Phase Behaviors of Water + Acetic Acid + Methyl Acetate + p-Xylene Mixture at 101.32 kPa

Liang-Sun Lee* and Ching-Hua Lin

Department of Chemical and Materials Engineering, National Central University, Chung-li 32001, Taiwan

Abstract: In this study, the experimental results exhibit that the mixture of water + acetic acid + methyl acetate + p-xylene has interesting phase behaviors of vapor-liquid equilibrium (VLE) and vapor-liquid-liquid equilibrium (VLLE) under pressure of 101.32 kPa. The VLE and VLLE data were obtained with a condensed-vapor-phase-recirculating still as described in the text. The experimental data are useful to the design and operation of the purification process of acetic acid.

The experimental VLE and VLLE data were then correlated with the NRTL and the UNIQUAC activity coefficient models, respectively, as described in the text. Attributed to the presence of acetic acid, which is a strong polar component, the association effect of molecules of this component in the vapor phase was considered and handled with the approach of Hayden and O'Connell for correlation.

Keywords: Acetic acid, p-xylene, VLE, VLLE.

INTRODUCTION

Acetic acid is a very important chemical reagent in chemical industry. It can be used as a solvent or an additive for producing paints, dyes, soft drink bottles, photographic film, wood glue, and synthetic fiber and fabrics. There are different commercial processes in chemical industry for acetic acid production. But the difficulty in purifying acetic acid is commonly encountered among these commercial processes due to the presence of azeotrope-like mixture of acetic acid and water in the acetic acid-rich region. To separate this mixture, the process of azetropic distillation using an entrainer to remove water by forming a water-entrainer azeotrope has usually been applied. Processes using different entrainers, such as by Othmer [1] using ethyl acetate, Tanaka and Yamada [2] using butyl acetate and propyl acetate, and Chien *et al*. [3] using isobutyl acetate, have been studied for a long time. In these azeotropic distillation processes, water is mainly removed by forming an entrainer-water azeotrope in the settler after the first separation column. A favorable entrainer is inexpensive and has the large water content in azeotrope. Unfortunately, among the entrainers mentioned above, none of them has both advantages or is superior to others. And besides, they are not the by products generated in the chemical reactions of acetic production processes. From the viewpoint of thermodynamics, an additional component such as the alien entrainer mentioned above will increase one more degree of freedom of the system and makes the separation more complicated. Thus, a more favorable entrainer is being searched to improve the acetic acid purification process. From literature, it is interesting to find that p-xylene, a by-product of reactions during acetic acid

production, will form a p-xylene-water azeotrope with water content larger than the azetropes of water-ethyl acetate, water-propyl acetate, water-isobutyl acetate, and water-butyl acetate. The advantage of the large water content and that of p-xylene is a by-product of reaction causes it to be considered as one of the feasible entrainer. To study the feasibility of using p-xylene as an entrainer, the thermodynamic data of the quaternary mixture of water + acetic acid + methyl acetate + p-xylene are necessary. Unfortunately, the phase equilibria of this mixture have not been reported in the literature. In this study, the phase behaviors of vapor-liquid equilibrium (VLE) and vapor-liquid-liquid equilibrium (VLLE) were observed and the experimental data of phase equilibrium of this quaternary mixture useful for process design were provided. Then the experimental VLE and VLLE data were correlated with the non-random two liquid (NRTL) and the universal quasi-chemical (UNIQUAC) activity coefficient models, respectively, as discussed in the latter part of this report.

EXPERIMENTS

Chemicals

The chemicals for this study are all GR grade of acetic acid (Riedel-deHaën Company, 99.8 mass%), p-xylene (Baker Company, 99.7 mass%), methyl acetate (Merck Company, 99.0 mass%), ethanol (Merck Company, 99.8 mass%), dibutyl phthalate (Aldrich Company, 99.0 mass%), and de-ionic water generated from a Millipore water generator with an electric resistance of less than $18.2 M\Omega \cdot cm^{-1}$.

Verification of a Very Slow Reaction

It is known that acetate and water, in the present of catalyst, will react reversibly, and will affect the VLE and VLLE behaviors. In order to obtain the correct and reliable VLE and VLLE data of water, acetic acid, methyl acetate, and p-xylene mixture, it must be verified whether the reaction ex-

*Address correspondence to this author at the Department of Chemical and Materials Engineering, National Central University, Chung-li 32001, Taiwan; Tel: 886-3-425-0224; Fax: 886-3-425-2296; E-mail: t3100206@ncu.edu.tw

ists during experiment. The verification was made by observing the composition change of a ternary mixture of acetic acid, water, and methyl acetate with a designated mole ratio of 1:1:1 without catalyst. This mixture was prepared in a flask and stirred more than 40 min. at the temperature of 343.15 K and then sample was taken from flask every 30 min. for gas chromatography (GC) analysis. The analysis results of the collected samples were plotted as Fig. (**1**). The total experiment time of 300 minutes was considered long enough for phase equilibrium experiment. When all the experimental points were plotted, it showed that the reaction effect on the phase equilibrium of this mixture was negligible.
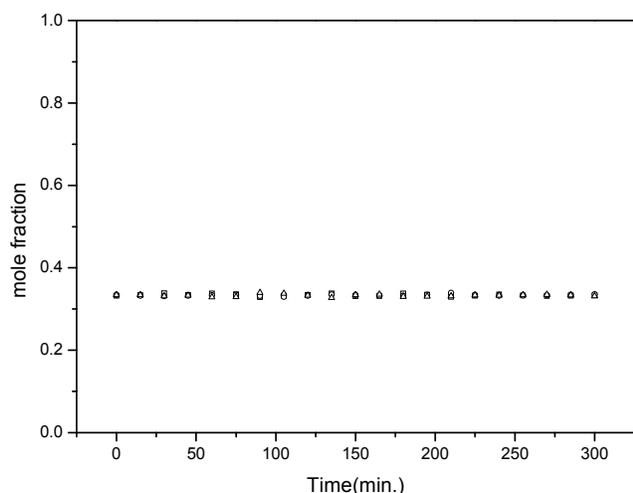
Fig. (1). Reaction experiment of water + acetic acid + methyl acetate + p-xylene mixture at 343.15 K. □: water; ◇: acetic acid; △: methyl acetate.

Composition Analysis of Mixtures

In this study, the compositions of vapor and liquid phases were determined by GC analysis. For this purpose, three binary calibration curves of constituent components, water-acetic acid, methyl acetate-acetic acid, and p-xylene-acetic acid, were separately prepared prior to phase equilibrium experiments. Each calibration curve related to the composition and peak area ratio obtained from GC analysis of each binary mixture was prepared. Based on these three calibration curves, the compositions of each component of the present quaternary mixture can be calculated through mathematical manipulations given in Appendix.

VLLE Experiments

The recirculation still used for VLLE experiments in this study is similar to that for our previous report [4] and also shown as Fig. (**2**). At the beginning of each experiment, the water + acetic acid + methyl acetate + p-xylene mixture was prepared with methyl acetate less than 0.01 mole percentage, which is the approximate composition of methyl acetate in the outlet stream of the process reactor. This quaternary mixture, about 350 mL, was fed into an equilibrium cell and then steadily heated by a hot plate. A stirrer in the equilibrium cell kept the temperature and composition of liquid mixture

uniform. According to our experience, heat was needed to the vapor phase to attain and maintain the constant equilibrium temperature of the mixture. It was supplied by circulating silicon oil in the inner jacket around the condenser in addition to an outer vacuum jacket to prevent heat loss. The vapor and liquid temperatures were measured using thermocouples (Macro Fortunate Company, Model TM-907A) with the uncertainty of ±0.01 K. During the VLLE experiments, two liquid phases were clearly observable in the equilibrium cell even with agitation. It is worth mentioning that in our experiments, the condensed vapor would split into two liquid phases and the lighter phase always remained above the denser phase and could not return to the equilibrium cell. To overcome this difficulty, a liquid pump was installed to force the condensate back to the cell. This operation would accelerate the experiment but not affect the VLE from the thermodynamic view point. It was observed that 40 minutes will be enough for ensuring VLLE, through analyzing the collected samples of test run at different time periods, after equilibrium temperature was reached. For analyzing the vapor samples, which split into two liquid phases when condensed, pure ethanol was used as cosolvent to homogenize the two liquids before GC analysis. The peak area of ethanol would be excluded from GC analysis while calculating the correct composition. For liquid phase composition determination, about 8 mL of liquid mixture was transferred with a syringe from equilibrium cell to a LLE bottle which was kept at the same temperature as that of VLLE experiment and allowed to settle and separate into two liquid phases. After liquid-liquid equilibrium (LLE) had been reached (minimum 50 minutes was required), two liquids were separately sampled for composition analysis.
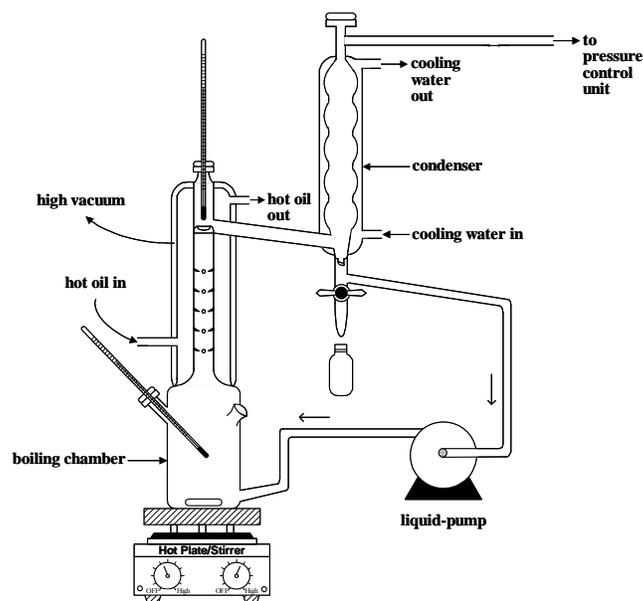
Fig. (2). VLE and VLLE experimental apparatus.

It should be mentioned that the VLLE experiments were conducted at the constant pressure of 101.32 kPa (760 mmHg) by a pressure control system, shown in Fig. (**3**), with a simple apparatus that took advantage of the local atmos-

pheric pressure being always lower than 101.32 kPa. In this apparatus, nitrogen gas was supplied at constant 101.32 kPa to the cell and a scaled glass column filled with dibutyl-phthalate whose level in glass column was determined by the daily local atmospheric pressure measured with a Fortin barometer. The uncertainty of pressure control was ±0.1333 kPa (1.0 mmHg). During experiments, the peaks of GC analysis were carefully examined to ensure that nitrogen, which was used in the pressure control system, did not dissolve in mixture and affected the phase equilibrium.
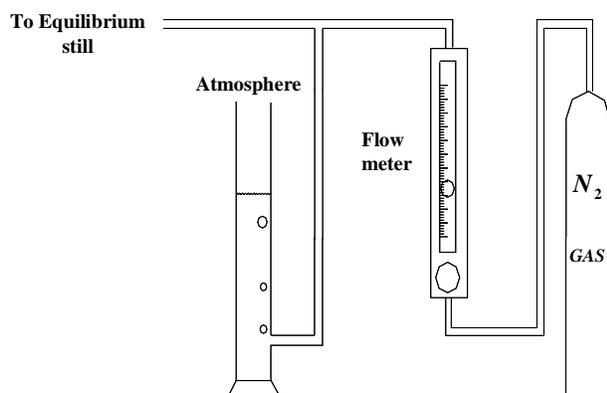
Fig. (3). Set up for constant pressure.

The compositions of all equilibrium phases were analyzed with a gas chromatography with a thermal conductivity detector (TCD) of a 2m × 1/8 in Porapak Q column. The optimum operation conditions of the present analysis were: injection port, 200°C; oven temperature, 160°C; detector temperature, 160°C; detector current 80 mA; carrier gas (helium, 99.9%) flow rate 30 mL · min⁻¹.

In order to ensure the reliability of apparatus, instrument, and experimental skill to obtain reliable experimental data, a test on the vapor-liquid equilibrium of water and acetic acid mixture was conducted at 101.32 kPa. The equilibrium compositions of the mixture of this test fairly match the literature data of Ohe [5] as shown in Fig. (**4**).
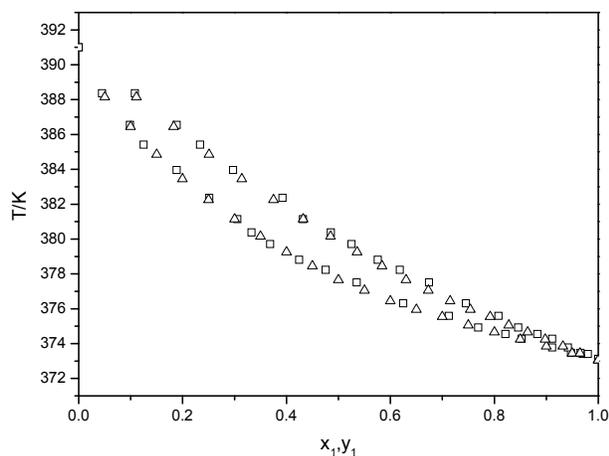
Fig. (4). Experimental and literature VLE data of water (1) and acetic acid (2) mixture at 101.32 kPa. □ : experimental data, △ : Ohe [5].

VLE Experiments

The VLE experiments were conducted with the same apparatus for VLLE experiments. With the same procedure as the VLLE experiments, a liquid mixture was prepared and fed into the equilibrium cell and then smoothly heated till the phase equilibrium was reached where the liquid and vapor temperatures must be maintained constant for more than 40 min. to ensure phase equilibrium was attained. During experiment, the observation of a homogeneous liquid phase ensured that the phase equilibrium is true VLE and samples of liquid and vapor phases were separately taken with syringes for GC analysis. During VLE experiments, assurance for the total return of condensed vapor was needed whether the condensed vapor was a single or a two-liquid phase. With the process similar to the VLLE experiment, a circulating pump was used to force the condensate back to the equilibrium cell in case two liquid phases occurred on the return path. The compositions of the vapor and liquid phases were analyzed with a gas chromatography as described in the previous paragraph for VLLE experiments.

EXPERIMENTAL RESULTS

VLE

30 experimental VLE data of water + acetic acid + methyl acetate + p-xylene mixture were collected and, based on the order of equilibrium temperature, listed in Table **1**. Unfortunately, a phase diagram similar to that for a binary or a ternary mixture could not depict these quaternary data, and thus, only the numerical values were presented.

VLLE

25 VLLE data of this quaternary mixture were collected and listed in Table **2** showing the compositions of aqueous phase, organic phase, and vapor phase. Similar to the VLE data, all these equilibrium data were difficult to depict by a phase diagram. Table **2** shows that the boiling point of VLLE varied in a small temperature range between 364.68 K and 376.60 K and the composition of p-xylene in vapor phase varied slightly.

THEORETICAL BACKGROUND

VLLE

The phase equilibrium criteria for VLLE of a quaternary mixture are the equal temperature and pressure through out all phases and the equal fugacity of each constituent component in each phase. If the fugacities of the vapor and liquid phases are expressed in terms of fugacity coefficient and activity coefficient, respectively, then the equation of equal fugacity for a component is expressed as Eq. (1).

$$y_i \hat{\phi}_i^v P = x_i^{lj} \gamma_i^{lj} f_i^{lo} \qquad i = 1,..,4; j = 1,2 \qquad (1)$$

where f_i^{lo} is the standard state of liquid phase of component i. If the condensed phase of pure component i at the system temperature and pressure is chosen as the standard state and assume that the condensed phase volume is a very weak function of pressure then the standard state is expressed as

$$f_i^{l0} = f_i^l = p_i^{sat} \phi_i^{sat} \exp\left[\frac{v_i^l (P - P_i^{sat})}{RT}\right] \qquad (2)$$

Table 1.   The Experimental Data of VLE of Water (1) + Acetic Acid (2) + Methyl Acetate (3) + p-Xylene (4) Mixture at 101.32 kPa

No.	T/K	x_1^f	x_2^f	x_3^f	x_1	x_2	x_3	y_1	y_2	y_3	y_4
1	367.14	0.6539	0.3188	0.0081	0.6521	0.3197	0.0083	0.5391	0.1102	0.0636	0.2871
2	367.78	0.7061	0.2729	0.0095	0.7054	0.2742	0.0098	0.5646	0.0929	0.0867	0.2557
3	368.95	0.6963	0.2815	0.0097	0.6937	0.2833	0.0099	0.5820	0.1131	0.0697	0.2352
4	368.98	0.6733	0.3055	0.0107	0.6737	0.3058	0.0104	0.5671	0.1176	0.0909	0.2244
5	369.00	0.6679	0.3115	0.0101	0.6669	0.3125	0.0106	0.5745	0.1284	0.0879	0.2093
6	369.07	0.7141	0.2625	0.0094	0.7119	0.2632	0.0099	0.5596	0.0938	0.0763	0.2703
7	370.05	0.6332	0.3442	0.0106	0.6319	0.3458	0.0102	0.5536	0.1405	0.0872	0.2187
8	370.53	0.6673	0.3109	0.011	0.6679	0.3119	0.0102	0.5903	0.1306	0.0871	0.1919
9	370.73	0.6330	0.3475	0.0095	0.6320	0.3487	0.0087	0.5680	0.1594	0.0747	0.1980
10	370.90	0.3946	0.5257	0.0088	0.3934	0.5266	0.0081	0.3572	0.2720	0.0430	0.3278
11	374.31	0.1519	0.5445	0.0118	0.1520	0.5453	0.0126	0.2168	0.4548	0.0475	0.2809
12	374.34	0.1213	0.4638	0.0128	0.1189	0.4657	0.0119	0.2253	0.4688	0.0453	0.2606
13	374.51	0.1420	0.5507	0.0109	0.1428	0.5492	0.0102	0.2105	0.4628	0.0384	0.2883
14	375.70	0.1028	0.4617	0.0108	0.1033	0.4628	0.0103	0.2012	0.4918	0.0398	0.2672
15	376.52	0.1757	0.6810	0.0108	0.1738	0.6827	0.0100	0.1836	0.4722	0.0423	0.3018
16	376.78	0.1705	0.6720	0.0095	0.1687	0.6730	0.0094	0.1739	0.4788	0.0384	0.3089
17	376.89	0.0802	0.3587	0.0112	0.0794	0.3574	0.0120	0.2258	0.4655	0.0505	0.2583
18	377.59	0.3472	0.6277	0.0121	0.3453	0.6286	0.0125	0.3375	0.4485	0.0858	0.1282
19	378.52	0.2067	0.7332	0.0113	0.2054	0.7343	0.0107	0.1873	0.5084	0.0566	0.2477
20	378.62	0.3233	0.6541	0.0115	0.3221	0.6562	0.0112	0.3234	0.4920	0.0798	0.1047
21	378.75	0.1986	0.7449	0.0095	0.1979	0.7434	0.0101	0.1786	0.5224	0.0548	0.2442
22	379.67	0.3023	0.6770	0.0102	0.3005	0.6794	0.0102	0.2968	0.5357	0.0714	0.0962
23	380.17	0.2711	0.7090	0.0092	0.2693	0.7100	0.0105	0.2695	0.5631	0.0730	0.0945
24	380.57	0.2454	0.7318	0.0128	0.2474	0.7303	0.0119	0.2525	0.5756	0.0807	0.0912
25	381.64	0.2182	0.7619	0.0098	0.2180	0.7608	0.0104	0.2144	0.6218	0.0703	0.0935
26	382.59	0.1845	0.7941	0.0119	0.1835	0.7953	0.0114	0.1789	0.6613	0.0763	0.0835
27	383.46	0.1646	0.8141	0.0104	0.1628	0.8156	0.0112	0.1607	0.6810	0.0740	0.0843
28	384.66	0.1217	0.8581	0.0108	0.1208	0.8593	0.0102	0.1175	0.7380	0.0679	0.0765
29	385.45	0.0924	0.8859	0.0102	0.0928	0.8848	0.0108	0.0862	0.7624	0.0684	0.0830
30	386.85	0.0570	0.9228	0.0111	0.0586	0.9210	0.0105	0.0562	0.8050	0.0663	0.0724

Table 2.   The Experimental Data of VLLE of Water (1) + Acetic Acid (2) + Methyl Acetate (3) + p-Xylene (4) Mixture at 101.32 kPa

No.	T/K	x_1^f	x_2^f	x_3^f	x_1^{aq}	x_2^{aq}	x_3^{aq}	x_1^{org}	x_2^{org}	x_3^{org}	y_1	y_2	y_3	y_4
1	364.68	0.8960	0.0664	0.0109	0.8882	0.0915	0.0072	0.0798	0.0325	0.0564	0.6386	0.0338	0.0942	0.2333
2	364.98	0.8948	0.0728	0.0108	0.9120	0.0587	0.0105	0.1133	0.0238	0.0653	0.6483	0.0253	0.0947	0.2318
3	365.52	0.8499	0.1106	0.0116	0.8908	0.0845	0.0085	0.1073	0.0376	0.0666	0.6198	0.0428	0.0961	0.2412
4	365.63	0.8200	0.1313	0.0115	0.7826	0.1835	0.0105	0.0527	0.0569	0.0433	0.5772	0.0675	0.1084	0.2469
5	366.06	0.7779	0.1572	0.0107	0.8006	0.1736	0.0070	0.0639	0.0602	0.0437	0.5777	0.0694	0.1023	0.2505
6	366.31	0.8263	0.1244	0.0109	0.7858	0.1818	0.0078	0.0665	0.0703	0.0451	0.5692	0.0765	0.1107	0.2436
7	366.75	0.8720	0.1161	0.0081	0.6802	0.2720	0.0121	0.0583	0.0819	0.0389	0.5633	0.1051	0.0902	0.2414
8	366.77	0.7984	0.1471	0.0129	0.7410	0.2235	0.0114	0.1080	0.0677	0.0451	0.5763	0.0737	0.1124	0.2376
9	367.61	0.4497	0.1442	0.0181	0.7244	0.2441	0.0099	0.0492	0.0705	0.0333	0.5588	0.0969	0.0878	0.2566
10	367.89	0.6204	0.2485	0.0092	0.5498	0.3913	0.0110	0.0406	0.1216	0.0203	0.5003	0.1681	0.0602	0.2714
11	367.96	0.5834	0.2492	0.0152	0.5348	0.3907	0.0190	0.0516	0.1292	0.0341	0.4864	0.1722	0.0790	0.2623
12	368.24	0.5631	0.2139	0.0115	0.4795	0.4184	0.0198	0.0603	0.1450	0.0261	0.4685	0.1866	0.0757	0.2693
13	368.38	0.5958	0.3623	0.0051	0.3865	0.5361	0.0119	0.0565	0.1966	0.0159	0.3647	0.3057	0.0525	0.2772
14	368.49	0.5089	0.2055	0.0124	0.5625	0.3818	0.0132	0.0632	0.1290	0.0265	0.4928	0.1617	0.0808	0.2647

No.	T/K	x_1^f	x_2^f	x_3^f	x_1^{aq}	x_2^{aq}	x_3^{aq}	x_1^{org}	x_2^{org}	x_3^{org}	y_1	y_2	y_3	y_4
15	368.66	0.4566	0.2240	0.0136	0.4976	0.4263	0.0160	0.0785	0.1560	0.0254	0.4507	0.1903	0.0820	0.2770
16	369.25	0.2370	0.3522	0.0173	0.2774	0.5997	0.0212	0.0491	0.2533	0.0245	0.3146	0.3344	0.0760	0.2750
17	369.45	0.4411	0.4409	0.0111	0.2686	0.6144	0.0214	0.0606	0.2543	0.0279	0.3191	0.3240	0.0705	0.2864
18	369.97	0.1489	0.3864	0.0336	0.2279	0.5948	0.0379	0.0546	0.3006	0.0408	0.2586	0.3616	0.1133	0.2665
19	370.07	0.2465	0.3173	0.0172	0.2837	0.5848	0.0206	0.0754	0.2428	0.0233	0.3356	0.3225	0.0780	0.2639
20	370.93	0.2071	0.3728	0.0325	0.1995	0.5932	0.0401	0.0555	0.3119	0.0416	0.2523	0.3580	0.1250	0.2647
21	371.27	0.1284	0.3934	0.0373	0.1607	0.6391	0.0481	0.0433	0.3471	0.0455	0.1946	0.4034	0.1335	0.2684
22	371.76	0.1266	0.3891	0.0121	0.2174	0.6304	0.0156	0.0498	0.2715	0.0177	0.2674	0.3825	0.0642	0.2859
23	371.93	0.1142	0.3465	0.0217	0.1959	0.6319	0.0205	0.0380	0.2967	0.0257	0.2313	0.3953	0.0844	0.2891
24	374.14	0.0912	0.3273	0.0135	0.2339	0.5733	0.0141	0.0409	0.2677	0.0182	0.2713	0.3653	0.0647	0.2986
25	376.60	0.0874	0.3655	0.0098	0.1693	0.6708	0.0145	0.0312	0.3069	0.0162	0.1983	0.4374	0.0609	0.3034

Where the exponential term is the Poynting factor negligible at low pressure and

Eq. (1) is then further expressed as

$$y_i \hat{\phi}_i^v P = x_i^{lj} \gamma_i^{lj} p_i^{sat} \phi_i^{sat} \qquad i = 1,..,4; \; j = 1,2 \qquad (3)$$

In the above equation, the fugacity coefficient is estimated with the equation where an equation of state (EOS) is needed,

$$\ln \hat{\phi}_i^v = \frac{1}{RT} \int_0^p \left[\left(\frac{\partial v}{\partial n_i} \right)_{T,P,N_{j \neq i}} - \frac{RT}{P} \right] dP \qquad (4)$$

In this study, the equation of state employed is the virial equation of state (EOS) expressed as

$$\frac{PV}{RT} = 1 + \frac{BP}{RT} \qquad (5)$$

In general, the fugacity coefficient of a system under one atmospheric pressure should be unity without doubt. But for the present mixture with acetic acid this consideration is not correct since even in vapor phase, acetic acid will self-associate to form dimmers and trimers and will affect the phase equilibrium estimation. To handle this effect, the Hayden and O'Connell approach [6] was adopted. This approach will not be repeated here since it is available in the open literature.

VLE

For VLE, the theoretical consideration is identical to that of VLLE except only one liquid phase is considered. Thus, a VLE system has the less number of equilibrium equations than a VLLE system does. The equations for VLE will not be repeated here. However, the association effect of acetic acid in vapor phase that will affect phase equilibrium calculation of the present mixture must be considered as done for the VLLE calculations.

CORRELATION OF EXPERIMENTAL DATA

The experimental VLE and VLLE data of water + acetic acid + methyl acetate + p-xylene quaternary mixture were correlated with liquid activity coefficient model. There are many mathematical techniques that can be applied for the

present data reductions. Here, the maximum likelihood principle, which assumed that the experimental errors were random and independent and had the advantages of accounting for each concerned variable, was employed. The objective function for the VLE data correlation is in the form of

$$Q = \sum_{i=1}^{N_T} \left[\frac{(P_i^{exp} - P_i^{cal})^2}{\sigma_{P_i}^2} + \frac{(T_i^{exp} - T_i^{cal})^2}{\sigma_{T_i}^2} + \frac{(y_{1i}^{exp} - y_{1i}^{cal})^2}{\sigma_{y_{1i}}^2} + \frac{(y_{2i}^{exp} - y_{2i}^{cal})^2}{\sigma_{y_{2i}}^2} \right.$$

$$\left. + \frac{(y_{3i}^{exp} - y_{3i}^{cal})^2}{\sigma_{y_{3i}}^2} + \frac{(x_{1i}^{exp} - x_{1i}^{cal})^2}{\sigma_{x_{1i}}^2} + \frac{(x_{2i}^{exp} - x_{2i}^{cal})^2}{\sigma_{x_{2i}}^2} + \frac{(x_{3i}^{exp} - x_{3i}^{cal})^2}{\sigma_{x_{3i}}^2} \right]$$

$$(10)$$

where N_T is the total number of data point and σ_i represents the standard deviation of variable *i*. The values of σ of temperature and pressure were determined by the accuracy of the measurements and the random errors of researchers. And those of vapor and liquid compositions were related to the measurement error and inaccuracies of calibration curves. For the present correlation, the values of the standard deviations in the objective function were $\sigma_x = 0.001$, $\sigma_y = 0.01$, $\sigma_T = 0.1$ K, and $\sigma_P = 1$ mmHg. The physical data and parameters required for correlation were listed in Table **3**.

For the correlation of VLE of this quaternary mixture, the models of UNIQUAC [7] and NRTL [8] had been used. Both models can be found from the open literature or textbooks, and will not be described here again. It is observed from the correlation results that the NRTL model [8] provided the better results. Thus, only the optimum binary parameters minimizing the above objective function obtained from this model were reported in Table **4**. And during correlating experimental data, a value of 0.3 was considered for the nonrandomness factor. Because experimental and calculated data involved were too extensive to be listed in data correlation, and with the consideration of the brevity of text, only the average absolute deviation (AAD), average absolute relative deviation percentage (AARD%), and root mean square deviation (RMSD) of the correlation results of boiling temperature, vapor and liquid compositions of each component were given in Table **5**. This table showed that the correlation re-

Table 3.   Physical Properties of Water, Acetic Acid, Methyl Acetate, and p-Xylene

	water	acetic acid	methyl acetate	p-xylene
M.W.	18.02	60.05	74.08	106.17
$T_b(K)$	373.15	391.05	330.09	411.51
$T_c(K)$	647.13	591.95	506.55	616.20
$P_c(bar)$	220.55	57.86	47.50	35.11
$V_c(ml/mol)$	55.9478	179.7000	228.0000	378.0000
Z_{ra}	0.2432	0.2239	0.2553	0.2591
DM(debyes)	1.8497	1.7388	1.6788	0.0
RD($\overset{\circ}{A}$)	0.615	2.610	2.996	3.831
r	0.92000	2.19512	2.80422	4.65788
q	1.400	2.072	2.576	3.536
q'	1.000	2.072	2.576	3.536
Antoine equation				
$\log_{10}P/mmHg = A - (B / (T/^oC + C))$				
C1	8.10765	7.18807	7.07874	6.99052
C2	1750.29	1416.7	1164.43	1453.43
C3	235	211	220.46	215.307

Z_{ra}: Rackett parameter for saturated-liquid molar volume correction [9].
ω: acentric factor [10].
DM: dipole moment [10].
RD: mean radius of gyration [10].
r: structure volume parameter for the UNIQUAC equation [9].
q: structure area parameter for the UNIQUAC equation [9].
q′: structure area parameter for the modified UNIQUAC equation [9].
η: association or solvation parameter [9].

sults were fairly well. The largest AARD among temperature and compositions was 6.79% of water component.

Table 4.   The UNIQUAC and NRTL Model Parameters for Water (1) + Acetic Acid (2) + Methyl Acetate (3) + p-Xylene (4) System

	VLE	VLLE
	NRTL Model	UNIQUAC Model
A_{12}	-976.23	-82.17
A_{21}	522.68	151.02
A_{13}	742.17	-10000.00
A_{31}	-6886.03	7405.70
A_{14}	-37.07	36.35
A_{41}	471.51	-2024.19
A_{23}	210.61	-452.31
A_{32}	73.92	233.57
A_{24}	995.59	-153.81
A_{42}	282.72	-194.56
A_{34}	167.30	-202.94
A_{43}	177.44	19.72

The objective function for the VLLE data correlation was expressed in the form of

$$Q = \sum_{i=1}^{N_T}\left[\frac{(P_i^{exp} - P_i^{cal})^2}{\sigma_{P_i}^2} + \frac{(T_i^{exp} - T_i^{cal})^2}{\sigma_{T_i}^2} + \frac{(y_{1i}^{exp} - y_{1i}^{cal})^2}{\sigma_{y_{1i}}^2} \right.$$

$$+ \frac{(y_{2i}^{exp} - y_{2i}^{cal})^2}{\sigma_{y_{2i}}^2}$$

$$\frac{(y_{3i}^{exp} - y_{3i}^{cal})^2}{\sigma_{y_{3i}}^2} + \frac{(x_{1i}^{exp'} - x_{1i}^{cal'})^2}{\sigma_{x_{1i}}^2} + \frac{(x_{2i}^{exp'} - x_{2i}^{cal'})^2}{\sigma_{x_{2i}}^2} + \frac{(x_{3i}^{exp'} - x_{3i}^{cal'})^2}{\sigma_{x_{3i}}^2}$$

$$+ \frac{(x_{1i}^{exp''} - x_{1i}^{cal''})^2}{\sigma_{x_{1i}}^2} + \frac{(x_{2i}^{exp''} - x_{2i}^{cal''})^2}{\sigma_{x_{2i}}^2} + \left. \frac{(x_{3i}^{exp''} - x_{3i}^{cal''})^2}{\sigma_{x_{3i}}^2} \right]$$

$$(11)$$

Where the standard deviation of each variable, σ, has the same meaning as explained in the previous paragraph of VLE correlation. The liquid activity coefficient models considered for correlation were also NRTL [8] and UNIQUAC

Table 5. **The AAD, AARD, and RMSD of Correlation of VLE by the NRTL Model**

	VLE								
	NRTL model								
	T/K	x_1	x_2	x_3	x_4	y_1	y_2	y_3	y_4
AAD	0.93	0.0003	0.0003	0.0000	0.0000	0.0173	0.0189	0.0016	0.0122
AARD(%)	0.25	0.09	0.08	0.02	0.04	6.79	5.84	2.29	5.49
RMSD	1.06	0.0004	0.0004	0.0000	0.0001	0.0199	0.0221	0.0025	0.0159

$AAD = \sum_{i=1}^{k} |M^{exp} - M^{cal}|/k$, $AARD = \sum_{i=1}^{k} \left[|M^{exp} - M^{cal}|/M^{exp} \right]/k$

$RMSD = (\sum_{i=1}^{k} (M^{exp} - M^{cal})^2 /k)^{1/2}$, Mexp = measured value, Mcal = calculated value

k = total number of points.

Table 6. **The AAD, AARD, and RMSD of the Correlation Results of VLLE by the UNIQUAC Model**

	VLLE											
	UNIQUAC model											
	T/K	x_1^{aq}	x_2^{aq}	x_3^{aq}	x_4^{aq}	x_1^{org}	x_2^{org}	x_3^{org}	x_4^{org}	y_1	y_2	y_3	y_4
AAD	0.41	0.0119	0.0171	0.0008	0.0123	0.0065	0.0042	0.0020	0.0067	0.0203	0.0083	0.0064	0.0273
AARD(%)	0.11	3.73	4.55	4.20	14.18	10.83	2.58	5.60	0.96	4.58	4.80	7.44	10.29
RMSD	0.56	0.0147	0.0247	0.0015	0.0193	0.0084	0.0061	0.0028	0.0103	0.0239	0.0106	0.0082	0.0282

$AAD = \sum_{i=1}^{k} |M^{exp} - M^{cal}|/k$, $AARD = \sum_{i=1}^{k} \left[|M^{exp} - M^{cal}|/M^{exp} \right]/k$, $RMSD = (\sum_{i=1}^{k} (M^{exp} - M^{cal})^2 /k)^{1/2}$, Mexp = measured value, Mcal = calculated value,

k = total number of points.

[7]. It was observed that the correlation with the NRTL model [8] was a failure and thus, only the results obtained from the UNIQUAC [7] model were reported. With the consideration of the brevity of text, only AAD, AARD, and RMSD of temperature, compositions of vapor and the two liquid phases were reported in Table **6**. The correlation results were fairly well with the exceptions of the compositions of p-xylene in aqueous phase, water in organic phase, and p-xylene in vapor phase for which AARD% was larger than 10.00%.

CONCLUSION

In this study, the quaternary mixture of water + acetic acid + methyl acetate + p-xylene was experimentally determined that it had the phase behaviors of VLE and VLLE at 101.32 kPa. The experimental data of VLE and VLLE were listed in Tables **1** and **2**, respectively. The former phase behavior exhibits between 367.14 K and 386.85 K and the latter behavior exhibits in a smaller temperature range between 364.68 K and 376.60 K. Before the experiments of phase equilibrium, the chemical reactions that would affect the phase study were checked and ensured that the reaction effect was negligible for the present mixture without catalyst. The experimental data of both phase behaviors were collected and reported numerically since it was difficult to depict a quaternary mixture by a phase diagram.

The VLE data sets were correlated with the NRTL [8] and UNIQUAC [7] models and only the results by the NRTL model were reported due to its superiority over the UNIQUAC model for this mixture. The data sets of VLLE were also correlated with the NRTL and UNIQUAC models, but only the results by the UNIQUAC model were reported due to the unsuccessful results of the NRTL model. Attributed to the presence of a strongly associating component, acetic acid, the polymerization effect of this compound on phase equilibrium was considered and handled with the Hayden-O'Connell approach [6].

NOMENCLATURE

A	=	peak area percentage of GC analysis
A_{ij}	=	interaction parameter of molecules i and j
B	=	second virial coefficient
DM	=	dipole moment, debyes
f_i^l	=	liquid fugacity of pure component i
n	=	number of components
P	=	pressure, kPa
P_i^{sat}	=	saturated vapor pressure of component i, kPa
Q	=	objection function for correlation
q	=	surface parameter of molecular structure in UNIQUAC model
q'	=	modified value of q
R	=	gas constant
RD	=	radius of gyration,

r	=	volume parameter of molecular structure in UNIQUAC model
T	=	temperature, K
T_b	=	boiling point, K
T_c	=	critical temperature, K
V	=	molar volume, cm^3/mol
v_i^l	=	saturated liquid volume of component *i*
x_i	=	liquid mole fraction of component *i*
y_i	=	vapor mole fraction of component *i*

Greek

ϕ_i^{sat}	=	saturated fugacity coefficient of component *i*
$\hat{\phi}_i^v$	=	vapor fugacity coefficient of component *i*
γ_i	=	liquid activity coefficient of component *i*
σ_p	=	standard deviation of pressure
σ_T	=	standard deviation of temperature
σ_x	=	standard deviation of liquid phase composition
σ_y	=	standard deviation of vapor phase composition

Superscript

aq	=	aqueous phase
cal	=	calculated value
exp	=	experimental value
j	=	*j-th* liquid phase

l	=	liquid phase
org	=	organic phase

REFERENCES

[1]   D. F. Othmer, "Azeotropic distillation for dehydrating acetic acid", *Chem. Metallurg. Eng.*, vol. 40, pp. 91-95, 1941.
[2]   S. Tanaka and J. Yamada, "Graphical calculation method for minimum Reflux ratio in azeotropic distillation", *J. Chem. Eng. Jpn.*, vol. 5, pp. 20-26, 1972.
[3]   I. L. Chien, K. L. Zeng, H. Y. Chao and J. H. Liu, "Design and control of acetic acid dehydration system via heterogeneous azeotropic distillation", *Chem. Eng. Sci.*, vol. 59, pp. 4547-4567, Nov. 2004.
[4]   L. S. Lee and H. C. Shen, "Azeotropic behavior of water + n-propanol + cyclohexane mixture and using cyclohexane as an entrainer for separation water + n-propanol mixture at 760 mmHg", *Ind. Eng. Chem. Res.*, vol. 42, pp. 5905-5914, Nov. 2003;
[5]   S. Ohe, *Vapor-liquid Equilibrium Data*. Tokyo: Elsevier, 1989.
[6]   J. G. Hayden and J. P. O'Connell, "A generalized method for predicting second virial coefficients", *Ind. Eng. Chem. Process Des. Dev.*, vol. 14, pp. 209-216, July 1975.
[7]   D. S. Abrams and J. M. Prausnitz, "Statistical thermodynamics of liquid mixtures: a new expression for the excess Gibbs energy of partly or completely miscible systems", *AIChE J.,* vol. 21, pp.116-128, Jan. 1975.
[8]   H. Renon and J. M. Prausnitz, "Local composition in thermodynamic excess functions for liquid mixtures", *AIChE J.,* vol. 14, pp. 135-144, Jan. 1968.
[9]   J. M. Prausnitz, T. F. Anderson, C. A. Grens, C. A. Eckert, R. Hsieh, and J.P. O'Connell, Computer Calculation for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria. New Jersey: Prentice-Hall, 1980.
[10] R. C. Reid, J. M. Prausnitz, and B. E. Poling, *The Properties of Gases and Liquids*. 4th Edition, New York: McGraw-Hill, 1987.

Appendix: Composition of a quaternary mixture by GC analysis

Assume that the results of GC analysis of a quaternary mixture were given the peak areas and mole fractions of each component in the below table

component	water(1)	acetic acid (2)	methyl acetate (3)	p-xylene (4)
Peak area %	A_1	A_2	A_3	A_4
Mole fraction	x_1	x_2	x_3	x_4

It is obvious that

$$A_1 + A_2 + A_3 + A_4 = 1 \qquad \text{(A1)}$$

and

$$x_1 + x_2 + x_3 + x_4 = 1. \qquad \text{(A2)}$$

The calibration curve of acetic acid + water mixture and $A_2/(A_1+A_2)$ will give x_2/x_1, that of acetic acid + methyl acetate mixture and $A_2/(A_2+A_3)$ will give x_2/x_3, and that of acetic acid + p-xylene mixture and $A_2/(A_2+A_4)$ will give x_2/x_4.

Let

$$\frac{x_2}{x_1} = a, \qquad \frac{x_2}{x_3} = b, \qquad \frac{x_2}{x_4} = c \qquad \text{(A3)}$$

Substituting Eq. (A3) into Eq. (A2) will obtain

$$\frac{x_2}{a} + x_2 + \frac{x_2}{b} + \frac{x_2}{c} = 1$$

or $\left[\dfrac{abc + bc + ca + ab}{abc} \right] x_2 = 1$

Finally, the compositions of each component are

$$x_1 = \frac{bc}{abc + bc + ca + ab}$$

$$x_2 = \frac{abc}{abc + bc + ca + ab}$$

$$x_3 = \frac{ca}{abc + bc + ca + ab}$$

and

$$x_4 = \frac{ab}{abc + bc + ca + ab}$$