RESEARCH NOTES

The Isobaric Vapor-Liquid Equilibrium of Butanone-DMF and Toluene-DMF at Reduced Pressures[*]

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Abstract   The isobaric vapor-liquid equilibrium data of butanone(1)-*N*, *N*-dimethylformamide (DMF)(2) at 100.92kPa, 93.32kPa, and 79.99kPa and of toluene(1)-DMF(2) at 100.92kPa were measured using a modified Rose–Williams still. The above data met the thermodynamic consistency test and were correlated with the Wilson, NRTL, and UNIQUAC equations. These data can be used in the analysis and design of the process that involves separating DMF from butanone and toluene in the leather synthesis industry.
Keywords   isobaric vapor-liquid equilibrium, *N*, *N*-dimethylformamide, DMF, butanone, toluene, Wilson equation, NRTL equation, UNIQUAC equation

1   INTRODUCTION

N, *N*-dimethylformamide (DMF) is an important organic compound and is an intermediate in the chemical industry and is also widely used in the petroleum, fiber synthesis, acrylic spinning, polyester synthesis leather, and dyestuff industries. In a typical synthesis leather factory, traditionally, DMF, butanone, and toluene are used as solvents and are finally emitted to the atmosphere with hot air.

In order to protect the environment, it is necessary to recover DMF, butanone, and toluene from the emissions of hot air. An effective recovery process is absorbing DMF, butanone, and toluene in a packed absorption column and then separating DMF from butanone and toluene in a distillation column under a reduced pressure. Therefore, the isobaric vapor-liquid equilibrium data of butanone-DMF and toluene-DMF are greatly needed for the industrial design of the recovery process. However, so far, the relevant isobaric VLE data have not been available in literature besides some limited isothermal VLE data of toluene-DMF[1].

In this study, the isobaric VLE data of butanone(1)-DMF(2) and of toluene (1)-DMF (2) were measured by a dynamic recirculating still to meet the requirement in the synthesis leather process. The isobaric data for these systems have not been reported in literature before.

2   EXPERIMENT
2.1   Materials

Analytical-grade butanone, toluene, and DMF were purchased from the Shanghai Reagent Factory. Butanone was used after rectification on an efficient column that was filled with metal packings. DMF was used after dehydration over activated molecular sieves. Toluene was used without further purification.

The purity of all the chemicals was checked by gas chromatography (GC) and the purities of butanone, toluene, and DMF were found to be 99.9%, 99.5%, and 99.9%, respectively.

2.2   Apparatus

The experimental apparatus used in this study was a modified Rose-Williams still, which was favored in previous works[2—4]. The details of the apparatus were described by Chen and Hu[5]. The pressure of the system was controlled within ± 0.065kPa (0.05mmHg) by a pressure regulator. The equilibrium temperature was measured with a calibrated thermometer with the accuracy of 0.1K.

The compositions of the vapor and liquid phase at equilibrium were analyzed by a GC7890 GC. The length of the capillary column was 15m, and the fixed liquid was SE54.

Before the measurement of the data, the VLE data of the binary system of 1-propanol-ethylbenzene was measured in a wide range of concentration at 66.66kPa (500mmHg) to make sure that the apparatus would function properly. The comparison of the results of the experiments and the literature data [6] of 1-propanol-ethylbenzene is shown in Fig.1. As evident, the experimental results are in good agreement with the literature data, which indicates that the functioning of the apparatus was good.

3   RESULTS AND DISCUSSION

Tables 2—5 show the isobaric vapor-liquid equilibrium data of butanone(1)-DMF(2) at 100.92kPa, 93.32kPa, and 79.99kPa and of toluene(1)-DMF(2) at 100.92kPa. The Wilson, NRTL, and UNIQUAC equations were used to correlate the experimental data of the two binary systems. The correlated results of the absolute average deviations in boiling points and vapor-phase mole fractions of the two binary systems at
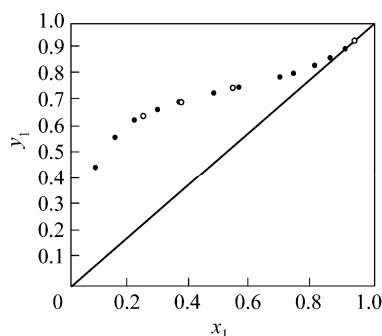
Figure 1   Comparison of the experimental results with the literature data of 1-propanol-ethylbenzene at 66.66kPa (500mmHg)

○ this study; ● Ellis and Froome[6]

Table 1   Antoine equation① coefficients of the pure components

Component	A	B	C
butanone [7]	3.9894	1150.207	−63.904
DMF[8]	3.93068	1337.716	−82.648
toluene[7]	4.07827	1343.943	−53.773

① $\lg P = A - B/(T+C)$

three pressures are presented in Table 6. The satisfactory correlated results were obtained from all the four groups of the experimental data using the three equations. Figs.2 and 3 depict the comparison between the experimental values (100.92kPa) and the calculated values using the Wilson, NRTL, and UNIQUAC equations.

Table 2   Experimental data of butanone (1)-DMF (2) at 100.92kPa

T, K	x_1	y_1
361.8	0.8741	0.9789
368.0	0.7797	0.9513
373.4	0.7053	0.9328
385.4	0.5280	0.8761
394.6	0.3998	0.8312
402.5	0.2941	0.8013
408.0	0.2062	0.7595
411.4	0.1608	0.7312
419.9	0.0614	0.5303
422.4	0.0405	0.4188
422.9	0.0254	0.3082
423.4	0.0221	0.2654
423.7	0.0168	0.2076
424.2	0.0128	0.1544
424.4	0.0109	0.1328
424.7	0.0076	0.0924
425.0	0.0055	0.0651

Table 3   Experimental data of butanone(1)-DMF(2) at 93.32kPa

T, K	x_1	y_1
357.0	0.8983	0.9804
363.5	0.7998	0.9604
370.1	0.7101	0.9411
375.5	0.6296	0.9223
381.8	0.5317	0.8635
390.8	0.4032	0.8045
397.1	0.2995	0.7811
403.3	0.2239	0.7307
409.9	0.1500	0.6289
415.4	0.0766	0.4531
418.4	0.0456	0.3092
420.5	0.0222	0.2004
420.7	0.0210	0.1763

Table 4   Experimental data of butanone(1)-DMF(2) at 79.99kPa

T, K	x_1	y_1
352.3	0.9052	0.9797
357.9	0.8234	0.9581
368.1	0.6596	0.9123
364.1	0.7187	0.9302
372.3	0.5901	0.8914
375.4	0.5506	0.8832
378.8	0.4995	0.8712
385.0	0.4046	0.8256
394.3	0.2570	0.7516
402.3	0.1572	0.6631
409.5	0.0799	0.4742
412.1	0.0483	0.3325
415.9	0.0170	0.1891

Table 5   Experimental data of toluene(1)-DMF(2) at 100.92kPa

T, K	x_1	y_1
386.4	0.9129	0.9412
387.8	0.7899	0.8763
389.4	0.6840	0.8402
390.6	0.6004	0.8015
392.6	0.5133	0.7701
394.6	0.4195	0.7417
397.8	0.3428	0.7109
402.4	0.2689	0.6584
408.9	0.1850	0.5723
414.2	0.1211	0.4795
418.2	0.05897	0.3152
420.3	0.04206	0.2134

Table 6 Absolute average deviations in boiling points and vapor-phase mole fractions of the two binary systems at three pressures

System	Pressure, kPa	Wilson Eq.		NRTL Eq.		UNIQUAC Eq.	
		ΔT	Δy	ΔT	Δy	ΔT	Δy
butanone(1)-DMF(2)	100.92	0.49	0.0050	0.63	0.0045	0.49	0.0077
butanone(1)-DMF(2)	93.32	0.34	0.0067	0.56	0.0024	0.58	0.0031
butanone(1)-DMF(2)	79.99	1.33	0.0049	1.34	0.0031	1.34	0.0049
toluene (1)-DMF(2)	100.92	0.55	0.0050	0.56	0.0071	0.55	0.0068

Note: $\Delta T = \dfrac{1}{N}\sum_{i}^{N}\left|(T_{\text{cal}} - T_{\text{exp}})_i\right|$, $\Delta y = \dfrac{1}{N}\sum_{i}^{N}\left|(y_{\text{cal}} - y_{\text{exp}})_i\right|$.

The general equilibrium relationship between the vapor phase and liquid phase can be expressed as:

$$\hat{\Phi}_i^{\text{V}} y_i P = x_i \gamma_i P_i^{\text{s}} \Phi_i^{\text{s}} \exp\left[\frac{V_i^{\text{L}}\left(P - P_i^{\text{s}}\right)}{RT}\right] \qquad (1)$$

As the binary system reaches vapor-liquid equilibrium at low pressures, the equilibrium relationship can be simplified to:

$$\hat{\Phi}_i^{\text{V}} y_i P = x_i \gamma_i P_i^{\text{s}} \qquad (2)$$

where x and y are the liquid and vapor mole fractions in equilibrium; γ_i is the activity coefficient; P_i^{s} is the vapor pressure of the pure component i, which can be obtained from the Antoine equation; $\hat{\Phi}_i^{\text{V}}$ is the vapor-phase fugacity coefficient, which can be calculated from the second Virial equation:

$$\ln\left(\hat{\Phi}_i^{\text{V}}\right) = \frac{P}{RT}\left(2\sum_j y_i B_{ij} - \sum_i \sum_j y_i y_j B_{ij}\right) \qquad (3)$$

where B is the second molar Virial coefficient, which can be estimated by means of Pitzer and Curl equations[9]. In this study, the Loreatz-Berthlot rules[10] were used for mixing parameters. The required pure component data such as critical properties and acentric factors were directly taken from Ref.[10]. The Antoine coefficients of butanone and toluene were taken from Ref.[7] and DMF from Ref.[8], as shown in Table 1.

The experimental data were tested by the Redlich-Kister thermodynamic consistency using the Herington analysis[11]. According to the analysis, the experimental data are consistent if the Herington's D-J was less than 10. The results of the butanone (1)-DMF (2) system for test in consideration were found to be 6.48 for 100.92kPa, 4.86 for 93.32kPa, and 2.32 for 79.99kPa, respectively. The result of the toluene (1)-DMF (2) system for test in consideration was found to be 5.12. All four sets of data satisfactorily passed the thermodynamic consistency test using the Herington analysis.

The experimental data of the binary systems were then used to obtain the binary parameters of the activity coefficient models. The VLE calculation algorithm was used in combination with the Maximum-Likelihood method. Thus, the pressure deviation was set to be less

than 0.1%, temperature deviation less than 0.1℃, liquid mole fraction deviation less than 0.1%, and the vapor mole fraction deviation to less than 1%.

The energy parameters of the Wilson, NRTL, and UNIQUAC equations were obtained using the following expressions:

Wilson $\qquad \ln\left(\Lambda_{ij}\right) = a_{ij} + \dfrac{b_{ij}}{T}$ $\qquad (4)$

NRTL $\qquad \tau_{ij} = a_{ij} + \dfrac{b_{ij}}{T}$ $\qquad (5)$

UNIQUAC $\qquad \ln\left(\tau_{ij}\right) = a_{ij} + \dfrac{b_{ij}}{T}$ $\qquad (6)$

where a_{ij} and b_{ij} are the binary model parameters regressed.

The parameters for all the models are listed in Tables 7 and 8. Figs.2 and 3 depict the comparison between the experimental values (100.92kPa) and the calculated values using the Wilson, NRTL, and UNIQUAC equations.

Table 7 Parameters for butanone-DMF

Equation	Parameters			
	a_{12}	a_{21}	b_{12}	b_{21}
Wilson	−3.2279	−1.4984	1813.7970	121.2147
NRTL	12.7143	7.1619	−3334.9900	−3306.0100
UNIQUAC	−1.8567	−1.5276	−342.2990	965.8725

Table 8 Parameters for toluene-DMF

Equation	Parameters			
	a_{12}	a_{21}	b_{12}	b_{21}
Wilson	1.5147	−9.6502	−504.4960	3350.8970
NRTL	1.0929	4.4341	−534.8191	−1567.2140
UNIQUAC	−5.0269	1.6001	1607.2620	−427.2884

In this study, a modified Rose–Williams still was used to measure the isobaric vapor-liquid equilibrium data of butanone (1)-DMF (2) at 100.92kPa, 93.32kPa, and 79.99kPa and of toluene (1)-DMF (2) at 100.92kPa. The temperature ranged from 352K to 425K and all the experimental data were tested for thermodynamic consistency. The activity coefficient models of Wilson,
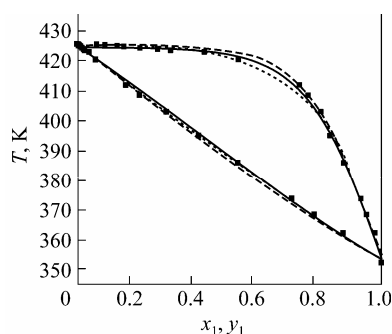
Figure 2 *T-x-y* diagram for butanone(1)- DMF(2) at
100.92kPa

■ experimental data; —— Wilson equation;
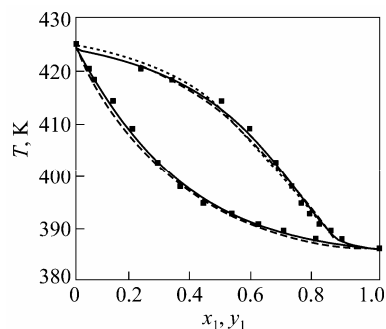– – – NRTL equation; ······ UNIQUAC equation

Figure 3 *T-x-y* diagram for toluene(1)- DMF(2) at
100.92kPa

■ experimental data; —— Wilson equation;
– – – NRTL equation; ······ UNIQUAC equation

NRTL and UNIQUAC equations were adopted to correlate the binary experimental data. The data in this study can be used in the design of the synthesis leather process, and can also enrich the VLE data bank of DMF.

NOMENCLATURE

a_{ij}, b_{ij} parameters
A, B, C Antoine coefficients
B_{ij} second molar Virial coefficient in Eq.(3), m³·mol⁻¹
N number of experimental points
P^S vapor pressure of pure component, Pa
R universal gas constant, J·mol⁻¹·K⁻¹
T equilibrium boiling temperature, K
x mole fraction in liquid phase

y mole fraction in vapor phase
γ liquid-phase activity coefficient
Φ fugacity coefficient

Superscripts
L   liquid phase
S   saturated state
V   vapor phase

Subscripts
cal   calculated value
exp   experimental value
1, 2, i, j components

REFERENCES

1 Gao, Z.H., Ma, Z.L., Chen, L.W.Q., "Isothermal vapor-liquid equilibria of benzene-dimethylformamide and toluene-dimethylformamide systems using a small modified ebulliometer", *Fluid Phase Equilibria*, **173**, 253—262(2000).
2 Chen, Z.X., Hu, W.M., Wang, L.H., Wu, Z.L., "Isobaric vapor-liquid equilibrium of *t*-butyl alcohol-cyclohexanol", *Fluid Phase Equilibria*, **70**, 227—238(1991).
3 Hu, W.M., Shen, L.M., Zhao, L.J., "Measurement of vapor-liquid equilibrium for binary mixtures of phenol-dimethyl carbonate and phenol-methanol at 101.3kPa", *Fluid Phase Equilibria*, **219**, 265—268 (2004).
4 Chen, Z.X., Hu, W.M., "Isobaric vapor-liquid equilibriums of octane-ethyl acetate and octane-isopropyl acetate systems", *Chin. J. Chem. Eng.*, **3**(3), 180—186(1995).
5 Chen, Z.X., Hu, W.M., Lu, J.G., Li, X.M., "Isobaric vapor-liquid equilibrium of systems containing triethyl orthoformate at 101.3 kPa", *Fluid Phase Equilibria*, **154**, 89—98(1999).
6 Ellis, S.R.M., Froome, B.A., "A vacuum vapor-liquid equilibrium still", Chem. Ind., **32**, 237—240(1954).
7 Nickerson, J.K., Kobe, K.A., Mcketta, J.J., "Thermodynamic properties of the methyl ketone series", *J. Phys. Chem.*, **65**, 1037—1043(1961).
8 Gopal, R., Rizvi, S.A., "Vapour pressures of some mono- and di-alkyl substituted aliphatic amides at different temperatures", *J. Indian Chem. Soc.*, **45**(1), 13—16(1968).
9 Pitzer, K.S., Curl, R.F., "The volumetric and thermodynamic properties of fluids. III. Empirical equation for the second virial coefficient1", *J. Am. Chem. Soc.*, **79**(10), 2369—2370(1957).
10 Reid, R.C., Prausnitz, J.M., Poling, B.E., The Properties of Gases and Liquid, 3rd ed., McGraw-Hill Book Company, New York(1977).
11 Fredenslund, A., Gmehling, J., Rasmussen, P., Vapor-Liquid Equilibria Using UNIFAC, Elsevier, Amsterdam(1977).