J. Chem. Eng. Data **2007,** *52,* 230−234

Vapor−Liquid Equilibria and H^E for Binary Systems of Dimethyl Ether (DME) with C_1−C_4 Alkan-1-ols at 323.15 K and Liquid−Liquid Equilibria for Ternary System of DME + Methanol + Water at 313.15 K

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Isothermal vapor−liquid equilibria (VLE) and excess molar enthalpies (H^E) at 323.15 K were measured for the binary mixtures of dimethyl ether (DME) with C_1 to C_4 alkan-1-ols. The measured VLE and H^E data were correlated well with G^E model equations and Redlich−Kister polynomial, respectively. Additionally liquid−liquid equilibrium (LLE) for the ternary system of DME + methanol + water was determined at 313.15 K. The measured LLE data were compared with the correlated values by using NRTL and UNIQUAC models, and they showed good agreements.

Introduction

Dimethyl ether (DME), also known as methoxy methane, is a colorless gaseous ether that has been used mainly as a refrigerant, solvent, and propellant for aerosol sprays. It also has the potential to be a major raw material in the chemical industry. Recently, DME has been considered as an attractive alternative GTL (gas to liquid product) fuel for compression ignition (diesel) engines because it has a high cetane number of 60, a low boiling point of −25 °C, and a high oxygen mass fraction of 35 %. However, since DME is a gas at ambient temperature and pressure, it easily becomes liquid under modest pressure since it has a vapor pressure of only 5 bar at 20 °C. In addition, it has some advantages as a fuel because it is environmentally benign, being virtually nontoxic, and is easily degraded in the troposphere and thus not harmful to the ozone layer. Furthermore, it gives the smallest amount of NO_x, CO, HC, and PM as an exhausted gas as compared to fossil fuels. Studies of DME are therefore of some significance.[1]

DME is usually made by the dehydration of methanol or directly from syn-gas. It also can be made from coal and biomass.[1] Thus the phase equilibria and physical properties of DME with methanol or with some higher alcohols and hydrocarbons are necessary for the DME manufacturing process. However, the published phase equilibrium data and pure or mixture properties of DME-contained systems are so far not enough.[2]

In this work, the isothermal vapor−liquid phase equilibria (VLE) and the excess enthalpies (H^E) for binary systems of DME + methanol, + ethanol, + 1-propanol, and + 1-butanol at 323.15 K have been investigated. A computer-driven static apparatus was used for the isothermal VLE measurements ($P-x$ data). While H^E at 323.15 K was measured using an isothermal flow calorimeter (model 7501, Hart Scientific). In addition, ternary LLE of the system DME + methanol + water at 313.15 K has been determined using a high-pressure static apparatus. The measured data were correlated well with common G^E model equations or the Redlich−Kister polynomial.

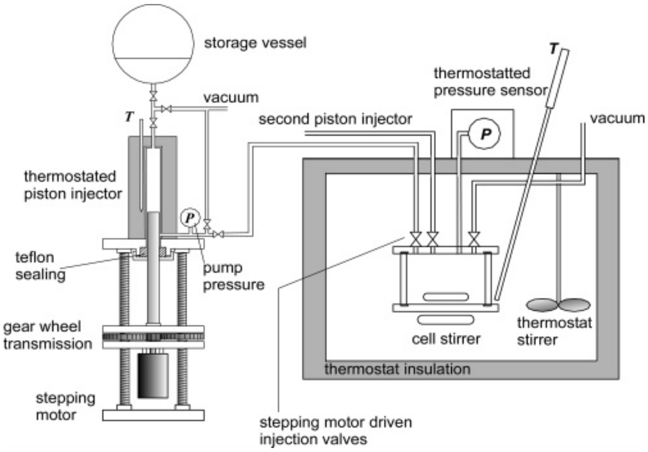

Figure 1. Computer-driven differential static apparatus for VLE measurement.

Experimental Section

Materials. DME was supplied by Sigma-Aldrich Co Ltd. The mass fraction purity specified by the manufacturer was greater than $w = 99.5$ %. The alkan-1-ols were supplied by Fischer. The purities of methanol and ethanol were better than $w = 99.8$ %, while the other alkan-1-ols were better than $w = 99.5$ %. Doubly distilled deionized water was used for the measurement. The C_2 to C_4 alkan-1-ols were dried over activated molecular sieves with a pore diameter of 0.4 nm, and for methanol, a molecular sieve type of 0.3 nm was used. The water mass fractions of chemicals by Karl Fischer titration (Metrohm 684 KF coulometer) were less than 7×10^{-5}.

Apparatus and Procedure. A computer-driven static apparatus was used for the isothermal VLE measurements ($P-x$ data). Figure 1 shows this apparatus. The evacuated VLE cell kept at constant temperature in a thermostatic oil bath was charged with purified and degassed sample compounds by using stepping motor-driven injection pumps and automatic valves.

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10.1021/je0603574 CCC: $37.00

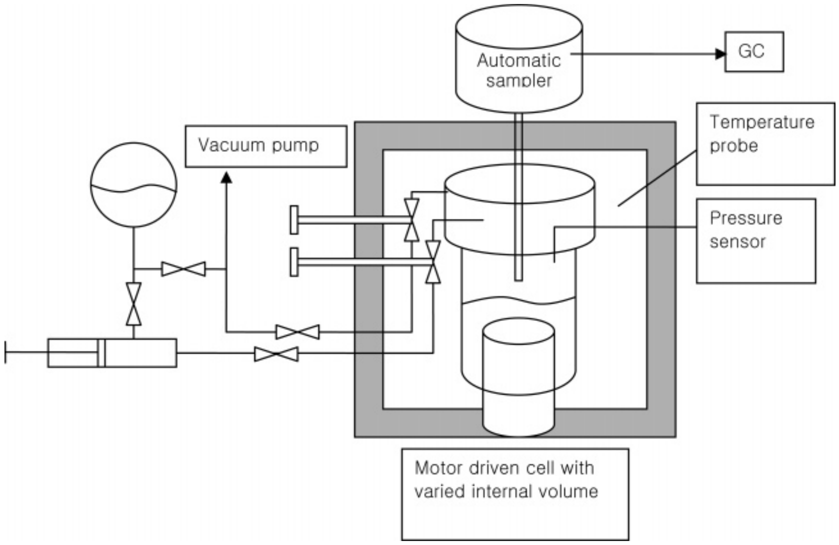

Figure 2. Schematic diagram of the static apparatus for the LLE measurement.

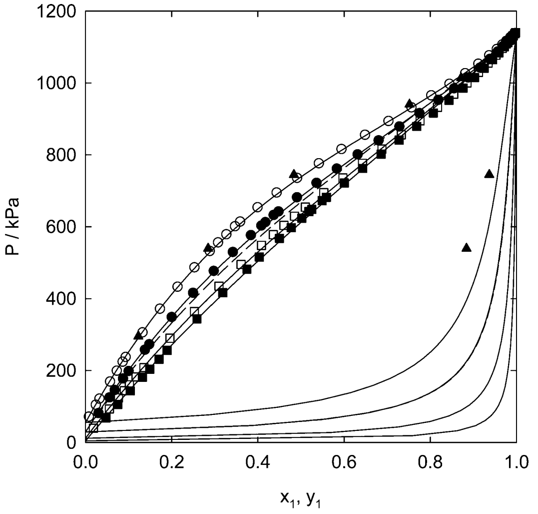

Figure 3. Isothermal VLE data for the binary systems of DME (1) + alkan-1-ol (C_1 to C_4) (2) at 323.15 K: ●, DME + methanol; ▲, DME + methanol from ref 9; ○, DME + ethanol; − −, DME + ethanol calculated by UNIQUAC binary parameters from ref 10; ■, DME + 1-propanol; □, DME + 1-butanol. Solid curves were calculated from Margules equation.

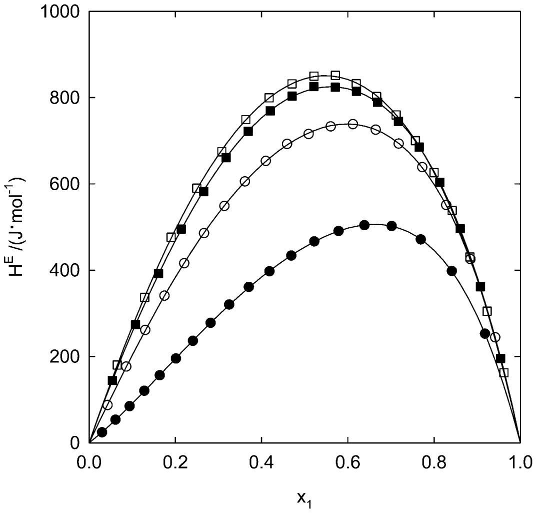

Figure 4. H^E for the binary systems of DME (1) + alkan-1-ol (C_1 to C_4) (2) at 323.15 K: ●, DME + methanol; ○, DME + ethanol; ■, DME + 1-propanol; □, DME + 1-butanol. Solid curves were calculated from Redlich−Kister polynomial.

It has been described in detail elsewhere.[3,4] The pressure in the equilibrium cell was measured using a Digiquartz pressure sensor (model 245A, Paroscientific). The temperature was measured with a Pt-100 resistance thermometer (model 1506, Hart Scientific).

The overall compositions were determined from the known volumes of liquids injected into the equilibrium cell. Then true liquid-phase compositions were obtained by solving mass and volume balance equations taking into account the VLE ($P-x$) behavior. The experimental uncertainties (σ) of this device are as follows: $\sigma(T) = 0.03$ K, $\sigma(P) = 20$ Pa $+ 0.0001$ (P/Pa), and $\sigma(x_i) = 0.0001$.

A commercial isothermal flow calorimeter (model 7501, Hart Scientific) was used for the measurement of excess enthalpy. This apparatus has already been described in detail.[5] The calorimeter consisted of two solvent pumps (ISCO, LC 2600, 260 cm^3), a temperature-regulated flow cell equipped with a pulsed heater, a Peltier cooler, and a back-pressure regulator to prevent evaporation. The Peltier cooler operated at constant power, producing constant heat loss from the calorimeter cell. The temperature of the cell was kept constant by adjusting the frequency of the pulsed heater to compensate for the cooling from the Peltier and the heat of mixing effect. The uncertainty of the experimental values was estimated to be less than ± 1 % of the H^E values measured.

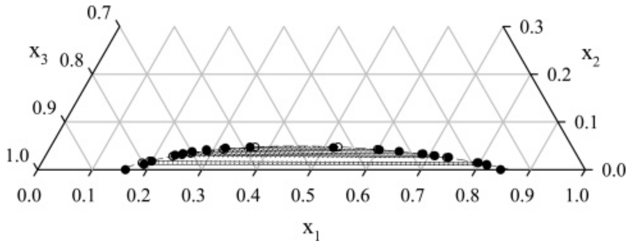

Figure 5. LLE for ternary system of DME (1) + methanol (2) + water (3) at 313.15 K: ●, experimental data point; ○, calculated data; −, experimental tie-line; ···, calculated tie-line; - - -, calculated binodal curve.

For the determination of LLE for the ternary system, an apparatus using the static measurement principle was used. The equilibrium cell was placed in an air bath and equipped with micro-sampling devices at the top of the cell. This sampler allowed taking very small sample amounts from (0.1 to 1) μL from the equilibrated liquid phases. The sampling procedure

Table 1. Isothermal Vapor−Liquid Equilibria for the DME + Alkan-1-ol (C_1 to C_4) (2) Systems at 323.15 K

P/kPa	x_1	P/kPa	x_1	P/kPa	x_1
DME + Methanol					
55.30	0.0000	556.4	0.3074	997.4	0.8443
71.99	0.0077	578.9	0.3267	1027.1	0.8810
104.9	0.0237	601.5	0.3468	1053.6	
122.0	0.0323		0.3589	1076.8	0.9367
169.7	0.0567	614.2	0.3992	1094.0	0.9542
199.9	0.0725	695	0.4434	1106.8	0.9670
224.9	0.0859	736	0.4909	1116.7	0.9763
237.9	0.0930	776.4	0.5413	1127.0	
306.3	0.1321	816.2	0.5940	1132.3	0.9904
371.9	0.1727	855	0.6486	1137.7	0.9952
433.2	0.2135	894	0.7029	1143.0	1.0000
487.3	0.2526	931.9	0.7563		
532.8	0.2881	965.4	0.8023		
DME + Ethanol					
29.37	0.0000	603	0.4078	1015.2	0.8879
81.99	0.0300	612.8	0.4174	1042.7	0.9156
125.4	0.0556	632.5	0.4364	1066.7	0.9382
145.8	0.0676	642.5	0.4479	1087.3	0.9564
177.9	0.0871	682	0.4905	1102.2	0.9689
198.8	0.1000	722	0.5359	1113.5	0.9779
258.0	0.1379	762.0	0.5830	1121.6	0.9842
273.3	0.1480	801.4	0.6313	1130.0	0.9906
348.7	0.1999	840.3	0.6800	1134.2	0.9938
416.2	0.2496	878.9	0.7284	1138.6	0.9969
477.3	0.2976	916.2	0.7748	1142.9	1.0000
529.9	0.3418	952.9	0.8188		
576.9	0.3837	985.0	0.8554		
DME + 1-Propanol					
12.32	0.0000	577.8	0.4357	1029.5	0.9120
39.85	0.0183	604.1	0.4605	1055.4	0.9344
93.57	0.0553	629	0.4851	1077.4	0.9524
124.3	0.0766	654.5	0.5101	1095.8	0.9668
144.0	0.0904	694.7	0.5529	1108.8	0.9764
160.6	0.1018	735	0.5974	1118.2	0.9832
182.5	0.1173	776.1	0.6427	1124.3	0.9874
208.4	0.1356	816.2	0.6880	1130.4	0.9915
290.2	0.1959	855.8	0.7327	1136.7	0.9958
364.0	0.2526	894.8	0.7760	1139.9	0.9979
434.7	0.3097	932	0.8167	1143.2	1.0000
495.0	0.3610	968.9	0.8544		
548.1	0.4082	1000.3	0.8852		
DME + 1-Butanol					
4.61	0.0000	597.7	0.4775	985.9	0.8761
68.28	0.0472	624.0	0.5021	1014.9	0.9026
105.8	0.0751	642.1	0.5182	1041.2	0.9255
143.8	0.1035	648.3	0.5251	1064.5	0.9445
181.7	0.1323	673.0	0.5489	1084.0	0.9596
204.0	0.1490	682.0	0.5590	1100.2	0.9716
231.9	0.1707	722.1	0.6006	1111.7	0.9797
256.1	0.1892	762.3	0.6433	1119.9	0.9853
344.0	0.2588	802.0	0.6859	1125.3	0.9890
416.8	0.3186	841.1	0.7279	1130.9	0.9926
482.4	0.3744	879.2	0.7685	1136.7	0.9963
515.8	0.4036	916.4	0.8074	1139.8	0.9982
567.9	0.4501	951.8	0.8433	1143.2	1.0000

was controlled via pressurized air, magnetic valves and either a timer-unit or by computerized control. The samples were injected and vaporized directly in the carrier gas stream of a gas chromatograph equipped with a TCD. The sample stream was superheated to avoid condensation of high boiling components. To calculate the compositions, the chromatograph was calibrated directly with known amounts of gaseous or liquid substance. The chromatographic signals, system pressure and temperature were recorded with an IBM PC. Pressure measurement was performed by means of an oil filled pressure transmitter (temperature and pressure dependent calibration). The experimental uncertainties of temperature, pressure, and mole composition are the same with those of VLE measurement. Figure 2 shows a scheme of this apparatus.

Table 2. Correlated Parameters for the Isothermal Vapor−Liquid Equilibria of DME (1) + Alkan-1-ol (C_1 to C_4) (2) at 323.15 K

model eq	A_{12}	A_{21}	α_{12}	ΔP^{b}/kPa
DME (1) + Methanol (2)				
Margules	0.6690	0.8687		19.7
Van Laar	0.6878	0.8765		24.3
Wilson[a]	−921.1478	3358.9457		28.6
NRTL[a]	2286.1978	74.6175	0.3005	24.3
UNIQUAC[a]	2303.2309	−509.7254		25.6
DME (1) + Ethanol (2)				
Margules	0.5063	0.6420		41.4
Van Laar	0.5239	0.6429		44.6
Wilson[a]	−142.1585	1897.9787		46.3
NRTL[a]	1804.7973	−73.4698	0.3011	44.3
UNIQUAC[a]	947.9082	−69.6874		45.1
DME (1) + 1-Propanol (2)				
Margules	0.3388	0.3958		54.4
Van Laar	0.3489	0.3932		56.0
Wilson[a]	429.5755	636.5596		56.3
NRTL[a]	1089.9090	−31.1541	0.3019	55.8
UNIQUAC[a]	−107.7982	640.2683		56.1
DME (1) + 1-Butanol (2)				
Margules	0.2363	0.2818		57.9
Van Laar	0.2468	0.2796		59.4
Wilson[a]	804.8589	−52.3837		59.5
NRTL[a]	990.0009	−230.9685	0.2932	59.1
UNIQUAC[a]	−481.3504	1003.7554		59.6

[a] The units of parameters are $J\cdot mol^{-1}$. [b] $\Delta P = \sum(P_{\text{exp}} - P_{\text{calcd}})/N$, where N is the number of data points.

Table 3. Excess Molar Enthalpies for the Binary Systems of DME (1) + Alkan-1-ol (C_1 to C_4) (2) at 323.15 K

x_1	$H^{E}/(J\cdot mol^{-1})$	x_1	$H^{E}/(J\cdot mol^{-1})$	x_1	$H^{E}/(J\cdot mol^{-1})$
DME (1) + Methanol (2)					
0.0300	24.4	0.2818	278	0.6384	504
0.0614	53.4	0.3250	320	0.7018	502
0.0941	84.8	0.3704	361	0.7693	471
0.1282	121	0.4183	397	0.8412	398
0.1640	157	0.4688	434	0.9179	253
0.2014	195	0.5222	467		
0.2406	236	0.5786	491		
DME (1) + Ethanol (2)					
0.0428	87.4	0.3614	606	0.7180	693
0.0862	177	0.4098	653	0.7725	639
0.1303	261	0.4591	693	0.8279	551
0.1750	341	0.5092	716	0.8842	426
0.2205	416	0.5601	733	0.9416	244
0.2667	486	0.6118	739		
0.3137	549	0.6645	725		
DME (1) + 1-Propanol (2)					
0.0541	144	0.4203	769	0.7654	685
0.1078	274	0.4708	804	0.8131	604
0.1610	392	0.5210	826	0.8604	496
0.2138	495	0.5707	824	0.9073	362
0.2661	583	0.6200	815	0.9538	195
0.3179	661	0.6688	789		
0.3693	722	0.7173	745		
DME (1) + 1-Butanol (2)					
0.0655	182	0.4705	832	0.7999	626
0.1290	337	0.5216	850	0.8420	538
0.1904	476	0.5713	852	0.8831	431
0.2499	590	0.6196	832	0.9230	305
0.3076	675	0.6666	802	0.9620	162
0.3635	749	0.7122	760		
0.4178	800	0.7567	700		

Results and Discussion

The measured isothermal VLE data ($P-x$) for four binary systems of DME + methanol, + ethanol, + 1-propanol and + 1-butanol at 323.15 K are listed in Table 1 and plotted in Figure

Table 4. Fitted Parameters[a] and Standard Mean Deviation[a] of the Redlich−Kister Polynomial and Partial Excess Molar Enthalpy at Infinite Dilution[a] for the Binary H^E of DME + Alkan-1-ol (C_1 to C_4) at 323.15 K

mixture	A_1	A_2	A_3	A_4	A_5	A_6	σ_{st}	$\bar{H}_1^{E,\infty}$	$\bar{H}_2^{E,\infty}$
DME + methanol	1814.5	1163.8	550.1	427.6	−74.5	−68.0	0.9	766.7	3813.5
DME + ethanol	2855.9	976.5	593.1	403.4			1.4	2069.1	4828.9
DME + 1-propanol	3259.3	678.9	481.1	569.1	−31.6	−377.9	1.8	2838.7	4578.9
DME + 1-butanol	3375.2	587.1	349.5	284.9			1.9	2852.7	4596.7

[a] The unit is J·mol^{-1}.

Table 5. LLE for the Ternary System of DME (1) + Methanol (2) + Water (3) at 313.15 K

organic phase				aqueous phase			
x_1	x_2	x_1	x_2	x_1	x_2	x_1	x_2
0.8453	0.0000	0.6904	0.0318	0.1606	0.0000	0.2501	0.0354
0.8157	0.0092	0.6874	0.033	0.1866	0.0113	0.2636	0.0374
0.7977	0.0142	0.6411	0.0379	0.1986	0.0178	0.2878	0.0415
0.7375	0.0258	0.6032	0.0414	0.2361	0.0302	0.3205	0.0452
0.7110	0.0289	0.5171	0.0459	0.2488	0.0334	0.3639	0.0467

Table 6. Fitted Binary Parameters of NRTL and UNIQUAC Model for LLE of DME (1) + Methanol (2) + Water (3) Ternary System

system	A_{ij}/K	A_{ji}/K	rmsd
	NRTL ($\alpha_{ij} = \alpha_{ji} = 0.2$)		
(1) + (2)	−1139.00	−644.03	0.0056
(2) + (3)	−950.26	−155.49	
(1) + (3)	477.54	419.36	
	UNIQUAC		
(1) + (2)	−243.31	−282.94	0.0037
(2) + (3)	−458.64	−109.36	
(1) + (3)	485.24	45.93	

3. The liquid phases of DME with alkan-1-ols systems show small positive deviations from Raoult's law. The experimental data were correlated with five common G^E model equationsand showed good agreements with calculated values. The objective function used to calculate the pressure is

$$\mathrm{OF} = \sum\left(1 - \frac{P_{\mathrm{calcd}}}{P_{\mathrm{exp}}}\right)^2 \le \epsilon \tag{1}$$

Table 2 shows these correlation results. The solid lines in Figure 3 were the calculated values by the best-fitted G^E model in each binary system. The measured VLE of DME + methanol were compared with literature data.[9] For the DME + ethanol system, VLE data were calculated from published UNIQUAC parameters[10] and compared with the experimental data. They were plotted in Figure 2 along with the experimental results.

The mixing process for the same binary systems at 323.15 K show endothermic behavior since they have the positive excess molar enthalpies as shown in Figure 4. Table 3 shows the measured H^E data. The H^E values in the measured systems have an upward tendency, which are increased as the carbon number of alkan-1-ols increased. The measured H^E data were correlated with eq 2, the Redlich−Kister polynomial:[6]

$$H_{12}^E/\mathrm{J{\cdot}mol^{-1}} = x_1 x_2 \sum_{i=1}^{n} A_i (x_1 - x_2)^{i-1} \tag{2}$$

where A_i is the adjustable parameter and n is the number of fitted parameters. The Redlich−Kister equation provided excellent correlation results for the measured H^E of all the binary mixtures. Their mean deviations of the correlated H^E values from the experimental data are less than 0.1 %. Table 4 shows fitted parameters and standard mean deviation using the Redlich−Kister polynomial and partial excess molar enthalpy at infinite dilution, which can be calculated with fitted parameters of eq 2 using eq 3. Calculated H^E values are shown as solid lines in Figure 4:

$$\bar{H}_1^{E,\infty}/\mathrm{J{\cdot}mol^{-1}} = A_1 - A_2 + A_3 - A_4 + A_5 - A_6$$

$$\bar{H}_2^{E,\infty}/\mathrm{J{\cdot}mol^{-1}} = A_1 + A_2 + A_3 + A_4 + A_5 + A_6 \tag{3}$$

The LLE at 313.15 K for the ternary mixture of DME + methanol + water were determined. They are listed in Table 5 and plotted in Figure 5. A very small immiscible region was found for this system as shown in Figure 5. The methanol distributes almost the same amount in the DME and the water phase. The experimental LLE data were also correlated with the NRTL[7] and UNIQUAC[8] G^E models. For each ternary mixture, six effective binary interaction parameters are required for G^E model correlation. The binary interaction parameters were determined by adjusting to minimize the differences between the experimental and calculated mole fractions for each of the components over all the tie lines. The objective function (OF) is

$$\mathrm{OF} = \sum_{k=1}^{n} \sum_{j=1}^{2} \sum_{i=1}^{3} [x_{ijk} - x_{ijk}^{\mathrm{cal}}]^2 \tag{4}$$

where n is the number of tie lines; x is the mole fraction; superscript cal means calculated value; and subscripts i, j, and k denote component, phase, and tie line, respectively.

The parameters determined are given in Table 6 together with the rmsd of these correlations:

$$\mathrm{rmsd} = \left(\sum_{k=1}^{n} \sum_{j=1}^{2} \sum_{i=1}^{3} \frac{(x_{ijk} - x_{ijk}^{\mathrm{cal}})^2}{6n}\right)^{1/2} \tag{5}$$

Table 6 shows the correlation parameters and rmsd between measured and calculated values. As shown in the table, the UNIQUAC equation provided a little more precise calculation result.

Conclusions

The isothermal VLE ($P-x$) and H^E at 323.15 K for the binary mixtures of DME with (C_1 to C_4) alkan-1-ols were determined by using a static VLE apparatus and an isothermal flow calorimeter, respectively. The liquid phase of equilibrium data showed positive deviations from the Raoult's law, and there is no azeotrope for all the mixtures. From H^E measurements, positive values of excess enthalpy were obtained for all the systems. The VLE data were correlated well with common G^E model equations, while the Redlich−Kister equation was used for the correlation of H^E values. The ternary LLE for the DME + methanol + water system showed a small region of immiscibility. The measured LLE were also correlated well with

NRTL and UNIQUAC models. The rmsd were less than 0.6 % between experimental and calculated values.

Acknowledgment

The authors are grateful to Mr. R. Bölts in the University of Oldenburg for his technical support.

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Received for review August 10, 2006. Accepted October 5, 2006. The authors are grateful to the KEMCO (Korea Energy Management Corporation) for financial support (Grant 2003-E-ID03-P-03-0-000).

JE0603574