Isothermal Binary Vapor−Liquid Equilibrium for 2-Methylpropane and *n*-Butane with 1,2-Ethanedithiol and 2-Methyl-2-propanethiol

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Isothermal vapor−liquid equilibrium was measured for 2-methylpropane + 1,2-ethanedithiol, 2-methylpropane + 2-methyl-2-propanethiol, *n*-butane + 1,2-ethanedithiol, and *n*-butane + 2-methyl-2-propanethiol at 346.97 K with a static total pressure apparatus. The measured data were reduced with Barker's method to obtain phase equilibrium data. The Legendre polynomial, Wilson, NRTL, UNIQUAC, UNIFAC, and Cosmo-SAC activity coefficients in infinite dilution and possible model parameters were reported. All binary data showed a positive deviation from Raoult's law.

Introduction

Butane is present in natural gas, liquefied petroleum gas (LPG), and hydrocarbon streams in petroleum refineries. Butane is a colorless and highly flammable gas,[1] and it has two isomers: *n*-butane and 2-methylpropane. The phase equilibrium behavior of butane enables the development of thermodynamic models that is fundamental in process design and development. 2-Methyl-2-propanethiol is a malodorous component that is added to natural gas in small quantities to aid in its detection.[2] 1,2-Ethanedithiol is a toxic compound widely used as a building block in organic chemistry. This compound is interesting as a test system for predictive activity coefficient models, due to its structure with thiols. For example, reliable fluid phase equilibrium prediction of diols requires separate interaction parameters and can not be modeled reliably by using two alcoholic functional groups.[3]

Experimental Section

Materials. The suppliers and purities of the materials used are presented in Table 1. The sulfur compounds were dried over Merck 3A molecular sieves for at least 24 h prior to degassing. The degassing was performed by vacuum rectification[6] with modifications.[7] 2-Methylpropane and *n*-butane were degassed by evacuation in a syringe pump. The vacuum line was opened 10 times in a 10 s period. The quality of the degassing procedure was checked by comparing the measured refractive indices and vapor pressures to values in the literature (Tables 1 and 2). In this work, 2-methylpropane and *n*-butane are always addressed as component (1) and the sulfur compounds as component (2).

Apparatus. The static total pressure apparatus is described in detail by Uusi-Kyyny et al.,[10] and the automation of the apparatus is described by Ouni et al.[11] The pressure of the cell was measured with a Digiquartz 2300A-101-CE pressure transducer. Temperature was measured by a temperature meter equipped with Pt-100 probes. The volume of the cell was 103.3 cm^3, and the cell was equipped with a magnetic stirrer and submerged into a water bath. Injections of the components into the cell were made with syringe pumps.

Procedure. After degassing, the first component was introduced to the cell, and the pure component vapor pressure was measured. Then, a predetermined volume of the second component was added into the cell, and after about 30 min, when the system reached equilibrium, the equilibrium pressure and temperature were measured. The procedure was repeated until an approximately equimolar composition was reached. The injections were predetermined so that the cell was nearly full of liquid at the end. Finally the cell was drained and emptied

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Table 1. Materials and Their Purities According to Suppliers

		GC-analysis	refractive index		
component	supplier	(mass fraction)	this work	ref 4	ref 5
2-methylpropane	Oy Aga Ab	0.9995			
n-butane	Oy Aga Ab	0.9995			
1,2-ethanedithiol	Fluka	0.9976	1.5562	1.5562	
2-methyl-2-propanethiol	Aldrich	0.9987	1.4200	1.42004	1.4200

Table 2. Measured Pure Component Vapor Pressures and Literature Correlations

		p/kPa				
component	*T*/K	this work	ref 4	ref 5	ref 8	ref 9
2-methylpropane	346.97	1178.6	1178.3	1180.7	1173.2	1181.0
	346.97	1179.9	1178.3	1180.7	1173.2	1181.0
n-butane	346.96	881.4	883.5	883.2	885.1	883.5
	346.96	879.3	883.5	883.2	885.1	883.5
1,2-ethanedithiol	346.97	8.2	8.7	–	–	8.7
	346.96	8.5	8.7	–	–	8.7
2-methyl-2-Propanethiol	346.97	134.4	135.9	136.0	–	128.4
	346.97	132.7	135.9	136.0	–	128.4

Table 3. Pure Component Physical Properties, Critical Temperature T_c,[7] Critical Pressure P_c,[7] Acentric Factor ω,[7] Liquid Molar Volume V_i,[3] Relative van der Waals Volume V,[3] and Relative van der Waals Surface Area A[3a]

component	2-methylpropane	*n*-butane	1,2-ethanedithiol	2-methyl-2-propanethiol
T_c/K	408.14	425.18	663	530.14
P_c/MPa	3.65	3.80	5.36	4.06
ω	0.1825	0.2008	0.2570	0.1966
V_i/$cm^3 \cdot mol^{-1}$	105.35	101.39	84.19	113.52
V/$cm^3 \cdot mol^{-1}$	47.79	47.80	50.08	59.15
A/$cm^2 \cdot mol^{-1}$	$6.93 \cdot 10^9$	$6.94 \cdot 10^9$	$7.25 \cdot 10^9$	$8.45 \cdot 10^9$
R_{UNIQ}	3.15	3.15	3.30	3.90
Q_{UNIQ}	2.77	2.78	2.90	3.38

[a] Volume RUNIQ and surface area QUNIQ parameters were calculated according to Abrams et al.[15]

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Table 4. VLE Data for 2-Methylpropane (1) + 1,2-Ethanedithiol (2)[a]

n_1	n_2		T	p_{exptl}	p_{leg}				
mol	mol	z_1	K	kPa	kPa	x_1	y_1	γ_1	γ_2
0.2332 ± 0.0026	0.0000 ± 0.0000	1.0000 ± 0.0000	346.97	1178.6	1178.6 ± 0.4	1.0000 ± 0.0000	1.0000 ± 0.0000	1.0000 ± 0.000	9.5483 ± 0.757
0.2332 ± 0.0026	0.0013 ± 0.0002	0.9913 ± 0.0009	346.97	1168.9	1169.2 ± 1.6	0.9933 ± 0.0013	0.9993 ± 0.0002	1.0001 ± 0.000	9.1902 ± 0.668
0.2332 ± 0.0026	0.0061 ± 0.0003	0.9729 ± 0.0013	346.97	1139.6	1139.3 ± 1.8	0.9700 ± 0.0018	0.9971 ± 0.0005	1.0025 ± 0.001	8.0743 ± 0.457
0.2332 ± 0.0026	0.0136 ± 0.0004	0.9542 ± 0.0016	346.97	1102.5	1102.1 ± 2.5	0.9357 ± 0.0024	0.9947 ± 0.0006	1.0114 ± 0.002	6.7584 ± 0.252
0.2332 ± 0.0026	0.0257 ± 0.0005	0.9146 ± 0.0023	346.97	1060.0	1060.1 ± 3.9	0.8862 ± 0.0033	0.9925 ± 0.0006	1.0347 ± 0.005	5.3488 ± 0.090
0.2332 ± 0.0026	0.0427 ± 0.0006	0.8663 ± 0.0031	346.97	1022.9	1023.5 ± 5.7	0.8255 ± 0.0042	0.9909 ± 0.0005	1.0796 ± 0.010	4.1534 ± 0.060
0.2332 ± 0.0026	0.0604 ± 0.0008	0.8206 ± 0.0037	346.97	1000.8	1001.1 ± 6.9	0.7709 ± 0.0049	0.9901 ± 0.0006	1.1355 ± 0.014	3.4015 ± 0.070
0.2332 ± 0.0026	0.0787 ± 0.0010	0.7730 ± 0.0042	346.97	987.0	987.1 ± 7.3	0.7219 ± 0.0053	0.9897 ± 0.0007	1.1988 ± 0.018	2.8990 ± 0.064
0.2332 ± 0.0026	0.1024 ± 0.0013	0.7271 ± 0.0046	346.97	977.0	976.6 ± 6.9	0.6673 ± 0.0057	0.9894 ± 0.0007	1.2855 ± 0.021	2.4730 ± 0.051
0.2332 ± 0.0026	0.1290 ± 0.0015	0.6801 ± 0.0050	346.97	970.5	970.0 ± 5.8	0.6156 ± 0.0059	0.9893 ± 0.0006	1.3858 ± 0.022	2.1617 ± 0.038
0.2332 ± 0.0026	0.1600 ± 0.0018	0.6318 ± 0.0053	346.97	965.7	965.5 ± 4.0	0.5650 ± 0.0060	0.9892 ± 0.0006	1.5043 ± 0.022	1.9207 ± 0.026
0.2332 ± 0.0026	0.1947 ± 0.0022	0.5832 ± 0.0054	346.97	961.7	962.0 ± 1.7	0.5179 ± 0.0060	0.9891 ± 0.0006	1.6365 ± 0.022	1.7388 ± 0.016
0.2332 ± 0.0026	0.2422 ± 0.0027	0.5342 ± 0.0055	346.97	957.2	957.9 ± 2.6	0.4656 ± 0.0058	0.9891 ± 0.0006	1.8144 ± 0.020	1.5735 ± 0.007
0.2327 ± 0.0026	0.2456 ± 0.0027	0.5331 ± 0.0055	346.97	955.4	957.2 ± 2.9	0.4617 ± 0.0058	0.9891 ± 0.0006	1.8292 ± 0.020	1.5625 ± 0.007
0.1910 ± 0.0022	0.2456 ± 0.0027	0.4830 ± 0.0056	346.97	949.0	950.5 ± 6.2	0.4048 ± 0.0058	0.9890 ± 0.0007	2.0744 ± 0.019	1.4194 ± 0.007
0.1561 ± 0.0018	0.2456 ± 0.0027	0.4328 ± 0.0055	346.97	937.7	938.0 ± 8.6	0.3474 ± 0.0056	0.9888 ± 0.0008	2.3907 ± 0.020	1.3030 ± 0.009
0.1258 ± 0.0015	0.2456 ± 0.0027	0.3816 ± 0.0054	346.97	915.3	913.7 ± 9.2	0.2890 ± 0.0053	0.9885 ± 0.0008	2.8125 ± 0.026	1.2079 ± 0.008
0.1009 ± 0.0012	0.2456 ± 0.0027	0.3295 ± 0.0052	346.97	875.3	872.1 ± 7.2	0.2345 ± 0.0049	0.9881 ± 0.0008	3.3350 ± 0.044	1.1372 ± 0.007
0.0782 ± 0.0010	0.2456 ± 0.0027	0.2765 ± 0.0048	346.97	803.2	800.1 ± 2.6	0.1808 ± 0.0043	0.9872 ± 0.0008	4.0277 ± 0.088	1.0824 ± 0.005
0.0600 ± 0.0008	0.2456 ± 0.0027	0.2248 ± 0.0043	346.97	706.3	704.8 ± 3.9	0.1367 ± 0.0037	0.9859 ± 0.0007	4.7855 ± 0.156	1.0478 ± 0.003
0.0429 ± 0.0006	0.2456 ± 0.0027	0.1707 ± 0.0037	346.97	572.0	573.2 ± 8.2	0.0956 ± 0.0030	0.9832 ± 0.0010	5.7083 ± 0.265	1.0238 ± 0.002
0.0275 ± 0.0005	0.2456 ± 0.0027	0.1157 ± 0.0029	346.97	409.5	412.8 ± 9.2	0.0599 ± 0.0023	0.9778 ± 0.0015	6.7442 ± 0.418	1.0096 ± 0.001
0.0152 ± 0.0003	0.2456 ± 0.0027	0.0602 ± 0.0021	346.97	247.7	250.9 ± 5.7	0.0323 ± 0.0016	0.9651 ± 0.0024	7.7452 ± 0.592	1.0028 ± 0.000
0.0080 ± 0.0003	0.2456 ± 0.0027	0.0315 ± 0.0016	346.97	141.5	140.8 ± 1.4	0.0166 ± 0.0012	0.9395 ± 0.0031	8.4147 ± 0.721	1.0008 ± 0.000
0.0029 ± 0.0002	0.2456 ± 0.0027	0.0146 ± 0.0012	346.97	58.8	58.1 ± 3.9	0.0060 ± 0.0009	0.8567 ± 0.0154	8.9137 ± 0.820	1.0001 ± 0.000
0.0000 ± 0.0000	0.2456 ± 0.0027	0.0000 ± 0.0000	346.97	8.2	8.2 ± 0.4	0.0000 ± 0.0000	0.0000 ± 0.0000	9.2141 ± 0.838	1.0000 ± 0.000

[a] n is moles of component i in the whole system; z is mole fraction of component i in the whole system; T is temperature in the system; p_{exptl} is experimental pressure; p_{leg} is calculated pressure obtained from the Legendre polynomial; x is mole fraction in liquid phase; y is mole fraction in vapor phase; and γ is activity coefficient of component i.

Table 5. VLE Data for 2-Methylpropane (1) + 2-Methyl-2-propanethiol (2)

n_1	n_2		T	p_{exptl}	p_{leg}				
mol	mol	z_1	K	kPa	kPa	x_1	y_1	γ_1	γ_2
0.2338 ± 0.0026	0.0000 ± 0.0000	1.0000 ± 0.0000	346.97	1179.9	1179.9 ± 0.4	1.0000 ± 0.0000	1.0000 ± 0.0000	1.0000 ± 0.000	1.4912 ± 0.040
0.2338 ± 0.0026	0.0020 ± 0.0002	0.9913 ± 0.0005	346.97	1167.6	1167.8 ± 1.3	0.9900 ± 0.0011	0.9975 ± 0.0003	1.0000 ± 0.000	1.4781 ± 0.037
0.2338 ± 0.0026	0.0065 ± 0.0002	0.9729 ± 0.0017	346.97	1143.1	1143.0 ± 1.5	0.9691 ± 0.0015	0.9924 ± 0.0006	1.0004 ± 0.000	1.4517 ± 0.035
0.2338 ± 0.0026	0.0112 ± 0.0003	0.9542 ± 0.0028	346.97	1119.1	1118.7 ± 1.6	0.9480 ± 0.0019	0.9874 ± 0.0008	1.0012 ± 0.000	1.4264 ± 0.032
0.2338 ± 0.0026	0.0218 ± 0.0004	0.9146 ± 0.0049	346.97	1070.3	1069.9 ± 1.8	0.9046 ± 0.0027	0.9770 ± 0.0012	1.0040 ± 0.000	1.3775 ± 0.028
0.2338 ± 0.0026	0.0361 ± 0.0005	0.8663 ± 0.0073	346.97	1015.3	1014.6 ± 2.0	0.8529 ± 0.0035	0.9648 ± 0.0016	1.0093 ± 0.001	1.3252 ± 0.023
0.2338 ± 0.0026	0.0511 ± 0.0007	0.8206 ± 0.0093	346.97	966.2	965.3 ± 2.0	0.8052 ± 0.0041	0.9534 ± 0.0019	1.0163 ± 0.002	1.2818 ± 0.020
0.2338 ± 0.0026	0.0687 ± 0.0009	0.7730 ± 0.0111	346.97	917.6	916.6 ± 1.9	0.7565 ± 0.0046	0.9417 ± 0.0021	1.0253 ± 0.002	1.2421 ± 0.017
0.2338 ± 0.0026	0.0877 ± 0.0011	0.7271 ± 0.0126	346.97	872.9	871.7 ± 1.8	0.7105 ± 0.0050	0.9303 ± 0.0023	1.0356 ± 0.003	1.2084 ± 0.014
0.2338 ± 0.0026	0.1100 ± 0.0013	0.6801 ± 0.0138	346.97	827.9	826.8 ± 1.5	0.6639 ± 0.0053	0.9182 ± 0.0024	1.0478 ± 0.005	1.1776 ± 0.012
0.2338 ± 0.0026	0.1363 ± 0.0016	0.6318 ± 0.0147	346.97	782.8	781.9 ± 1.3	0.6167 ± 0.0055	0.9053 ± 0.0025	1.0620 ± 0.006	1.1498 ± 0.010
0.2338 ± 0.0026	0.1671 ± 0.0019	0.5832 ± 0.0154	346.97	738.1	737.5 ± 0.9	0.5697 ± 0.0056	0.8914 ± 0.0025	1.0780 ± 0.007	1.1250 ± 0.008
0.2338 ± 0.0026	0.2039 ± 0.0022	0.5342 ± 0.0158	346.97	693.5	692.9 ± 0.8	0.5226 ± 0.0057	0.8763 ± 0.0025	1.0958 ± 0.009	1.1030 ± 0.007
0.2325 ± 0.0026	0.2037 ± 0.0022	0.5331 ± 0.0158	346.97	691.8	691.7 ± 0.8	0.5214 ± 0.0057	0.8759 ± 0.0025	1.0963 ± 0.009	1.1025 ± 0.007
0.1902 ± 0.0022	0.2037 ± 0.0022	0.4830 ± 0.0158	346.97	641.7	641.6 ± 0.7	0.4686 ± 0.0057	0.8570 ± 0.0025	1.1186 ± 0.011	1.0809 ± 0.005
0.1554 ± 0.0018	0.2037 ± 0.0022	0.4328 ± 0.0155	346.97	591.0	591.1 ± 0.7	0.4163 ± 0.0057	0.8353 ± 0.0025	1.1431 ± 0.014	1.0625 ± 0.004
0.1257 ± 0.0015	0.2037 ± 0.0022	0.3816 ± 0.0149	346.97	538.7	539.1 ± 0.9	0.3632 ± 0.0055	0.8095 ± 0.0024	1.1703 ± 0.016	1.0466 ± 0.003
0.1001 ± 0.0012	0.2037 ± 0.0022	0.3295 ± 0.0140	346.97	484.9	485.6 ± 1.0	0.3101 ± 0.0052	0.7779 ± 0.0023	1.2002 ± 0.019	1.0333 ± 0.002
0.0778 ± 0.0010	0.2037 ± 0.0022	0.2765 ± 0.0127	346.97	429.9	430.5 ± 1.1	0.2568 ± 0.0048	0.7379 ± 0.0022	1.2328 ± 0.023	1.0224 ± 0.001
0.0590 ± 0.0008	0.2037 ± 0.0022	0.2248 ± 0.0110	346.97	375.5	376.2 ± 1.0	0.2060 ± 0.0043	0.6880 ± 0.0020	1.2664 ± 0.026	1.0142 ± 0.001
0.0419 ± 0.0006	0.2037 ± 0.0022	0.1707 ± 0.0090	346.97	318.4	318.8 ± 0.9	0.1541 ± 0.0036	0.6176 ± 0.0020	1.3033 ± 0.030	1.0078 ± 0.001
0.0267 ± 0.0005	0.2037 ± 0.0022	0.1157 ± 0.0065	346.97	259.6	259.8 ± 0.6	0.1027 ± 0.0029	0.5142 ± 0.0021	1.3424 ± 0.035	1.0034 ± 0.000
0.0130 ± 0.0003	0.2037 ± 0.0022	0.0602 ± 0.0036	346.97	200.4	199.8 ± 0.8	0.0524 ± 0.0020	0.3475 ± 0.0032	1.3834 ± 0.039	1.0009 ± 0.000
0.0066 ± 0.0003	0.2037 ± 0.0022	0.0315 ± 0.0019	346.97	169.2	168.6 ± 1.1	0.0272 ± 0.0014	0.2151 ± 0.0048	1.4051 ± 0.042	1.0002 ± 0.000
0.0030 ± 0.0002	0.2037 ± 0.0022	0.0146 ± 0.0009	346.97	150.7	150.3 ± 1.3	0.0125 ± 0.0011	0.1119 ± 0.0063	1.4179 ± 0.043	1.0000 ± 0.000
0.0000 ± 0.0000	0.2037 ± 0.0022	0.0000 ± 0.0000	346.97	134.4	134.4 ± 0.4	0.0000 ± 0.0000	0.0000 ± 0.0000	1.4291 ± 0.044	1.0000 ± 0.000

with a vacuum. The procedure was repeated in a reversed order so that the second component was introduced first and then the first component was injected.

Data Reduction. The measured data consisted of the temperature and the total pressure of the cell, the volumes of the injected components, and the temperature of the injection pumps. The total composition inside the cell at equilibrium was calculated from pump injections, and then the mole fractions of the components in the vapor and liquid phases were obtained by using the Barker method.[12] The Barker method assumes that there is an activity coefficient model that calculates the bubble point pressure with better accuracy than experimental pressure measurement. The Legendre polynomial[13] was used as an activity coefficient model for the data reduction with the Barker method. The vapor and liquid compositions obtained from the data reduction and experimental pressure and temperature were set to the input data for regression of the parameters for the Wilson,[14] NRTL,[15] and UNIQUAC[16] activity coefficient models. The obtained liquid compositions were also used for

Table 6. VLE Data for *n*-Butane (1) + 1,2-Ethanedithiol (2)

n_1	n_2		T	p_{exptl}	p_{leg}				
mol	mol	z_1	K	kPa	kPa	x_1	y_1	γ_1	γ_2
0.2471 ± 0.0027	0.0000 ± 0.0000	1.0000 ± 0.0000	346.96	881.4	881.4 ± 0.4	1.0000 ± 0.0000	1.0000 ± 0.0000	1.0000 ± 0.000	7.9498 ± 0.486
0.2471 ± 0.0027	0.0029 ± 0.0002	0.9885 ± 0.0011	346.98	869.9	869.3 ± 1.3	0.9872 ± 0.0013	0.9986 ± 0.0003	1.0004 ± 0.000	7.4584 ± 0.356
0.2471 ± 0.0027	0.0079 ± 0.0003	0.9690 ± 0.0015	346.97	850.9	850.4 ± 1.3	0.9657 ± 0.0017	0.9967 ± 0.0004	1.0029 ± 0.001	6.7243 ± 0.257
0.2471 ± 0.0027	0.0133 ± 0.0004	0.9490 ± 0.0018	346.97	832.9	833.0 ± 1.6	0.9438 ± 0.0021	0.9950 ± 0.0005	1.0077 ± 0.001	6.0787 ± 0.181
0.2471 ± 0.0027	0.0275 ± 0.0005	0.8998 ± 0.0026	346.97	798.1	798.3 ± 2.3	0.8907 ± 0.0030	0.9920 ± 0.0006	1.0284 ± 0.004	4.8479 ± 0.068
0.2471 ± 0.0027	0.0439 ± 0.0007	0.8491 ± 0.0034	346.97	770.9	771.4 ± 3.0	0.8370 ± 0.0038	0.9901 ± 0.0006	1.0622 ± 0.007	3.9489 ± 0.034
0.2471 ± 0.0027	0.0621 ± 0.0008	0.7992 ± 0.0040	346.97	751.2	751.5 ± 3.6	0.7847 ± 0.0045	0.9889 ± 0.0006	1.1073 ± 0.010	3.3026 ± 0.047
0.2471 ± 0.0027	0.0824 ± 0.0011	0.7499 ± 0.0045	346.97	736.7	736.7 ± 3.8	0.7338 ± 0.0050	0.9881 ± 0.0007	1.1638 ± 0.013	2.8229 ± 0.046
0.2471 ± 0.0027	0.1070 ± 0.0013	0.6979 ± 0.0049	346.97	725.2	724.9 ± 3.7	0.6808 ± 0.0054	0.9875 ± 0.0007	1.2368 ± 0.016	2.4365 ± 0.038
0.2471 ± 0.0027	0.1342 ± 0.0016	0.6480 ± 0.0052	346.98	716.6	716.1 ± 3.2	0.6304 ± 0.0056	0.9872 ± 0.0007	1.3215 ± 0.018	2.1477 ± 0.029
0.2471 ± 0.0027	0.1659 ± 0.0019	0.5983 ± 0.0054	346.97	709.5	709.0 ± 2.4	0.5808 ± 0.0058	0.9869 ± 0.0007	1.4221 ± 0.019	1.9188 ± 0.021
0.2471 ± 0.0027	0.2029 ± 0.0023	0.5491 ± 0.0055	346.97	703.1	702.9 ± 1.3	0.5324 ± 0.0058	0.9867 ± 0.0007	1.5400 ± 0.020	1.7362 ± 0.014
0.2471 ± 0.0027	0.2477 ± 0.0027	0.4995 ± 0.0055	346.97	696.5	696.7 ± 1.1	0.4840 ± 0.0057	0.9865 ± 0.0007	1.6815 ± 0.020	1.5855 ± 0.008
0.2477 ± 0.0027	0.2519 ± 0.0028	0.4958 ± 0.0055	346.97	696.2	696.3 ± 1.2	0.4804 ± 0.0057	0.9865 ± 0.0007	1.6928 ± 0.020	1.5756 ± 0.007
0.2018 ± 0.0023	0.2519 ± 0.0028	0.4447 ± 0.0055	346.97	687.4	687.9 ± 2.8	0.4244 ± 0.0057	0.9863 ± 0.0008	1.8965 ± 0.021	1.4345 ± 0.006
0.1647 ± 0.0019	0.2519 ± 0.0028	0.3953 ± 0.0054	346.97	676.0	676.6 ± 4.0	0.3698 ± 0.0055	0.9860 ± 0.0009	2.1457 ± 0.023	1.3224 ± 0.007
0.1328 ± 0.0016	0.2519 ± 0.0028	0.3451 ± 0.0052	346.97	658.7	659.0 ± 4.5	0.3142 ± 0.0053	0.9856 ± 0.0009	2.4684 ± 0.027	1.2296 ± 0.007
0.1060 ± 0.0013	0.2519 ± 0.0028	0.2961 ± 0.0048	346.97	632.1	631.9 ± 4.0	0.2604 ± 0.0049	0.9849 ± 0.0009	2.8716 ± 0.039	1.1569 ± 0.006
0.0828 ± 0.0010	0.2519 ± 0.0028	0.2474 ± 0.0044	346.97	590.5	589.9 ± 2.2	0.2082 ± 0.0044	0.9839 ± 0.0009	3.3805 ± 0.063	1.1006 ± 0.004
0.0626 ± 0.0008	0.2519 ± 0.0028	0.1989 ± 0.0039	346.97	528.0	527.5 ± 1.5	0.1587 ± 0.0038	0.9821 ± 0.0009	4.0126 ± 0.106	1.0591 ± 0.003
0.0449 ± 0.0007	0.2519 ± 0.0028	0.1514 ± 0.0033	346.96	442.3	441.9 ± 4.0	0.1137 ± 0.0031	0.9789 ± 0.0011	4.7657 ± 0.174	1.0308 ± 0.002
0.0290 ± 0.0005	0.2519 ± 0.0028	0.1033 ± 0.0026	346.97	328.4	329.4 ± 5.1	0.0727 ± 0.0024	0.9723 ± 0.0016	5.6557 ± 0.277	1.0128 ± 0.001
0.0144 ± 0.0003	0.2519 ± 0.0028	0.0541 ± 0.0018	346.97	188.2	188.3 ± 3.0	0.0355 ± 0.0016	0.9530 ± 0.0027	6.6953 ± 0.424	1.0031 ± 0.000
0.0091 ± 0.0003	0.2519 ± 0.0028	0.0347 ± 0.0015	346.97	127.0	126.5 ± 1.1	0.0221 ± 0.0013	0.9310 ± 0.0033	7.1362 ± 0.493	1.0012 ± 0.000
0.0038 ± 0.0002	0.2519 ± 0.0028	0.0150 ± 0.0011	346.97	60.4	60.5 ± 2.4	0.0093 ± 0.0010	0.8579 ± 0.0109	7.5998 ± 0.569	1.0002 ± 0.000
0.0000 ± 0.0000	0.2519 ± 0.0028	0.0000 ± 0.0000	346.96	8.5	8.5 ± 0.4	0.0000 ± 0.0000	0.0000 ± 0.0000	7.9627 ± 0.597	1.0000 ± 0.000

Table 7. VLE Data for *n*-Butane (1) + 2-Methyl-2-propanethiol (2)

n_1	n_2		T	p_{exptl}	p_{leg}				
mol	mol	z_1	K	kPa	kPa	x_1	y_1	γ_1	γ_2
0.4051 ± 0.0026	0.0000 ± 0.0000	1.0000 ± 0.0000	346.96	879.3	879.3 ± 0.4	1.0000 ± 0.0000	1.0000 ± 0.0000	1.0000 ± 0.000	1.4114 ± 0.021
0.4051 ± 0.0026	0.0039 ± 0.0002	0.9904 ± 0.0005	346.98	871.0	871.3 ± 0.7	0.9900 ± 0.0006	0.9972 ± 0.0002	1.0000 ± 0.000	1.4004 ± 0.020
0.4051 ± 0.0026	0.0114 ± 0.0002	0.9726 ± 0.0007	346.97	856.4	856.7 ± 0.8	0.9716 ± 0.0008	0.9922 ± 0.0003	1.0003 ± 0.000	1.3806 ± 0.019
0.4051 ± 0.0026	0.0191 ± 0.0003	0.9551 ± 0.0009	346.98	842.6	842.7 ± 0.8	0.9535 ± 0.0010	0.9872 ± 0.0005	1.0008 ± 0.000	1.3619 ± 0.018
0.4051 ± 0.0026	0.0389 ± 0.0004	0.9123 ± 0.0013	346.97	809.7	809.5 ± 0.9	0.9097 ± 0.0014	0.9752 ± 0.0007	1.0032 ± 0.000	1.3197 ± 0.015
0.4051 ± 0.0026	0.0621 ± 0.0005	0.8671 ± 0.0018	346.97	776.3	775.7 ± 1.0	0.8637 ± 0.0018	0.9627 ± 0.0010	1.0071 ± 0.000	1.2796 ± 0.013
0.4051 ± 0.0026	0.0879 ± 0.0007	0.8217 ± 0.0021	346.97	743.4	742.8 ± 1.0	0.8178 ± 0.0022	0.9500 ± 0.0012	1.0126 ± 0.001	1.2434 ± 0.011
0.4051 ± 0.0026	0.1177 ± 0.0009	0.7749 ± 0.0024	346.97	710.7	709.8 ± 0.9	0.7709 ± 0.0025	0.9367 ± 0.0014	1.0197 ± 0.001	1.2102 ± 0.009
0.4051 ± 0.0026	0.1515 ± 0.0011	0.7278 ± 0.0027	346.97	678.2	677.2 ± 0.9	0.7240 ± 0.0027	0.9229 ± 0.0015	1.0284 ± 0.002	1.1802 ± 0.008
0.4051 ± 0.0026	0.1894 ± 0.0013	0.6814 ± 0.0029	346.97	646.4	645.5 ± 0.8	0.6779 ± 0.0029	0.9088 ± 0.0016	1.0384 ± 0.002	1.1538 ± 0.007
0.4051 ± 0.0026	0.2347 ± 0.0016	0.6332 ± 0.0030	346.97	613.7	613.0 ± 0.7	0.6303 ± 0.0031	0.8933 ± 0.0017	1.0502 ± 0.003	1.1294 ± 0.006
0.4051 ± 0.0026	0.2879 ± 0.0019	0.5846 ± 0.0031	346.97	580.9	580.3 ± 0.6	0.5824 ± 0.0032	0.8767 ± 0.0018	1.0635 ± 0.004	1.1077 ± 0.005
0.4051 ± 0.0026	0.3523 ± 0.0022	0.5349 ± 0.0032	346.96	547.3	546.7 ± 0.5	0.5336 ± 0.0032	0.8580 ± 0.0018	1.0787 ± 0.005	1.0881 ± 0.004
0.4048 ± 0.0026	0.3524 ± 0.0022	0.5346 ± 0.0032	346.97	546.2	546.4 ± 0.5	0.5333 ± 0.0032	0.8580 ± 0.0018	1.0787 ± 0.005	1.0880 ± 0.004
0.3313 ± 0.0022	0.3524 ± 0.0022	0.4846 ± 0.0032	346.97	510.7	511.1 ± 0.5	0.4823 ± 0.0032	0.8363 ± 0.0018	1.0962 ± 0.006	1.0701 ± 0.003
0.2705 ± 0.0018	0.3524 ± 0.0022	0.4343 ± 0.0032	346.97	474.6	475.0 ± 0.5	0.4310 ± 0.0032	0.8117 ± 0.0018	1.1155 ± 0.007	1.0545 ± 0.002
0.2193 ± 0.0015	0.3524 ± 0.0022	0.3836 ± 0.0031	346.98	437.6	438.1 ± 0.6	0.3794 ± 0.0031	0.7829 ± 0.0018	1.1365 ± 0.008	1.0412 ± 0.002
0.1745 ± 0.0012	0.3524 ± 0.0022	0.3312 ± 0.0030	346.98	398.8	399.2 ± 0.6	0.3262 ± 0.0030	0.7476 ± 0.0018	1.1598 ± 0.010	1.0297 ± 0.001
0.1363 ± 0.0010	0.3524 ± 0.0022	0.2790 ± 0.0028	346.97	359.2	359.6 ± 0.6	0.2735 ± 0.0028	0.7047 ± 0.0017	1.1847 ± 0.011	1.0204 ± 0.001
0.1036 ± 0.0008	0.3524 ± 0.0022	0.2272 ± 0.0025	346.97	319.2	319.5 ± 0.6	0.2217 ± 0.0025	0.6512 ± 0.0017	1.2109 ± 0.013	1.0131 ± 0.001
0.0730 ± 0.0006	0.3524 ± 0.0022	0.1716 ± 0.0021	346.97	275.3	275.4 ± 0.6	0.1665 ± 0.0021	0.5755 ± 0.0016	1.2405 ± 0.015	1.0072 ± 0.000
0.0470 ± 0.0005	0.3524 ± 0.0022	0.1177 ± 0.0017	346.97	231.8	231.7 ± 0.5	0.1135 ± 0.0017	0.4732 ± 0.0017	1.2706 ± 0.017	1.0033 ± 0.000
0.0240 ± 0.0003	0.3524 ± 0.0022	0.0637 ± 0.0012	346.98	187.2	186.8 ± 0.6	0.0610 ± 0.0012	0.3199 ± 0.0020	1.3020 ± 0.019	1.0009 ± 0.000
0.0155 ± 0.0003	0.3524 ± 0.0022	0.0422 ± 0.0010	346.97	168.9	168.7 ± 0.6	0.0402 ± 0.0009	0.2352 ± 0.0022	1.3148 ± 0.020	1.0004 ± 0.000
0.0064 ± 0.0002	0.3524 ± 0.0022	0.0180 ± 0.0008	346.97	148.2	148.1 ± 0.8	0.0171 ± 0.0007	0.1145 ± 0.0031	1.3294 ± 0.021	1.0001 ± 0.000
0.0000 ± 0.0000	0.3524 ± 0.0022	0.0000 ± 0.0000	346.97	132.7	132.7 ± 0.4	0.0000 ± 0.0000	0.0000 ± 0.0000	1.3404 ± 0.021	1.0000 ± 0.000

calculation with the UNIFAC[17] method. As an objective function in performing the regression, eq 1 was used

$$\text{O.F.} = \sum \left| \frac{\gamma_{calc} - \gamma_{meas}}{\gamma_{calc}} \right| \quad (1)$$

The vapor phase fugacity coefficients were calculated by means of the Soave−Redlich−Kwong[18] equation of state. The quality of the measurements was verified by approaching the equimolar composition from both sides of the vapor pressure scale. If the vapor pressures coincided at equimolar composition, the measurements were considered to be of good quality. Pure component vapor pressures were also compared with the literature values as shown in Table 2. The component properties used in the data reduction are reported in Table 3. The calculations were made with the in-house simulator VLEFIT[19] that is developed at the Helsinki University of Technology.

Error Analysis. The uncertainty of the temperature measurements was ± 0.02 K for the water bath and ± 0.1 K for the syringe pumps. The uncertainty in the pressure measurements was ± 0.4 kPa for the cell and ± 20 kPa for the syringe pumps.

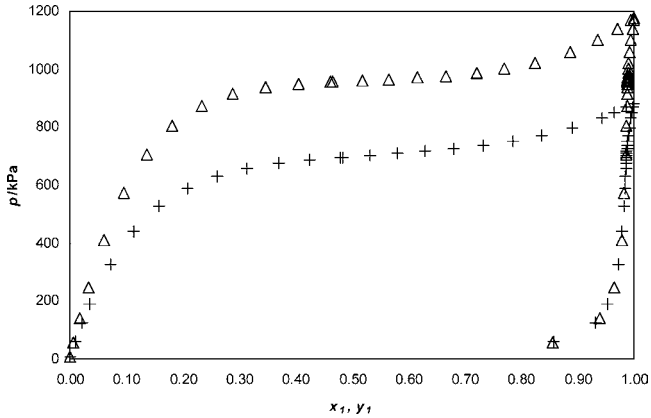

Figure 1. Pressure−composition diagram for Δ, 2-methylpropane + 1,2-ethanedithiol; +, *n*-butane + 1,2-ethanedithiol. Mole fraction on the *x*-axis is either 2-methylpropane or *n*-butane.

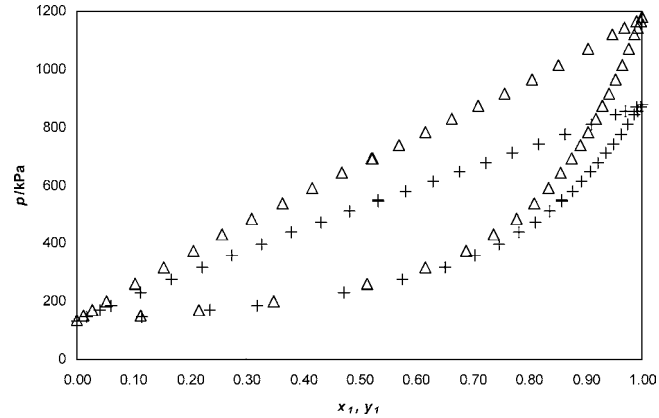

Figure 2. Pressure−composition diagram for Δ, 2-methylpropane + 2-methyl-2-propanethiol; +, *n*-butane + 2-methyl-2-propanethiol. Mole fraction on the *x*-axis is either 2-methylpropane or *n*-butane.

The uncertainty of the injected volumes was ± 0.02 cm^3 which was obtained from calibration with distilled water. The densities of the components were calculated from the Hankinson−Brobst−Thompson[20] density correlation. The uncertainties for 2-methylpropane and *n*-butane were less than 1 % and for 1,2-ethanedithiol and 2-methyl-2-propanethiol less than 5 %. The theoretical maximum error for the overall molar composition was calculated by the method presented by Hynynen et al.[21] The uncertainties for x_i, y_i, p_{leg}, and γ_i depended on the uncertainties of the measured values, and their values were from full 2^4 factorial analysis implemented in the VLEFIT software.

Results and Discussion

Results from VLE measurements, the Legendre polynomial fit, and the Barker data reduction with estimated maximum errors are presented in Tables 4 to 7. The experimental pressure as a function of vapor and liquid composition is shown in Figures 1 and 2. Total pressure data were also fitted using the Wilson, NRTL, and UNIQUAC activity coefficient models, and their results can be seen in Table 8. Table 8 shows that in cases of Wilson and UNIQUAC activity coefficient models the average pressure residual is slightly higher for the binary pairs

Table 8. Liquid Activity Coefficient Model Parameters for Legendre, Wilson, NRTL, and UNIQUAC, Activity Coefficient in Infinite Dilution γ^∞, Average Pressure Residual Δp and Absolute Average Pressure Residual $|\Delta p|$[a]

component 1 component 2	2-methylpropane 1,2-ethanedithiol	2-methylpropane 2-methyl-2-propanethiol	*n*-butane 1,2-ethanedithiol	*n*-butane 2-methyl-2-propanethiol
Legendre, $\alpha_{1,0}$	2.16421	0.38438	2.01739	0.32152
Legendre, $\alpha_{2,0}$	0.01588	0.01274	−0.00442	0.02169
Legendre, $\alpha_{3,0}$	0.14380	-	0.10735	-
γ^∞_1	9.21	1.43	7.96	1.34
γ^∞_2	9.55	1.49	7.95	1.41
Δp/kPa	0.0	0.2	0.0	0.1
$\lvert\Delta p\rvert$/kPa	1.0	0.5	0.3	0.4
Wilson, $\lambda_{1,2}$/K	447.05	92.43	426.73	92.03
Wilson, $\lambda_{2,1}$/K	635.23	45.84	551.76	22.53
Wilson volume ratio	1.25	0.93	1.20	0.89
Δp/kPa	14.5	0.3	7.2	1.1
$\lvert\Delta p\rvert$/kPa	21.0	0.6	11.3	1.6
γ^∞_1	10.10	1.43	8.76	1.37
γ^∞_2	10.87	1.49	8.68	1.38
NRTL, $\lambda_{1,2}$/K	512.87	116.61	455.80	127.35
NRTL, $\lambda_{2,1}$/K	491.56	23.05	453.52	−7.64
NRTL ($\alpha_{1,2} = \alpha_{2,1}$)	0.4	0.4	0.4	0.4
Δp/kPa	1.4	0.3	1.0	0.1
$\lvert\Delta p\rvert$/kPa	3.3	0.6	1.8	0.4
γ^∞_1	9.35	1.43	8.04	1.34
γ^∞_2	9.80	1.49	8.07	1.41
UNIQUAC, $\lambda_{1,2}$/K	128.95	−7.84	115.65	4.99
UNIQUAC, $\lambda_{2,1}$/K	160.92	55.48	152.92	34.34
Δp/kPa	−3.0	0.3	−1.5	0.1
$\lvert\Delta p\rvert$/kPa	11.8	0.6	6.2	0.4
γ^∞_1	8.54	1.43	7.46	1.34
γ^∞_2	8.61	1.49	7.38	1.41
UNIFAC, γ^∞_1	3.02	-	3.03	-
UNIFAC, γ^∞_2	4.13	-	4.14	-
Δp/kPa	157.22	-	92.39	-
$\lvert\Delta p\rvert$/kPa	157.22	-	92.39	-
Cosmo-SAC, γ^∞_1	2.90	1.28	3.10	1.33
Cosmo-SAC, γ^∞_2	3.98	1.38	4.25	1.45

[a] Wilson volume ratio is defined as v_1/v_2.

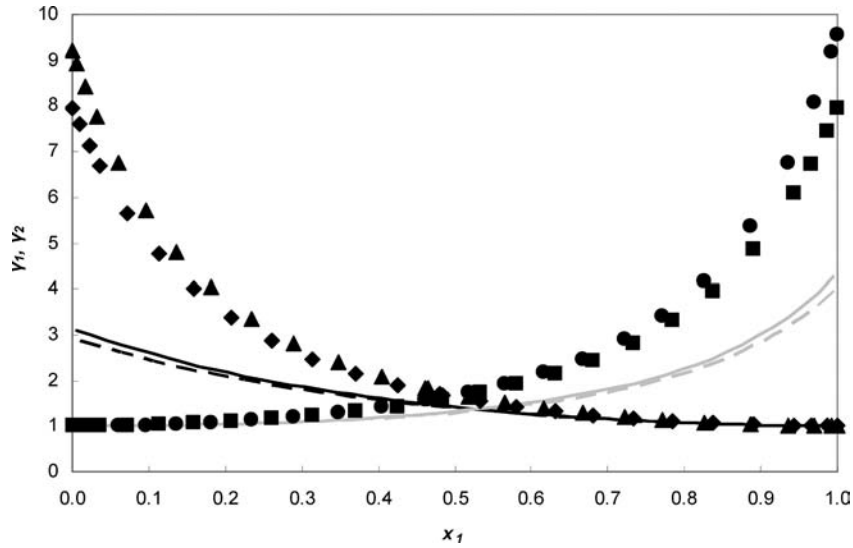

Figure 3. Liquid activity coefficient−composition diagram for the Legendre activity coefficient model of ▲, 2-methylpropane; ●, + 1,2-ethanedithiol; ◆, *n*-butane; ■, + 1,2-ethanedithiol; and for predictive Cosmo-SAC activity coefficient model of - - -, 2-methylpropane; gray dashed line, + 1,2-ethanedithiol; —, *n*-butane; gray solid line, + 1,2-ethanedithiol. Mole fraction on the *x*-axis is either 2-methylpropane or *n*-butane.

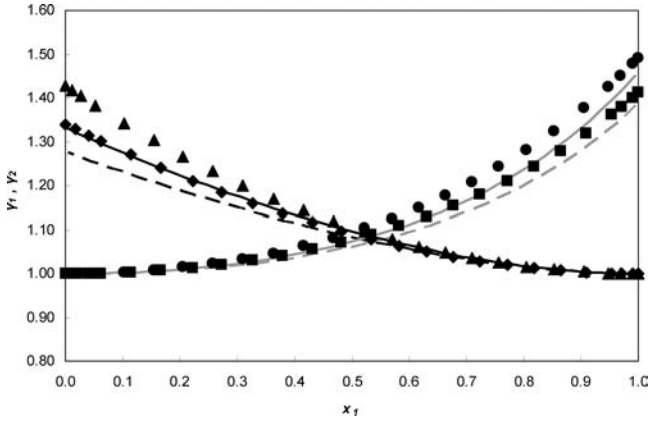

Figure 4. Liquid activity coefficient−composition diagram for the Legendre activity coefficient model correlation of ▲, 2-methylpropane; ●, + 2-methyl-2-propanethiol; ◆, *n*-butane; ■, + 2-methyl-2-propanethiol and for predictive Cosmo-SAC activity coefficient model of - - -, 2-methylpropane; gray dashed line, + 2-methyl-2-propanethiol; —, *n*-butane; gray solid line, + 2-methyl-2-propanethiol. Mole fraction on the *x*-axis is either 2-methylpropane or *n*-butane.

of 2-methylpropane + 1,2-ethanedithiol and *n*-butane + 1,2-ethanedithiol than for two other binary pairs. It can also be seen that the activity coefficients in infinite dilution are almost equal. No azeotropic behavior was found, and all four binary pairs showed positive deviation from Raoult's law.

Activity coefficients were also calculated using the predictive UNIFAC and Cosmo-SAC[22] models, and their results are reported in Table 8. In Figures 3 and 4, the Legendre polynomial and Cosmo-SAC activity coefficients are compared as a function of liquid composition. The figures show that the predictive Cosmo-SAC model gives lower activity coefficient values compared to the Legendre polynomial. The difference between activity coefficients is bigger with the binary systems where 1,2-ethanedithiol is involved. In the *n*-butane + 2-methyl-2-propanethiol system, the activity coefficient prediction of the Cosmo-SAC model agrees well with the Legendre polynomial regression. The UNIFAC model can be compared with the Cosmo-SAC model only for the systems 2-methylpropane + 1,2-ethanedithiol and *n*-butane + 1,2-ethanedithiol because part of the UNIFAC model subgroups for 2-methyl-2-propanethiol were not available. According to Table 8, the values of infinite dilution activity coefficients of the UNIFAC and Cosmo-SAC models are the same order of magnitude, and they differ greatly from Legendre infinite dilution activity coefficients.

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