14
Wilson, λ_{12}/K[d]	−74.70	195.81		74.70
Wilson, λ_{21}/K[d]	189.28	−31.86		332.16
Δp/kPa[b]	0.13	0.03		−0.06
$\lvert\Delta p\rvert$/kPa[c]	1.24	1.58		0.44
NRTL, λ_{12}/K[e]	177.06	178.14		169.06
NRTL, λ_{21}/K[e]	−59.89	−17.54		226.23
NRTL, $\alpha_{12} = \alpha_{21}$	0.4	0.4		0.4
Δp/kPa[b]	0.40	−0.02		0.15
$\lvert\Delta p\rvert$/kPa[c]	1.31	1.95		0.61
UNIQUAC, λ_{12}[f]	113.42	−55.015		240.71
UNIQUAC, λ_{21}[f]	−53.37	155.93		16.43
Δp/kPa[b]	0.16	0.24		−0.08
$\lvert\Delta p\rvert$/kPa[c]	1.26	1.72		0.52
UNIFAC, Δp/kPa[b]	−15.75	6.65		−2.63
UNIFAC, $\lvert\Delta p\rvert$/kPa[c]	16.96	7.25		2.78

[a] $a_{i,0}$ is the Legendre model parameter for one temperature. [b] Δp/kPa is the average pressure residual. [c] $\lvert\Delta p\rvert$/kPa is the average pressure deviation. [d] λ_{ij} is the Wilson model parameter for all measured temperatures. [e] λ_{ij} is the NRTL model parameter for all measured temperatures. [f] λ_{ij} is the UNIQUAC model parameter for all measured temperatures.

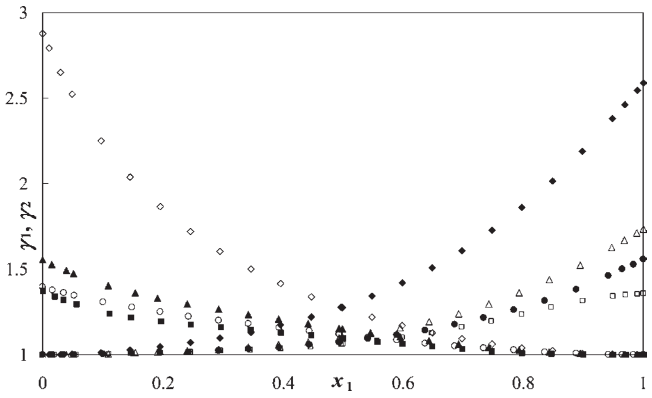

Figure 3. Liquid activity coefficients. Methyl formate (1), ◇, + methanol, ◆, system at 358.94 K; methoxymethane (1), ▲, + hexane, △, system at 308.13 K; methoxymethane(1), ○, + hexane, ●, system at 335.66 K; methoxymethane(1), ■, + methyl formate, □, system at 308.11 K.

Table 8. Comparison of Measured Methyl Formate + Methanol System to Literature

ref	T/K	$\|\Delta y\|^a$	Δp^b/kPa	$\|\Delta p\|^c$/kPa
20	303.20	0.0089	−1.38	1.52
21	298.15	0.0109	−3.02	3.02
23	318.15	NA	1.14	2.16
14[f]	358.94	0.007	−7.75	7.75
ref	p/kPa	$\|\Delta y\|$	ΔT^d/K	$\|\Delta T\|^e$/K
20	101.33	0.0067	0.32	0.47
22	101.33	0.0048	0.58	0.67
22	202.67	0.0065	0.33	0.47

[a] $|\Delta p|$/kPa is the average molar fraction deviation of the vapor phase. [b] Δp/kPa is the average pressure residual. [c] $|\Delta p|$/kPa is the average pressure deviation. [d] ΔT/K is the average temperature residual. [e] $|\Delta T|$/K is the average temperature deviation. [f] Calculated from the Wilson model parameters given in the refeerence using the DIPPR[15] correlation to calculate the vapor pressure.

which used more parameters than the local composition models, described the system at only one temperature, and cannot be used to describe multicomponent mixtures. The modified universal functional (UNIFAC, Dortmund) model[10] could describe the methoxymethane + hexane and methyl formate + methanol binary systems accurately but was less accurate with the methoxymethanoate + methyl formate binary system. The fitted parameters for Legendre,[4] Wilson,[11] nonrandom two-liquid (NRTL),[12] and universal quasichemical (UNIQUAC)[13] and the UNIFAC[10] pressure residuals are shown in Table 7. With the local composition models the average pressure deviation was no higher than 2.0 kPa. With the Legendre polynomials, the pressure average deviation was no higher than 0.7 kPa. The Wilson model could describe the literature values[20−23] well as shown in Table 8, with the exception of Sohlo and Holma.[14] As the work of Sohlo and Holma consisted of only the Wilson model parameters without measured vapor pressure data, the DIPPR[15] vapor pressure correlation was used to calculate the vapor pressure. This lack of experimentally determined pure component vapor pressure data may explain the large pressure residuals. For the methoxymethane + methyl formate binary system the vapor phase composition average deviation, calculated with the model of Sohlo and Holma,[14] was 0.0126, the average pressure residual was 34.3 kPa, and the pressure average deviation was 34.9 kPa.

The methyl formate + methanol binary system showed pressure maximum azeotropic behavior at a methyl formate concentration of 0.937 at 358.94 K. The concentration was determined with the Wilson model using parameters presented in Table 7. A regression of the data by Zeng et al.[22] showed similar behavior.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: aarne.sundberg@aalto.fi.

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■ REFERENCES

(1) International DME Association, Frequently Asked Questions. http://www.aboutdme.org/index.asp?bid=234#Q2.1 (accessed Jan 24, 2010).

(2) *Ullmann's Encyclopedia of Industrial Chemistry*, 7th ed.; Wiley-VCH, John Wiley & Sons: New York, 2011.

(3) Uusi-Kyyny, P.; Pokki, J.-P.; Laakkonen, M.; Aittamaa, J.; Liukkonen, S. Vapor liquid equilibrium for the binary systems 2-methylpentane + 2-butanol at 329.2 K and n-hexane + 2-butanol at 329.2 and 373.2 K with a static apparatus. *Fluid Phase Equilib.* **2002**, *201*, 343–358.

(4) Gmehling, J.; Onken, U. *Vapour-Liquid Data Collection*, DECHEMA Chemistry Data Series, Vol. 1, Part 1; DECHEMA: Frankfurt/Main, 1977.

(5) Soave, G. Equilibrium constants from a modified Redlich-Kwong equation of state. *Chem. Eng. Sci.* **1972**, *27*, 1197–1203.

(6) Barker, J. A. Determination of activity coefficients from total pressure measurements. *Aust. J. Chem.* **1953**, *6*, 207–210.

(7) Aittamaa, J.; Pokki, J.-P. *User Manual of Program VLEFIT*; Helsinki University of Technology: Espoo, Finland, 2003.

(8) Hynynen, K.; Uusi-Kyyny, P.; Pokki, J.-P.; Pakkanen, M.; Aittamaa, J.Isothermal Vapor Liquid Equilibrium for 2-Methylpropene + Methanol, + 1-Propanol, + 2-Propanol, + 2-Butanol, and + 2-Methyl-2-propanol Binary Systems at 364.5 K. *J. Chem. Eng. Data* **2006**, *51*, 562–568.

(9) Laakkonen, M.; Pokki, J.-P.; Uusi-Kyyny, P.; Aittamaa, J. Vapor-liquid equilibrium for the 1-butene + methanol, + ethanol, + 2-propanol, + 2-butanol and + 2-methyl-2-propanol systems at 326 K. *Fluid Phase Equilib.* **2003**, *212*, 237–252.

(10) Weidlich, U.; Gmehling, J. A modified UNIFAC model. 1. Prediction of VLE, h^E, and γ^∞. *Ind. Eng. Chem. Res.* **1987**, *26*, 1372–1381.

(11) Wilson, G. M. Vapor-Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing. *J. Am. Chem. Soc.* **1964**, *86*, 127–130.

(12) Renon, H.; Prausnitz, J. M. Local compositions in thermodynamic excess functions for liquid mixtures. *AIChE J.* **1978**, *14*, 135–144.

(13) Abrams, D. S.; Prausnitz, J. M. Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems. *AIChE J.* **1975**, *21*, 116–128.

(14) Sohlo, J.; Holma, H. Calculation of a ternary component distillation. *Kem. Teollisuus* **1973**, *8*, 346–350.

(15) Design Institute for Physical Properties. *DIPPR Project 801 - Full Version*; Design Institute for Physical Property Data/AIChE: New York, 2005.

(16) Bartholomew, R. J.; Irish, D. E. Study of the Raman noncoincidence effect from methyl formate − acetonitrile solutions. *J. Raman Spectrosc.* **1998**, *29*, 115–122.

(17) Ortega, J. Densities and refractive indices of pure alcohols as a function of temperature. *J. Chem. Eng. Data* **1982**, *27*, 312–317.

(18) Reid, R. C.; Prausnitz, J. M.; Poling, B. E. *The properties of gases and liquids*, 4th ed.; McGraw-Hill: New York, 1988.

(19) Yaws, C. L. *Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Components*; Gulf Publishing: Houston, TX, 2003.

(20) Kozub, N.; Schuberth, H.; Leibnitz, E. Phasengleichgewichtsuntersuchungen dampfförmig-flüssig am system methanol/methylformiat unter verwendung einer gaschromatographischen analysenmethode. *J. Prakt. Chem.* **1962**, *17*, 282–292.

(21) Polak, J.; Lu, B. C.-Y. Excess Gibbs free energies and excess volumes of methyl formate + methanol and methyl formate + ethanol at 298.15 K. *J. Chem. Thermodyn.* **1972**, *4*, 469–476.

(22) Zeng, J.; Fu, C.; Hu, W.-L. Study of the VLE for methyl formate − methanol system. *Tianranqi Huagong* **2000**, *25*, 54–56.

(23) Zharov, V. T.; Pervukhin, O. K. Structure of the vapor-liquid equilibrium diaghrams of reactive systems II. Methanol−formic acid −methyl formate system. *Zh. Fiz. Khim.* **1972**, *46*, 1970–1973.