VAPOR-LIQUID EQUILIBRIA AND EXCESS MOLAR PROPERTIES OF MTBE+METHANOL AND +ETHANOL MIXTURES

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Abstract—The isothermal vapor-liquid equilibrium (VLE) data, the excess molar enthalpy (h^E) and the excess molar volume (V^E) of binary liquid mixtures of methyl tert-buthyl ether (MTBE) with methanol and ethanol were reported. The VLE data were measured at 313.15 K using head space gas chromatography and h^E data were measured at 363.15 K by means of an isothermal flow calorimeter. The V^E data were also determined at 298.15 K with the densities which were measured by a vibrating tube densitometer. The experimental data were correlated with some g^E models or empirical polynomial.

Key words: *Vapor-liquid Equilibria, Excess Molar Volume, Excess Molar Enthalpy, MTBE, Octane Booster*

INTRODUCTION

Methyl tert-buthyl ether (MTBE) is a non-toxic and non-polluting oxygenated petrochemical compound, produced by the catalytic reaction of isobutylene and methanol and used as an octane booster for lead free or low-leaded gasolines. MTBE is also increasingly valued as a solvent and a chemical reactive [1, 2]. Fluid phase equilibria and thermodynamic excess properties of the mixtures containing MTBE are necessary to optimize the use of MTBE as a blending agent. However, there is a paucity of phase equilibrium and thermodynamic property data for MTBE mixtures.

This work is a part of the thermophysical study of the MTBE systems with methanol and ethanol. The isothermal vapor-liquid equilibrium (VLE) data at 313.15 K were measured directly by the head space gas chromatographic method, and the excess molar enthalpy (h^E) at 363.15 K under pressurized conditions was determined by means of an isothermal flow calorimeter. Measured densities using a digital vibrating tube densitometer were used to determine the excess molar volume (V^E) at 298.15 K under atmospheric pressure. The experimental VLE data was correlated with the g^E models of Margules [3], van Laar [4], Wilson [5], NRTL [6], UNIQUAC [7]. The excess properties (h^E, V^E) were also correlated by means of the Redlich-Kister polynomial [8].

EXPERIMENTAL

1. Materials

Commercial grade MTBE and alcohols from Aldrich and Merck were used. They were carefully dried with Union Carbide type 3 Å molecular sieves (from Fluka) and then distilled and degassed using a ca. 20 theoretical staged fractionating column. Their purities were more than 99.9 wt % by gas chromatographic analysis. The observed densities (ρ) of pure components at 298.15 K are given in Table 1, along with the published values [9-10] for com-

Table 1. Experimental densities (ρ) of pure components with literature data

Chemicals	Supplier	Densities(ρ) at 298.15 K	
		This work	Lit. value
MTBE	Aldrich	0.73533	0.73530[a]
Methanol	Merck	0.78645	0.78637[b]
Ethanol	Merck	0.78503	0.78500[b]

[a]: Reference 9. [b]: Reference 10.

parison.

2. Phase Equilibria Measurement

Precise determination of phase equilibrium data is still important to the thermodynamist and engineers in spite of an abundance of phase equlibrium data. The recently developed modified head space gas chromatographic method [11] is one of the rapid and precise determination method of VLE data. The VLE data of MTBE-alcohol systems at 313.15 K was measured by this method with the Hewlett-Packard (HP) 19395A head space sampler, which has the electropneumatic sampling system and the accurate thermostat, and the HP 5890 gas chromatography. About 3 ml of the liquid sample mixture of a known composition was added to the glass vial with an accuracy of 1×10^{-4} g by Mettler Balance. The glass vials were sealed with a teflon/rubber septum and aluminium cap and then kept in the thermostat, in which the temperature was regulated as a system temperature, 313.15 K, with the accuracy of ± 0.01°C. After the equilibrium was achieved, the vapor phase (head space) in the sample vial was then analyzed automatically by gas chromatography. Highly pure N_2 (99.9999%) was used as a carrier gas in the analysis of sample mixtures. Determination methods and operating procedures have been described previously [12].

3. Calorimetric Measurement

The excess molar enthalpies (h^E) for MTBE-alcohol mixtures were measured directly at 363.15 K under 7 bar using the Hart Scientific isothermal flow calorimeter. This flow calorimeter was equipped with syringe pumps capable of delivering accurately

small pulse-free flows. It also has several advantages over batch calorimeters with which most currently available h^E data have been measured. This flow calorimeter works by monitoring the power required by the control heater to keep the flow cell under isothermal conditions. The calorimeter has been checked against the ethanol-water system at the temperature of 298.15 K. The results obtained were in agreement with literature values. The operating procedure is described in Ref. [13].

4. Density Measurement

The vibrating tube digital densitometer (Anton Paar DMA 602) was employed to determine the densities of the pure components and binary mixtures. The densitometer was calibrated for each measurement using doubly distilled water and dried air at atmospheric pressure. About 3.5 ml of sample mixtures were prepared by weight with precisions of $\pm 1 \times 10^{-4}$ g. In order to escape the significant experimental error due to evaporated mass, 4 ml small glass vials were used as mixture vessels. The experimental systematic error was estimated to be less than 1×10^{-4} mole fraction. All the measurements were carried out at atmospheric pressure. The temperature of the vibrating U tube was regulated by Lauda thermostat of which the temperature was calibrated against a HP resistance thermometer with an accuracy of $\pm 0.01°C$. The time interval of measurements was chosen to be 15 min to attain a constant temperature and stability in oscillation. Apparatus and operating procedure are described elsewhere [14, 15].

RESULTS AND DISCUSSION

Experimental VLE data was calculated with the simplified Eq. (1) for the VLE determination. By the modified head space gas chromatographic method, true liquid mole fraction must be recalculated along with the flow diagram of Fig. 1 and the thermodynamic relations and calculation procedure have been previously described [16, 17].

$$y_1 P = x_1 \gamma_1 P^s{}_1 \tag{1}$$

The excess molar volume of mixing V^E is defined as

Fig. 1. Flow diagram for the calculation of liquid & vapor phase mole fraction.

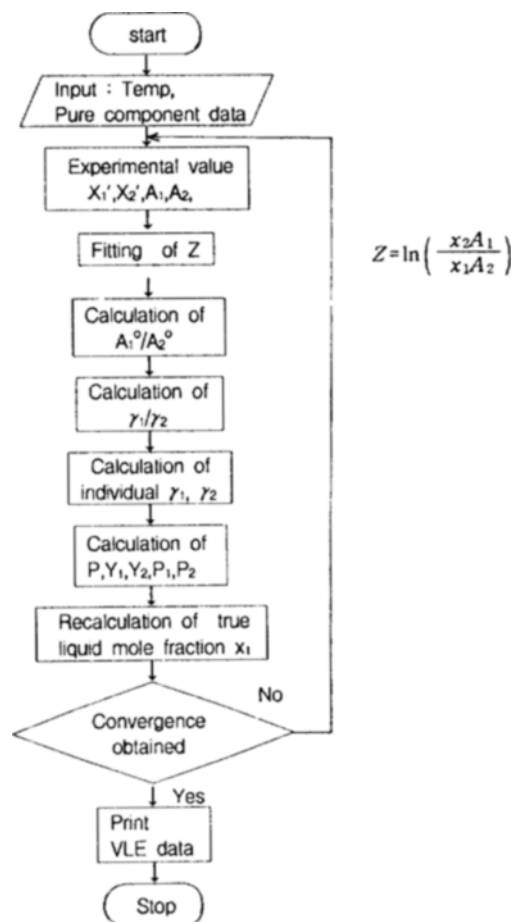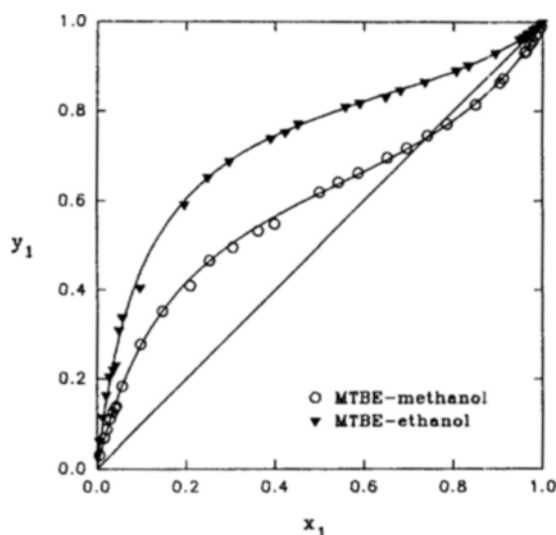$$V^E = \left(\frac{x_1 M_1 + x_2 M_2}{\rho_m} \right) - \frac{x_1 M_1}{\rho_1} - \frac{x_2 M_2}{\rho_2} \tag{2}$$

Table 2. Vapor-liquid equilibrium data of the MTBE systems with alcohols at 313.15 K

P (mmHg)	x_1	y_1	P (mmHg)	x_1	y_1	P (mmHg)	x_1	y_1	P (mmHg)	x_1	y_1
						MTBE-methanol					
289.09	.0065	.0304	380.57	.1471	.3509	471.93	.5425	.6418	470.21	.9113	.8740
297.89	.0158	.0671	400.13	.2090	.4090	475.78	.5876	.6626	460.78	.9595	.9328
302.35	.0217	.0853	419.95	.2521	.4663	480.10	.6530	.6963	460.20	.9626	.9357
308.31	.0290	.1091	430.19	.3054	.4955	481.71	.6963	.7179	457.29	.9712	.9498
312.12	.0345	.1240	441.89	.3620	.5324	482.56	.7424	.7460	455.47	.9773	.9586
314.73	.0404	.1342	446.34	.3987	.5483	482.18	.7860	.7716	452.52	.9845	.9717
315.57	.0433	.1375	465.27	.4533	.6132	478.95	.8495	.8144	449.86	.9949	.9906
327.40	.0557	.1826	467.16	.5008	.6193	471.89	.9034	.8635	449.92	.9953	.9903
356.31	.0978	.2768									
						MTBE-ethanol					
134.47	.0065	.0604	245.31	.1479	.5554	384.20	.5586	.8093	443.02	.9487	.9618
141.44	.0133	.1124	260.43	.1969	.5913	389.20	.5915	.8176	443.98	.9578	.9681
148.80	.0206	.1623	289.25	.2490	.6532	397.01	.6489	.8318	444.71	.9655	.9733
155.68	.0276	.2047	308.38	.2978	.6885	405.04	.6822	.8473	445.10	.9698	.9763
158.30	.0357	.2200	346.32	.4237	.7526	414.04	.7366	.8655	445.91	.9790	.9831
159.98	.0417	.2300	338.19	.3914	.7393	424.70	.8072	.8914	446.42	.9850	.9878
174.96	.0493	.3087	357.80	.4524	.7708	428.75	.8340	.9029	447.14	.9935	.9947
181.38	.0568	.3377	377.73	.4955	.8000	436.98	.8945	.9309	447.52	.9983	.9986
197.24	.0967	.4048									

Table 3. Fitted parameters and mean deviations of the MTBE systems with alcohols at 313.15 K

g^E model	A_{12}	A_{21}	α	Mean Dev. Δy
	MTBE-methanol			
MARGULES	0.9566	1.0172		0.0057
VAN LAAR	0.9560	1.0191		0.0056
WILSON	−375.5559	1090.1059		0.0050
NRTL	403.1583	266.4534	0.30	0.0055
UNIQUAC	784.4802	−177.8058		0.0061
	MTBE-ethanol			
MARGULES	0.8520	1.0537		0.0074
VAN LAAR	0.8579	1.0670		0.0072
WILSON	−316.4365	1024.2742		0.0069
NRTL	492.8187	288.7632	0.76	0.0068
UNIQUAC	623.1758	−201.4265		0.0075

Table 4. Excess molar enthalpies of the MTBE systems with alcohols at 363.15 K

x_1	h^E (J/mol)	x_1	h^E (J/mol)	x_1	h^E (J/mol)	x_1	h^E (J/mol)
			MTBE-methanol				
0.0364	42.47	0.1286	177.08	0.3405	509.99	0.8377	558.17
0.0368	42.69	0.1840	269.71	0.4425	639.59	0.9307	229.33
0.0784	101.86	0.2538	381.75	0.5764	741.11	0.9645	165.80
0.0792	101.78	0.2561	384.94	0.7538	694.50	0.9821	87.68
0.1272	174.41	0.3378	509.17	0.7560	696.03		
			MTBE-ethanol				
0.0521	113.02	0.3310	700.45	0.6644	956.04	0.8252	629.56
0.1101	243.70	0.4261	842.08	0.7371	889.49	0.9270	373.58
0.1750	388.50	0.5359	943.70	0.8166	746.52	0.9751	138.60
0.2481	544.15						

Fig. 2. Vapor-liquid equilibrium compositions for the systems of MTBE (1)-methanol(2) and MTBE(1)-ethanol(2) at 313.15 K.

Fig. 3. Excess molar enthalpies for the systems of MTBE(1)-methanol (2) and MTBE(1)-ethanol(2) at 363.15 K.

The Redlich-Kister polynomial function was used to correlate the experimental excess molar properties, $M^E(h^E, V^E)$.

$$M^E = x_1 x_2 \sum_{i=1}^{n} A_i (x_1 - x_2)^{i-1} \quad (3)$$

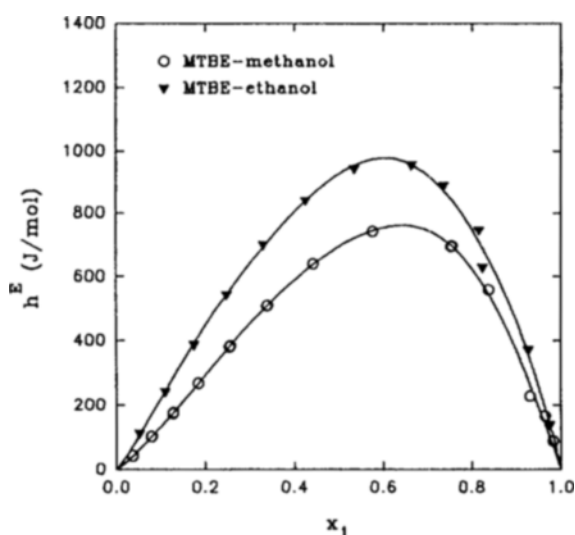Standard deviation of the fits S_d for excess molar properties [18] is defined as

$$S_d = \left[\frac{\sum_i (M^E_{calc} - M^E_{exp})_i^2}{(N-n)} \right]^{1/2} \quad (4)$$

where M^E_{calc} is the excess molar property, which is calculated by Eq. (3) and M^E_{exp} is an experimental excess property.

The experimental vapor-liquid equilibrium compositions at 313.15 K of MTBE-alcohol systems are listed in Table 2. The activity coefficients were correlated using g^E models. The definitions of the model equations and the pure component parameters are given in Ref. [19]. The evaluated model parameters A_{ij} and the mean deviations in y, Δy are given in Table 3. The mean deviation Δy means $|y_{exp} - y_{calc}|/N$ and parameter A_{ij} for the Wilson, NRTL and UNIQUAC equations are expressed as

$A_{ij} = (\lambda_{ij} - \lambda_{ii})$ in cal/mole

$A_{ij} = (g_{ij} - g_{ii})$ in cal/mole

$A_{ij} = (u_{ij} - u_{ii})$ in cal/mole

All the measured VLE data were thermodynamically consistent by the Redlich-Kister integral method. According to the data reported in Table 2, the MTBE-methanol system has a minimum boiling azeotrope, while the MTBE-ethanol system exhibit normal positive deviations from the Raoult's law.

Fig. 2 shows the vapor-liquid equilibrium compositions of each binary for easy comparison. In the Fig. 2, solid lines represent the data calculated with the best fitted model parameters.

Table 4 gives the experimental h^E data of MTBE with methanol and ethanol. This data was smoothed by the least-square method to Redlich-Kister equation. Fig. 3 shows the excess molar enthalpies of these binaries. Continuous lines represent the calculated data by means of Eq. (3).

In the Fig. 3, the mixing enthalpies of MTBE-alcohol mixtures show relatively large positive values. It is assumed that H-bonds between alcohol molecules are destroyed by increasing MTBE concentration, but the association in these binary mixtures does
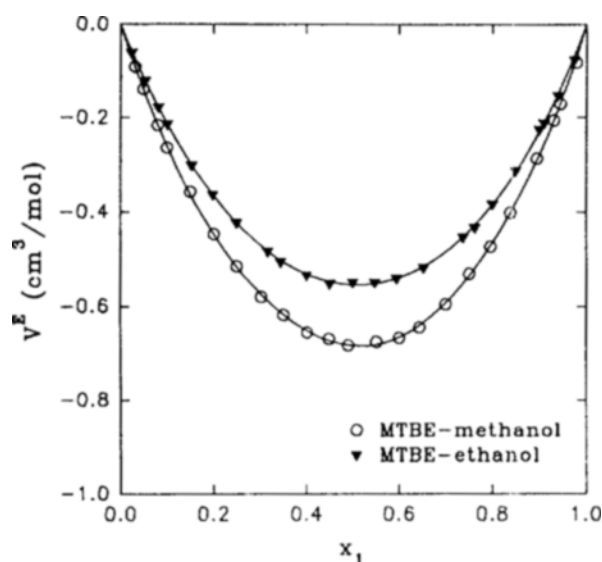
Fig. 4. Excess molar volumes for the systems of MTBE(1)-methanol (2) and MTBE(1)-ethanol(2) at 298.15 K.

not significantly increase, because more energy is required in these mixing processes. Table 5 shows the fitted parameters of the Redlich-Kister equation and the standard deviation S_d related to Eq. (4).

The volume changes of mixing of MTBE-alcohols are given in Table 6 and the values of fitted Redlich-Kister parameters A_i and standard deviation S_d are presented in Table 7. Fig. 4 shows the fitted V^E curves, together with the experimental points. In both systems V^E data appears to be negative over the entire range of concentration of MTBE and the curves are approximately symmetric with a minimum at a mole fraction of about 0.5. The negative deviations from the linear volumetric behavior is assumed to be caused by a strong hydrogen bonding or the different molecular size.

NOMENCLATURE

A_i	: peak area of chromatogram for component i in solution
A_i''	: peak area of chromatogram for pure component i
A_i	: parameter in the smoothing equation
A_{ij}	: parameter used in Margules, van Laar, Wilson, NRTL, UNIQUAC equation
g_{ij}	: interaction energy in the NRTL equation
h^E	: excess molar enthalpy
M^E	: excess molar property
M_i	: molecular weight of component i
N	: no. of experimental values
n	: no. of parameters A_i
P	: total pressure
P_i^o	: vapor pressure of pure component i
S_d	: standard deviation
u_{ij}	: interaction energy in the UNIQUAC equation
V^E	: excess molar volume
x_i	: liquid phase mole fraction of component i
x_i'	: liquid phase mole fraction of component i of injected sample mixture to glass vial
y_i	: vapor phase mole fraction of component i

Greek Letters

α	: nonrandomness parameter in the NRTL equation
γ_i	: activity coefficient of component i
ρ_i	: density of component i
ρ_m	: density of binary mixture
λ_{ij}	: interaction energy in the Wilson equation

Table 5. Fitted parameters and standard deviations (S_d) for the excess molar enthalpies of the MTBE systems with alcohols at 363.15 K

Systems	A_1	A_2	A_3	A_4	A_5	A_6	S_d (J/mol)
MTBE-methanol	2784.8	1681.5	328.16	142.36	−59.867	210.23	1.65
MTBE-ethanol	3675.3	1594.1	550.51	660.39	−261.21	−425.50	1.60

Table 6. Excess molar volumes of the MTBE systems with alcohols at 298.15 K

x_1	V^E (cm³/mol)	x_1	V^E (cm³/mol)	x_1	V^E (cm³/mol)	x_1	V^E (cm³/mol)
			MTBE-methanol				
0.0313	−0.0910	0.2503	−0.5144	0.5511	−0.6749	0.8393	−0.4013
0.0491	−0.1389	0.3020	−0.5787	0.5999	−0.6659	0.8958	−0.2868
0.0803	−0.2150	0.3503	−0.6177	0.6438	−0.6441	0.9315	−0.2054
0.1005	−0.2635	0.4014	−0.6545	0.6994	−0.5954	0.9448	−0.1709
0.1501	−0.3565	0.4491	−0.6683	0.7503	−0.5296	0.9737	−0.0812
0.2008	−0.4462	0.4902	−0.6817	0.7965	−0.4731		
			MTBE-ethanol				
0.0241	−0.0600	0.2497	−0.4210	0.5486	−0.5483	0.8505	−0.3122
0.0528	−0.1210	0.3170	−0.4817	0.5952	−0.5399	0.9007	−0.2248
0.0817	−0.1774	0.3446	−0.5047	0.6531	−0.5165	0.9108	−0.2108
0.1011	−0.2129	0.4008	−0.5328	0.7381	−0.4525	0.9402	−0.1522
0.1536	−0.3002	0.4514	−0.5507	0.7632	−0.4318	0.9750	−0.0742
0.1992	−0.3632	0.5011	−0.5476	0.8010	−0.3829		

Table 7. Fitted parameters and standard deviations (S_d) for the excess molar volumes of the MTBE systems with alcohols at 298.15 K

Systems	A_1	A_2	A_3	A_4	A_5	A_6	S_d (cm³/mol)
MTBE-methanol	−2.7322	−0.1557	−0.1812	0.3082	0.3818	−0.4541	0.0040
MTBE-ethanol	−2.2143	−0.0718	−0.3223	−0.0915	0.1027	−0.0130	0.0035

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