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Isobaric Vapour-Liquid Equilibrium for Binary System of Trifluoroacetic Acid and Acetone

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Isobaric vapour-liquid equilibrium (VLE) data for trifluoroacetic acid (TFA) and acetone system was measured at 101.33 kPa by using equilibrium still. The results show that TFA and acetone system can form a maximum temperature azeotrope. Thermodynamic consistency of the experimental data was confirmed by means of Herington method. The data was then correlated and calculated by Wilson equation and Vanlaar equation, respectively. Wilson equation is little better than the Vanlaar equation based on the average deviations of temperature and the vapour-phase composition. By Wilson equation the boiling temperature of the azeotrope for the experimental system was identified to be 77.62 ºC and the corresponding composition is 0.2459. These agree well with the experimental data.

Key Words: Acetone, Trifluoroacetic acid, Vapour-liquid equilibrium.

INTRODUCTION

Trifluoroacetic acid (TFA) is an important organic compound and an intermediate in chemical industry and is also widely used in chemical engineering fields because of strong oxidation capability, excellent solubility and high reactive activity[1], so many factories are being confronted with the recovery of TFA from fluid mixtures. However, so far, few relevant isobaric vapour liquid equilibrium (VLE) data have been available in the open literature. No VLE data have been found for the binary systems of TFA + acetone. In this work, the isobaric VLE data were measured for the TFA + acetone binary system using a VLE still. The data will provide a beneficial reference for separation and recovery of TFA from fluid mixtures.

EXPERIMENTAL

All the reagents were of analytical purity grade. The purity of TFA (Shanghai Fu Zhe Chemical Ltd.) is higher than 0.995 (mass fraction, the same below) and 0.999 for acetone (Tianjin University Ke Wei Company), so no further purification was needed.

Apparatus and procedure: An equilibrium still was used to determine the VLE data and it was shown in Fig. 1. About 20-30 mL of TFA + acetone binary liquid mixture was put into the equilibrium still. Then the sample was heated slowly to a certain temperature for about 1 h to make sure that the vapour-liquid equilibrium has been achieved and the temperature was controlled by a small voltage adjuster. A mercury thermometer calibrated by Shanghai Metrology Institution was used for temperature measurement within the accuracy of ± 0.1 ºC. The actual atmospheric pressure was measured by a mercury barometer with the accuracy of ± 50 Pa. When the temperature and the amount of reflux drops (2-3 drops/s) reached stable for more than 5 min, it was believed that the vapour and liquid phases has achieved balance and the corresponding bubble point temperature were recorded. The vapour and liquid samples were determined by acid-base titration[2].

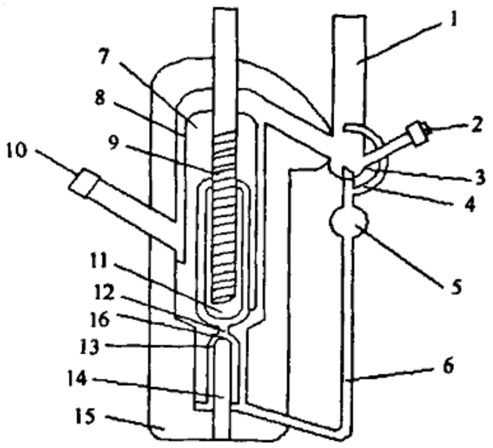

Fig. 1. Diagrammatic sketch of the equilibrium still. (1) Vapour condenser, (2) Vapour sampling port, (3) Vapour sampling cell, (4) Equilibrium tube, (5) Mixing chamber, (6) Reflux tube, (7) Equilibrium chamber, (8) Glass cover, (9) Thermometer well, (10) Liquid sampling port, (11) Liquid storing cell, (12) Lift tube, (13) Boiling room, (14) Heating mantle, (15) Vacuum jacket, (16) Feeding level

In order to verify the reliability of this device, the VLE data of the ethanol + cyclohexane binary system was measured by this device and compared with the literature data[3]. It was found that there was a small deviation between the experimental value and the literature value, which proved the reliability of this device.

RESULTS AND DISCUSSION

Table-1 showed the values of the quantities that characterize the equilibrium states of the liquid and vapour phases, x_i, y_i and t at a pressure of p = 101.33 kPa. The corresponding phase diagram was shown in Fig. 2. As can be seen from Fig. 2, the system TFA + acetone at 101.33 kPa exhibited negative deviation from Raoult's law and a maximum temperature azeotrope was found.

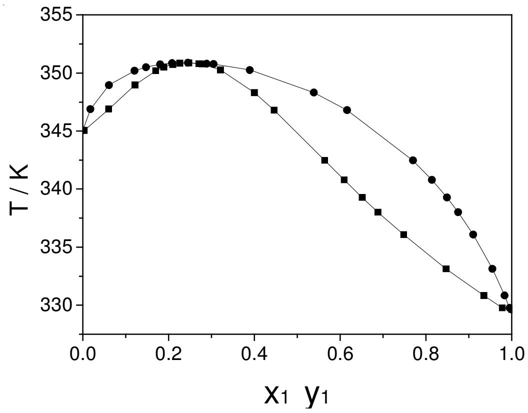

Fig. 2. Vapour-liquid equilibrium phase diagram for the TFA + acetone system at 101.33 kPa

Thermodynamics consistency verification: All experimental data were verified by means of the Herington method to see whether it was in accordance with thermodynamic consistency. According to the Herington method[4], the experimental data are consistent if the Herington's (D – J) was less than 10.

$$D = \frac{|I|}{\Sigma} \times 100$$

$$J = 150 \times \frac{\theta}{T_{min}}$$

where $I = \int_0^1 \ln\left(\frac{\gamma_1}{\gamma_2}\right) dx_1$, $\Sigma = \int_0^1 \left|\ln\left(\frac{\gamma_1}{\gamma_2}\right)\right| dx_1$. $\theta = T_{max} - T_{min}$, T_{max} and T_{min} were the highest and the lowest boiling points in the system, respectively, K. The calculation result was that $|D - J| = 7.692 < 10$, which indicated that all experimental data were in accordance with thermodynamic consistency.

Estimation of critical parameters: Due to the lack of thermodynamic parameters for the TFA, the critical parameters were predicted with the reported method[5]. The critical volume V_c and acentric factor ω were calculated using MXXC and Lee-Kesler method, respectively, the results were: $V_c = 203.2$ cm^3/mol and ω = 0.569.

Correlation: The activity coefficients were calculated from the equation:

$$\gamma_i = \frac{y_i \phi_i p}{x_i \phi_i^s p_i^s}$$

where γ_i is the activity coefficient of component i. p, x_i and y_i are total pressure of the system and the liquid and vapour phase mole fractions in equilibrium. p_i^s is the saturated vapour pressure of pure component i at the system temperature, calculated with the Antoine equation

TABLE-1
VLE DATA OF THE TFA + ACETONE BINARY SYSTEM AND DEVIATIONS AT 101.33 kPa

Temp. (°C)	Experimental value		Wilson equation		Vanlaar equation	
	x_1	y_1	$\|\Delta t\|$	$\|\Delta Y\|$	$\|\Delta t\|$	$\|\Delta Y\|$
71.91	0.3790×10^{-2}	0.0559×10^{-2}	0.34	0.0314	0.53	0.0070
73.74	0.6043×10^{-1}	0.1780×10^{-1}	0.27	0.0108	0.98	0.0157
75.81	0.1219	0.6152×10^{-1}	0.12	0.0178	0.67	0.0035
77.05	0.1700	0.1207	0.16	0.0138	0.16	0.0145
77.36	0.1892	0.1476	0.15	0.0128	0.17	0.0116
77.59	0.2102	0.1807	0.13	0.0131	0.14	0.0066
77.69	0.2267	0.2086	0.11	0.0128	0.16	0.0033
77.73	0.2472	0.2452	0.16	0.0124	0.14	0.0002
77.65	0.2707	0.2891	0.1	0.0107	0.13	0.0027
77.62	0.2786	0.3049	0.12	0.0078	0.01	0.0007
77.11	0.3212	0.3894	0.16	0.0007	0.31	0.0009
75.17	0.4002	0.5390	0.11	0.0053	0.41	0.0016
73.65	0.4465	0.6163	0.28	0.0066	0.55	0.0011
69.32	0.5643	0.7699	0.31	0.0042	0.37	0.0002
67.65	0.6098	0.8141	0.23	0.0030	0.31	0.0005
66.13	0.6520	0.8490	0.24	0.0022	0.23	0.0006
64.87	0.6883	0.8749	0.35	0.0017	0.32	0.0006
62.94	0.7484	0.9106	0.21	0.0008	0.25	0.0008
59.99	0.8471	0.9550	0.01	0.0002	0.12	0.0004
57.68	0.9353	0.9837	0.04	0.0001	0.07	0.0002
56.62	0.9783	0.9949	0.22	0.0002	0.02	0.00004
56.50	1.0000	1.0000	0.40	–	0.40	–

$|\Delta Y| = |y^{exp} - y^{cal}| / y^{cal}$; $|\Delta t| = |t^{exp} - t^{cal}|$.

TABLE-2
BASIC PROPERTIES OF PURE SUBSTANCES

Component	A	B	C	T_c (K)	P_c (KPa)	V_c (cm^3 mol^{-1})
Acetone	7.11714	1210.595	229.664	508.1	4763.29	209
Trifluoroacetic acid	7.47481	1408.69	234.861	491.3	3262.67	203.2

$$\log p_i^s(\text{mmHg}) = A - \frac{B}{T(K)+C}$$

where A, B and C are Antoine constants and T is the temperature in Kelvin. The Antoine constants and critical parameters for TFA and acetone were obtained from the literature[3,6] and were presented in Table-2. ϕ_i, ϕ_i^s are the fugacity coefficients of component i in the vapour mixtures and at saturation, respectively, estimated by using the second virial coefficients state equation[7].

Because the experiment was carried out at 101.33 kPa, the vapour phase could be regarded as ideal gas and the boiling point difference between TFA and acetone was not more than 30 K, so the Wilson and the Vanlaar parameters could be regarded as constant values. In order to find parameters of the equations, activity coefficients were correlated with the Wilson equation and the Vanlaar equation[7]. Estimation of the parameters of the equations was based on minimization of the following objective function (OF):

$$OF = \sum_k \sum_i (\ln \gamma_i^{cal} - \ln \gamma_i^{exp})_k^2 \qquad (2)$$

where k is the number of data points and i the number of components in the mixture. The experimental and calculated values are denoted by the superscripts 'exp' and 'cal', respectively. γ_i^{exp} is calculated with eqn. 1 and γ_i^{cal} is calculated with Wilson equation or by using the Vanlaar equation. The results obtained through simplex search were: $\Lambda_{12} = 4.2061$ and $\Lambda_{21} = 0.484463$ for the Wilson equation, $A_{12} = -2.48139$ and $A_{21} = -0.921$ for the Vanlaar equation. It was, then, used to calculate y_1^{cal} and t^{cal} under corresponding liquid compositions and pressure (101.33 kPa). The temperature and vapour-phase composition obtained from the theoretical calculations using the Wilson equation and the Vanlaar equation were compared with the experimental data. The comparative result was shown in Table-1. The deviations in temperature and vapour-phase composition were given and the max deviations of temperature and the vapour-phase composition between the experimental and the calculated values were: $|\Delta t| = 0.98$ ºC and $|\Delta Y| = 0.0314$, respectively. The differences indicated that Wilson equation and Vanlaar equation can be used to calculate VLE data for TFA and acetone. The calculation of the results can meet the requirements of chemical engineering for the separation of TFA and acetone.

From the data analysis, the average deviations of temperature and the vapour-phase composition between the experimental and the calculated values using the Wilson equation were not more than 0.1918 and 0.0080 ºC, respectively. However, the average deviations of temperature and the vapour-phase composition between the experimental and the calculated values by Vanlaar equation were 0.2932 and 0.0035 ºC. When these results are compared, it can be seen that the Wilson equation is a little better than the Vanlaar equation based on the average deviations of $|\Delta Y|$ and $|\Delta t|$.

Prediction of boiling temperature and composition of azeotrope: As can be seen from Fig. 2, the mixtures of TFA and acetone formed a maximum temperature azeotrope. The location of the azeotropic point was made by using $y_1 - x_1$ *versus* x_1 diagrams in order to determine x_1^{az} at $(y_1 - x_1) = 0$ together with T *versus* x_1 diagrams where T^{az} should be maximum at x_1^{az}. The composition and boiling temperature of the azeotrope obtained were: 0.248 and 77.7 ºC, respectively. The calculated values using the Wilson equation were 0.2459 and 77.62 ºC at 101.33 kPa, which accorded well with the experimental data. The results indicate that the Wilson equation gives satisfactory prediction of the vapour-liquid equilibrium for TFA + acetone binary systems. Moreover, the method will provide theoretical guidance for the research of VLE data in non-ideal behaviour.

Conclusion

The isobaric VLE data were determined for the TFA + acetone binary system and thermodynamic consistency of the experimental VLE data was confirmed by means of Herington method. The isobaric VLE data for the TFA + acetone binary system were correlated and calculated by Wilson equation and Vanlaar equation, respectively and the corresponding model parameters were obtained. The correlation results indicated that Wilson equation and Vanlaar equation can be used to calculate VLE data for TFA and acetone. The Wilson equation is a little better than the Vanlaar equation based on the average deviations of $|\Delta Y|$ and $|\Delta t|$. The results indicated that the models were suitable for the binary system and the data were reliable, so the experimental data and correlation results provided a basic data for separation of the binary systems of TFA + acetone. The TFA and acetone system formed a maximum temperature azeotrope. By Wilson equation the boiling temperature of the azeotrope for the experimental system was identified to be 77.62 ºC and the corresponding composition is 0.2459. These agree well with the experimental data.

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