

Isothermal vapor-liquid equilibria for the binary systems of ethylene glycol monopropyl ether with 2,2-dimethylbutane and 2,3-dimethylbutane

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Abstract—Isothermal vapor liquid equilibria for the binary system of ethylene glycol monopropyl ether with 2,2-dimethylbutane and 2,3-dimethylbutane were measured in a circulating water bath at 303.15, 318.15, and 333.15 K. The apparatus was in-house designed and manufactured. Consistency testing of the apparatus was done by comparing the measured vapor pressures to the calculated vapor pressures from the Antoine equation. The measured systems were correlated with a Peng-Robinson equation of state (PR) combined with Wong-Sandler mixing rule for the vapor phase, and NRTL, UNIQUAC, and Wilson activity coefficient models for the liquid phase. All the measured systems showed good agreement with the correlation results.

Key words: Vapor-liquid Equilibria, Surfactant, Ethylene Glycol Monopropyl Ether, 2,2-Dimethylbutane, 2,3-Dimethylbutane

INTRODUCTION

Surfactants are industrially important materials because of their wide ranging applications in the petrochemical, pharmaceutical, agrichemical and cosmetic industries. For these applications, measuring the phase behavior of surfactants and their mixtures is very important. Prediction of phase behavior is difficult for alkoxy ethanol, which includes both ether (O) and hydroxyl (OH) groups in the one molecule, since the simultaneous presence of both groups causes intra-molecular self-association and inter-molecular association for the mixtures of alkoxy ethanol and hydrocarbons or alcohols. Extensive phase behavior data are available for alkoxy ethanol+water [1-4], whereas little data are available for mixtures of alkoxy ethanol and hydrocarbons [5,6] or alcohols [7]. Previously, we measured vapor liquid equilibria (VLE) for the binary systems of hydrocarbons with surfactants [e.g., ethylene glycol monopropyl ether (C3E1) or ethylene glycol isopropyl ether (*i*C3E1)] [8-10] and alcohols with C3E1 systems [11] at isothermal or isobaric condition, to investigate the branch effect of hydrocarbons or alcohols in the alkoxy ethanol mixture.

In this work, to study the branch effect of hexane isomer in the C3E1 mixture, we measured the VLE for the binary system of ethylene glycol monopropyl ether with 2,2-dimethylbutane and 2,3-dimethylbutane at three constant temperatures: 303.15K, 318.15 K and 333.15 K. The measured systems were correlated with the Peng-Robinson equation of state (PR) [12] combined with the Wong-Sandler mixing rule [13] for the vapor phase, and NRTL [14], UNIQUAC [15], and Wilson [16] activity coefficient models for the liquid phase.

EXPERIMENTAL SECTION

1. Chemicals

2,2-Dimethylbutane and C3E1 were supplied by Sigma Aldrich (U.S.A.) and 2,3-dimethylbutane was supplied by Tokyo Chemical Industry (Japan). The minimum purity exceeded 99% (GC grade) for 2,2-dimethylbutane and 2,3-dimethylbutane, and was 99.4% (GC grade) for C3E1. These materials were used without further purification because no other peaks were detected in the gas chromatography (GC) analysis.

2. Apparatus and Procedure

The apparatus (Fig. 1) was designed and manufactured. The designed metal cell was connected to a pressure sensor, temperature sensor, vacuum pump, and feed chamber through a fitting, and was installed in a circulating water bath. The material of the designed cylindrical metal cell was stainless 'Sus 316', and the inner volume

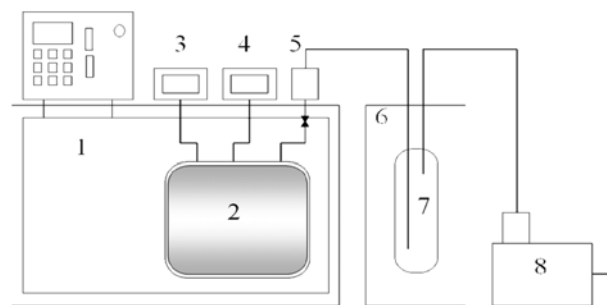


Fig. 1. Schematic diagram of the experimental apparatus.

- | | |
|--------------------------|----------------------------|
| 1. Isothermal water bath | 5. Vacuum valve |
| 2. Equilibrium cell | 6. Cooling bath circulator |
| 3. Temperature indicator | 7. Trap |
| 4. Pressure indicator | 8. Vacuum pump |

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was about 125 ml. The pressure sensor was supplied by Honeywell and the values were measured by a digital indicator, supplied by Red Lion, with an uncertainty of 0.11 kPa. The temperatures were measured using a thermometer supplied by Fluke with an uncertainty of 0.005 K. The uncertainties of the pressure and the temperature sensor were provided from the manufacturer. The circulating water bath that was controllable to 0.01 K was provided by Polyscience, the vacuum pump by Woosung Vacuum, and the trap by Daihan Scientific. The valves (female type) used in fitting of the cell were supplied by Swagelok (6LVV-DPRFR4-P), and were manufactured for very low pressure.

First, we fed the components to the cell from the feed chamber after degassing. The cell was then placed in the circulating water bath and the temperature was set to the desired value. The system was considered to have reached phase equilibrium when the pressure fluctuated within 0.1 kPa during every 15 minutes. The equilibrium pressure was obtained by repeating measurements 3-5 times, and the readings were averaged. After measuring the equilibrium pressure at the other specified temperatures, we sampled the small portion of liquid phase from the cell using a syringe. The samples were analyzed by GC with an installed thermal conductivity detector and a Porapak Q column (length: 1.83 m, diameter: 3.18 mm, mesh range: 80/100) with helium as a carrier gas. Finally, the composition was changed and the entire procedure was repeated.

RESULTS AND DISCUSSION

Isothermal VLE was measured for the binary systems of ethylene glycol monopropyl ether with 2,2-dimethylbutane and 2,3-dimethylbutane at constant temperatures of 303.15, 318.15, and 333.15 K. The systems were measured by static method. Results (\pm standard deviation) are displayed in Tables 1 and 2. The experimental points were measured more than three times and each series of values was averaged. Expanded uncertainties, U , and coverage factor, k , of the results are presented in Table 3, and were calculated from NIST

Table 1. Experimental VLE data for the binary system of 2,2-dimethylbutane (1)+ethylene glycol monopropyl ether at 303.15 K, 318.15 K, and 333.15 K, and those standard deviations

x_1	P (kPa)		
	303.15 K	318.15 K	333.15 K
0.000	0.466	1.227	2.880
0.045	11.757	18.867	28.967
0.094	20.643	33.023	50.303
0.147	27.220	43.857	67.037
0.202	32.033	52.213	80.637
0.259	36.337	59.210	91.690
0.309	39.017	63.767	99.180
0.384	41.477	68.380	106.893
0.466	43.713	72.200	113.047
0.646	46.313	77.007	121.607
0.823	48.670	80.817	127.863
0.889	49.397	82.493	131.497
0.948	50.147	84.877	136.010
1.000	51.453	87.213	140.167

Table 2. Experimental VLE data for the binary system of 2,3-dimethylbutane (1)+ethylene glycol monopropyl ether (2) at 303.15 K, 318.15 K, and 333.15 K, and the standard deviations

x_1	P (kPa)		
	303.15 K	318.15 K	333.15 K
0.000	0.466	1.227	2.880
0.031	6.683	11.280	18.193
0.066	12.017	19.743	31.023
0.098	16.193	26.737	41.667
0.139	19.913	32.873	51.497
0.197	23.880	39.663	62.447
0.292	28.120	47.217	74.857
0.383	30.733	51.867	82.657
0.463	32.070	54.417	87.280
0.543	33.330	56.643	91.073
0.645	34.730	59.007	95.230
0.799	36.447	62.257	100.547
0.878	37.120	63.447	103.183
0.956	37.847	65.297	106.370
1.000	38.523	66.241	108.164

Table 3. Expanded uncertainty (U) and coverage factor (k) of the experimental results

System	T (K)	Coverage factor (k)	Expanded uncertainty (U)		
			T	P	x_1
2,2-Dimethylbutane +C3E1	303.15	2	0.017	0.2202	0.0014
	318.15		0.018	0.2206	
	333.15		0.019	0.2222	
2,3-Dimethylbutane +C3E1	303.15	2	0.017	0.2204	0.0012
	318.15		0.018	0.2203	
	333.15		0.019	0.2211	

uncertainty guidelines [17]. According to the guidelines, accuracy, readability and repeatability of the indicator and accuracy of the probe were used for the temperature and the pressure. Also, readability, repeatability and non-linearity of GC calibration were used for the liquid phase composition.

The vapor pressures of pure components were calculated from the Antoine equation and the constants, obtained from NIST web data [18], are presented in Table 4. The measured vapor pressures were compared to the calculated vapor pressure. As shown in Table 4, the deviations of the measured and calculated vapor pressures were $<1\%$, indicating that the cell was suitable for the experiment. Comparison between measured and calculated vapor pressures for ethylene glycol monopropyl ether is not given here, because the vapor pressure was too low to adequately compare. Also, the temperature range of the Antoine constants deviated from the system temperature.

The measured data were correlated using the PR EOS [12], combined with conventional mixing rule, expressed as Eq. (2), for the vapor phase. For the liquid phase, the PR model combined with

Table 4. Antoine constants and vapor pressures of pure components

Temperature (K)		2,2-Dimethylbutane	2,3-Dimethylbutane
Antoine constants ^a	A	3.87973	3.93473
	B	1081.176	1127.187
	C	-43.807	-44.2
303.15	Experiment (kPa)	51.453	38.523
	Calculation (kPa) ^b	51.383	38.178
	Deviation (%) ^c	0.136	0.896
318.15	Experiment (kPa)	87.213	66.241
	Calculation (kPa) ^b	86.849	66.093
	Deviation (%) ^c	0.417	0.223
333.15	Experiment (kPa)	140.167	108.164
	Calculation (kPa) ^b	139.018	108.082
	Deviation (%) ^c	0.820	0.076

^aNIST web data [18] (2011. 12. 02)^bCalculated by Antoine equation

$$^c \text{Deviation (\%)} = \left| \frac{P^{\text{exp}} - P^{\text{cal}}}{P^{\text{exp}}} \right| \times 100$$

Wong-Sandler mixing rule [13], expressed as Eq. (6), including activity coefficient models, NRTL, UNIQUAC, and Wilson, was used.

The fugacity coefficient for the vapor phase was introduced in Peng and Robinson [12], and was expressed as:

$$\ln \phi_i^V = \frac{b_i}{b} (z-1) - \ln(z-B) - \frac{A}{2\sqrt{2}B} \left(\frac{2\sum_k x_k a_{ik}}{a} - \frac{b_i}{b} \right) \ln \frac{z + (1+\sqrt{2})B}{z + (1-\sqrt{2})B} \quad (1)$$

where A and B are defined as:

$$A = \frac{Pa}{(RT)^2} \quad B = \frac{Pb}{RT} \quad (2)$$

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad b = \sum_i x_i b_i \quad (3)$$

The parameters used in this correlation are presented in Table 5. The critical points, T_c , P_c , and boiling points, T_b , were obtained from NIST web data [18], and the acentric factor, ω , was obtained from the DIPPR database [19].

The fugacity coefficient for the liquid phase [13] is expressed as:

$$\ln \phi_i^L = \frac{1}{b_m} \left(\frac{\partial n b_m}{\partial n_i} \right) (z-1) - \ln(z-B) - \frac{A}{2\sqrt{2}B} \times \left(\frac{1}{a_m} \left(\frac{1}{n} \frac{\partial n^2 a_m}{\partial n_i} \right) - \frac{1}{b_m} \left(\frac{\partial n b_m}{\partial n_i} \right) \right) \ln \frac{z + (1+\sqrt{2})B}{z + (1-\sqrt{2})B} \quad (4)$$

Table 5. Parameters for the Peng-Robinson (PR) equation of state

	T_b (K) ^a	T_c (K) ^a	P_c (bar) ^a	ω ^b
2,2-Dimethylbutane	328.48	488.78	30.81	0.23497
2,3-Dimethylbutane	330.67	499.98	31.27	0.24610
C3E1	422.73	615.2	36.51	0.48676

^aNIST web data [18] (2011. 12. 02)^bDIPPR 801 database [19]

where A and B are defined as:

$$A = \frac{Pa_m}{(RT)^2} \quad B = \frac{Pb_m}{RT} \quad (5)$$

$$\frac{a_m}{RT} = Q \frac{D}{(1-D)} \quad b_m = \frac{Q}{(1-D)} \quad (6)$$

and where Q and D are defined as:

$$Q = \sum_i \sum_j x_i x_j \left(b - \frac{a}{RT} \right)_{ij} \quad D = \sum_i x_i \frac{a_i}{b_i RT} + \frac{A^E}{CRT} \quad (7)$$

and where C and A^E are defined as:

$$C = \frac{1}{\sqrt{2}} \ln(\sqrt{2}-1) \quad (8)$$

$$\frac{A^E}{RT} = \sum_i x_i \left(\frac{\sum_j x_j \tau_{ji} g_{ji}}{\sum_k x_k g_{ki}} \right) \quad (9)$$

The partial derivatives of a_m and b_m are expressed as:

$$\frac{1}{RT} \left(\frac{1}{n} \frac{\partial n^2 a_m}{\partial n_i} \right) = D \frac{\partial n b_m}{\partial n_i} + b_m \frac{\partial n D}{\partial n_i} \quad (10)$$

$$\frac{\partial n b_m}{\partial n_i} = \frac{1}{(1-D)} \left(\frac{1}{n} \frac{\partial n^2 Q}{\partial n_i} \right) - \frac{Q}{(1-D)^2} \left(1 - \frac{\partial n D}{\partial n_i} \right) \quad (11)$$

where the partial derivatives Q and D are expressed as:

$$\left(\frac{1}{n} \frac{\partial n^2 Q}{\partial n_i} \right) = 2 \sum_j x_j \left(b - \frac{a}{RT} \right)_{ij} \quad (12)$$

$$\frac{\partial n Q}{\partial n_i} = \frac{a_i}{b_i RT} + \frac{\ln \gamma_{\infty i}}{C} \quad (13)$$

where, in order to obtain $\ln \gamma_{\infty i}$, NRTL, UNIQUAC, and Wilson activity coefficient models were used. As shown in Table 6, the area parameter, q, the volume parameter, r, the liquid molar volume, and the binary energy parameter, α_{ij} , were indicated. The parameters, q

Table 6. Parameters used in the correlation by NRTL, UNIQUAC, and Wilson EOS

Component	Area parameter (q) ^a	Volume parameter (r) ^a	Liquid molar volume (cm ³ /mol) ^a	α_{12} in NRTL with C3E1 ^b
2,2-Dimethylbutane	3.932	4.498	133.712	0.3
2,3-Dimethylbutane	3.848	4.498	131.157	0.3
C3E1	3.832	4.372	114.78	-

^aDIPPR 801 Database [19]^bRenon and Prausnitz [14]

and r , were calculated by the method of Abrams and Prausnitz [15], and the van der Waals area and volume used in the method were obtained from the DIPPR database [19]. Also, the liquid molar volume of the components, used in Wilson EOS, was obtained from DIPPR [19]. According to Renon and Prausnitz [14], although, the

binary parameter, α_{ij} , was fixed at 0.3 in most available vapor-liquid equilibrium data, it can be fixed at 0.47 when the mixture includes strong self-associated substance. Thus, in our previous studies including ethylene glycol monopropyl ether, the α_{ij} was fixed at 0.47. However, in this work, the calculation result displayed a better agreement when the α_{ij} was fixed at 0.3. Thus, we presently used 0.3 for the α_{ij} values.

The results of the correlations are summarized in Table 7 with average absolute deviations of pressure (AADP) and interaction parameters for each system and activity model. The excess Gibbs free energy for all systems was regressed and optimized by following objective function:

$$OBJ = \sum_{i=1}^N \left| \frac{P_i^{exp} - P_i^{cal}}{P_i^{exp}} \right| \quad (14)$$

As shown in Table 7, almost all the AADP values obtained by the NRTL and Wilson activity models were <1%, but the values obtained by UNIQUAC activity model were not. Generally, the performance of the NRTL model is the best among the NRTL, UNIQUAC, and Wilson activity coefficient models. However, the Wilson activity model presently gave the best results (Figs. 2 and 3). In these phase diagram, the experimental data were compared to each correlated model. As shown in figures, the correlated results displayed good agreement with the experimental data. Moreover,

Table 7. The interaction parameters for the activity coefficient models and average absolute deviations of pressure

Model	Parameters ^a		k_{ij} ^b	AADP (%) ^c
	A_{12}	A_{21}		
2,2-Dimethylbutane (1)+ethylene glycol monopropyl ether (2) at 303.15 K				
NRTL	1341.858	423.131	-0.306	0.580
UNIQUAC	252.582	-25.787	-0.018	2.823
Wilson	212.271	1453.322	0.069	0.440
2,2-Dimethylbutane (1)+ethylene glycol monopropyl ether (2) at 318.15 K				
NRTL	1301.290	398.820	-0.274	0.451
UNIQUAC	294.119	-35.239	-0.070	2.435
Wilson	204.040	1203.925	0.081	0.392
2,2-Dimethylbutane (1)+ethylene glycol monopropyl ether (2) at 333.15 K				
NRTL	1278.474	373.106	-0.240	0.469
UNIQUAC	334.950	-45.492	-0.107	2.104
Wilson	189.875	1177.456	0.088	0.443
2,3-Dimethylbutane (1)+ethylene glycol monopropyl ether (2) at 303.15 K				
NRTL	985.889	368.367	-0.240	1.276
UNIQUAC	222.968	2.054	-0.042	2.934
Wilson	254.078	1433.233	0.032	0.320
2,3-Dimethylbutane (1)+ethylene glycol monopropyl ether (2) at 318.15 K				
NRTL	1271.099	456.909	-0.338	0.574
UNIQUAC	246.139	-4.750	-0.056	2.782
Wilson	244.951	1369.616	0.038	0.404
2,3-Dimethylbutane (1)+ethylene glycol monopropyl ether (2) at 333.15 K				
NRTL	1363.932	465.598	-0.334	0.497
UNIQUAC	262.913	-10.986	-0.053	2.680
Wilson	237.521	1339.618	0.039	0.408

^aNRTL, $A_{12}=(g_{12}-g_{11})/R$, $A_{21}=(g_{21}-g_{22})/R$; UNIQUAC, $A_{12}=\Delta u_{12}/R$, $A_{21}=\Delta u_{21}/R$; Wilson, $A_{12}=(\lambda_{12}-\lambda_{11})/R$, $A_{21}=(\lambda_{12}-\lambda_{11})/R$

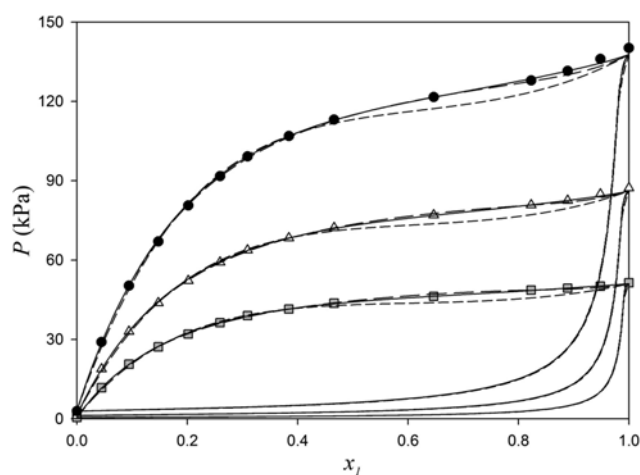
^bBinary interaction parameter^cAverage absolute deviation of the pressure

Fig. 2. Experimental data and calculated lines for the system of 2,2-dimethylbutane (1)+ethylene glycol monopropyl ether (2) at 303.15 K, 318.15 K, and 333.15 K. Symbols: \square , 303.15 K; \triangle , 318.15 K; \bullet , 333.15 K; solid curves, PR-WS-Wilson model; long dashed curves, PR-WS-NRTL model; short dashed curves, PR-WS-UNIQUAC model.

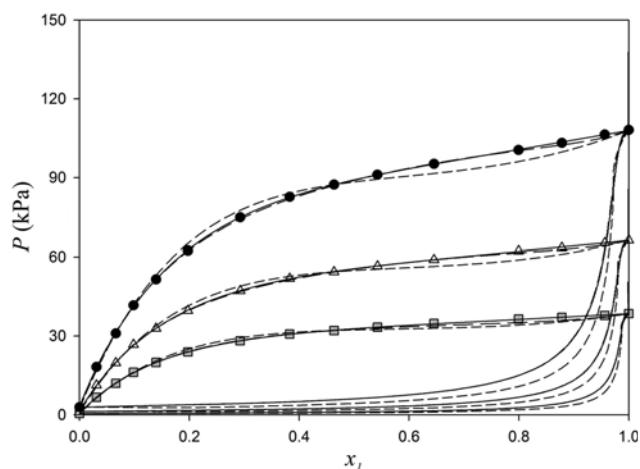


Fig. 3. Experimental data and calculated lines for the system of 2,3-dimethylbutane (1)+ethylene glycol monopropyl ether (2) at 303.15 K, 318.15 K, and 333.15 K. Symbols: \square , 303.15 K; \triangle , 318.15 K; \bullet , 333.15 K; solid curves, PR-WS-Wilson model; long dashed curves, PR-WS-NRTL model; short dashed curves, PR-WS-UNIQUAC model.

the solid curves calculated by the PR-WS-Wilson model, showed the best results, especially at the light component-rich region.

CONCLUSION

Isothermal VLE data were measured at 303.15, 318.15, and 333.15 K for the 2,2-dimethylbutane+ethylene glycol monopropyl ether and 2,3-dimethylbutane+ethylene glycol monopropyl ether systems. Consistency of the manufactured cell was verified through the comparison of the measured vapor pressure to the calculated values. The manufactured cell was suitable for the study, because the deviations of vapor pressures were <1%.

Correlations of the measured data were made by using the PR EOS model combined with conventional mixing rule for the vapor phase, and the PR model combined with the Wong-Sandler mixing rule including NRTL, UNIQUAC, and Wilson activity coefficient models was used for the liquid phase. Overall, the calculated model showed a good agreement with the experimental data, with the Wilson model being superior, especially at the light component-rich region.

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NOMENCLATURE

- a : equation of state “energy” parameter
- A, B, C : antoine equation constants
- A, B : dimensionless terms
- A_{∞}^E : excess molar Helmholtz free energy
- b : equation of state “excluded volume” parameter

- C : numerical constant defined in Eq. (8)
- D : summation term defined in Eq. (7)
- k_{ij} : binary interaction parameter
- P : pressure [bar]
- q : area parameter in UNIQUAC model
- Q : quadratic sum of second virial coefficients in Eq. (7)
- r : volume parameter in UNIQUAC model
- R : gas constant
- T : temperature [K]
- x_i : compositions of component i in the liquid phase
- Z : compressibility factor

Greek Letters

- α_{ij} : non-randomness constant for binary i, j interactions
- Δg_{ij} : NRTL model parameter
- Δu_{ij} : UNIQUAC model parameter
- $\Delta \lambda_{ij}$: Wilson model parameter
- φ_i^V : fugacity coefficient of component i in the vapor phase
- φ_i^L : fugacity coefficient of component i in the liquid phase
- γ_i : activity coefficient of component i
- τ_{ij} : NRTL model parameter
- ω : acentric factor

Superscripts

- cal : calculated value
- exp : experimental value

Subscripts

- b : at boiling conditions
- c : at critical conditions
- i, j, k : molecular species
- m : mixture
- ∞ : infinite pressure state

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