

## Study and applications of binary and ternary azeotropes<sup>☆</sup>

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### Abstract

Using apparatus designed by ourselves, we obtained data on 11 binary azeotropic systems at normal pressure, and 20 binary and 7 ternary azeotropic systems at subatmospheric pressures. The data obtained for binary azeotropes, were used to predict the azeotropic data and vapor–liquid equilibria for ternary systems, and the heats of vaporization for azeotropic mixtures. In general, the results obtained gave linear plots of the logarithm of pressure versus the reciprocal of temperature and of the azeotrope composition versus temperature. A minimum boiling point azeotrope is usually formed by hydrocarbon–alcohol binary systems. The alcohol content of the azeotropic mixture increases as the pressure is raised, and decreases as the number of carbon atoms is increased (constant pressure).

*Keywords:* Azeotrope; Binary system; Heat of vaporization; Ternary system; VLE

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### 1. Introduction

The properties and behavior of azeotropic mixtures are of key importance in fluid-phase equilibria and solution thermodynamics. There must be a very close relationship between the nature of the azeotropic mixture and its thermodynamic properties. Therefore, the determination of the relationships between the temperature and pressure and the composition of azeotropic mixtures, and using these data

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from binary systems to predict the azeotropic data and the vapor–liquid equilibrium relationship for ternary systems and the heats of vaporization for azeotropic mixtures, is both of general interest in solution theory and of practical value in the azeotropic rectification and production of high-purity chemicals in industry. Much work has been done on azeotropic solutions [1–3], the available data are insufficient to satisfy the needs of research and development.

In the present study azeotropic data were obtained, using the apparatus designed by ourselves, for a total of 38 systems (including binary and ternary systems composed of alcohols, alkanes, ketones and esters) and the inherent regularities of the azeotropic solution were studied. The results obtained were used to predict the vapor–liquid equilibria and heats of vaporization of some related systems. The results thus obtained are in good agreement with data obtained experimentally.

## 2. Experimental

Data were determined experimentally for 11 binary azeotropic systems at atmospheric pressure and 20 systems at subatmospheric pressure, using the differential ebulliometer designed by us [4] and the azeotropy apparatus with rectification method [5], see (Fig. 1). In addition, data were obtained for 7 ternary azeotropic systems at subatmospheric pressure, using the latter apparatus. The experimental data are presented in Tables 1–3. The azeotropic temperature was measured using a standard platinum resistance thermometer with a Keithley 195A 6-digit multi-meter (accuracy 0.001  $\Omega$ , equivalent to 0.01 K). Pressure was measured and controlled by a pressure transducer (accuracy 0.1 kPa). The accuracy of the composition analysis was 0.001 (mole fraction) for binary mixtures and 0.002 for ternary ones. All the chemicals used in the experimental work were examined for impurities by using gas chromatography; no impurity peaks were detected.

## 3. Correlation and prediction of azeotropic data

### 3.1. Correlation of data for binary azeotropic systems

Four variables (temperature, pressure, and the composition of the liquid and the vapor phases) describe the vapor–liquid equilibrium behavior of a binary system. Three of these variables are independent, as shown by the Gibbs–Duhem relationship. At the azeotropic point, the composition of the vapor is the same as that of liquid, and thus only two variables are independent. Therefore, two equations are required to correlate the data on the binary azeotropes. Our results indicate that plots of the logarithm of pressure versus the reciprocal of the azeotropic temperature and of the azeotropic composition versus temperature are generally linear. In the present work, the variation in the azeotropic temperature ( $T_{az}$ ) with the pressure ( $P$ ) is correlated by

$$\ln P = A - B/T_{az} \quad (1)$$

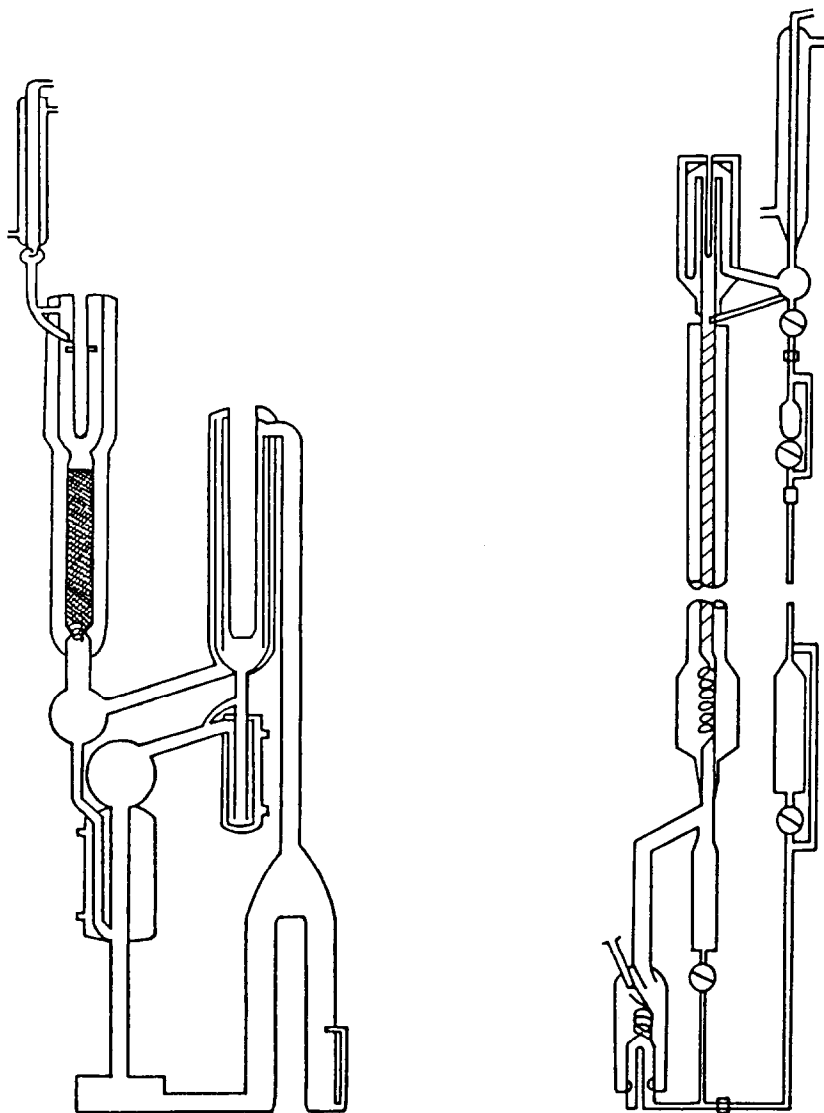


Fig. 1. Scheme of the azeotropy apparatus.

or

$$\ln P = A - B/(T_{az} + C) \quad (2)$$

and the relationship between the azeotropic composition ( $x_{1,az}$ ) and temperature is

$$x_{1,az} = a + bT_{az} \quad (3)$$

Table 1  
Experimental data for binary azeotropic systems obtained at 101.33 kPa

System	<i>T</i> /K	<i>x</i> <sub>1</sub>
Water(1)–ethanol	351.34	0.1089
Water(1)–tetrahydrofuran	336.32	0.1923
Methanol(1)–toluene	336.41	0.6172
Methanol(1)–benzene	330.83	0.4886
Ethanol(1)–n-hexane	331.96	0.2639
Methyl acetate(1)–cyclohexane	344.43	0.3454
Ethanol(1)–cyclohexane	338.05	0.4509
1-Propanol(1)–cyclohexane	347.58	0.2482
1-Butanol(1)–cyclohexane	352.70	0.0830
1-Propanol(1)–benzene	350.00	0.2064
Benzene(1)–cyclohexane	350.65	0.4515

Comparison of calculated values with experimentally determined data shows that Eq. (2) is better than Eq. (1) at predicting the azeotropic temperature and pressure of binary systems. The average relative deviation in the calculated values from the experimental pressure data is less than 0.1%, and the average absolute deviation in azeotropic compositions is not greater than a mole fraction of 0.001.

### 3.2. Prediction of multicomponent azeotropic data

Multicomponent data can be predicted by using the activity-coefficient method and the corresponding binary azeotropic data. In the present study the Wilson model was employed. According to the equilibrium criterion, the fugacities of the vapor and liquid phases must be equal when equilibrium is achieved. At the azeotropic point, the composition of the vapor is the same as that of the liquid, and thus the vapor–liquid equilibrium relationship becomes

$$\gamma_i = Z_i P / p_i^0 \quad (4)$$

where the correction factor for the vapor phase ( $Z_i$ ) is given by the  $B$ -truncated virial equation:

$$Z_i = \exp [(B_i - V_i^L)(P - p_i^0) / RT]$$

The second virial coefficients ( $B_i$ ) were calculated by using the Tsonopoulos [6] method, and the vapor pressure ( $p_i^0$ ) was calculated using Antoine equation. A pair of activity coefficients can be exactly calculated from temperature and pressure data (except composition data) by using Eq. (4). The activity coefficients and azeotropic composition obtained are substituted in the two-component Wilson equation which is solved iteratively to obtain a pair of Wilson energy parameters.

An attempt has been made to predict multicomponent azeotropes, including ternary systems, by using only the corresponding binary azeotropic data. The azeotropic point is a special point in the vapor–liquid equilibrium, at which the

Table 2

Experimental data for binary azeotropic systems, obtained at subatmospheric pressures

<i>P</i> /kPa	<i>T</i> /K	<i>x</i> <sub>1</sub>	<i>P</i> /kPa	<i>T</i> /K	<i>x</i> <sub>1</sub>	<i>P</i> /kPa	<i>T</i> /K	<i>x</i> <sub>1</sub>	<i>P</i> /kPa	<i>T</i> /K	<i>x</i> <sub>1</sub>
<i>Methanol</i> (1)– <i>n</i> -hexane			<i>1-Propanol</i> (1)– <i>n</i> -heptane								
26.66	292.01	0.4441	66.66	312.38	0.4851	19.60	316.78	0.3246	56.28	341.47	0.4030
39.99	300.59	0.4622	79.99	317.02	0.4919	25.94	322.90	0.3432	70.50	347.59	0.4242
53.33	307.17	0.4757	101.32	322.64	0.5018	33.67	328.93	0.3625	88.60	353.69	0.4428
<i>Methanol</i> (1)– <i>n</i> -heptane			<i>1-Butanol</i> (1)– <i>n</i> -hexane								
26.66	300.75	0.7314	66.66	321.80	0.7420	31.12	308.39	0.0190	67.92	329.24	0.0300
39.99	309.56	0.7366	79.99	326.37	0.7498	36.61	312.55	0.0210	77.83	333.38	0.0340
53.33	316.42	0.7406	101.32	331.96	0.7532	45.29	318.07	0.0250	89.05	337.49	0.0370
<i>Methanol</i> (1)–acetone			<i>t-Butanol</i> (1)–benzene								
26.66	294.69	0.0711	66.66	316.91	0.1813	54.03	322.86	0.0270	101.33	341.46	0.0390
39.99	304.09	0.1061	79.99	321.80	0.2112	64.20	327.75	0.0290			
53.33	311.13	0.1469	101.32	328.43	0.2506	13.59	296.96	0.1975	66.69	335.37	0.3348
<i>Methanol</i> (1)–methylacetate			<i>1-Pentanol</i> (1)– <i>n</i> -heptane								
26.66	294.09	0.2756	66.66	315.63	0.3089	26.43	312.16	0.2504	79.76	340.34	0.3548
39.99	303.16	0.2949	79.99	320.49	0.3247	40.23	322.16	0.2892	101.51	347.19	0.3775
53.33	309.99	0.3011	101.32	326.82	0.3390	53.29	329.36	0.3129			
<i>Ethanol</i> (1)– <i>n</i> -hexane			<i>t-Butanol</i> (1)–cyclohexane								
45.34	311.07	0.2787	68.88	321.35	0.3089	13.46	295.35	0.1563	66.62	332.92	0.3218
56.43	316.39	0.2949	87.31	327.49	0.3249	26.51	310.37	0.2205	80.16	337.83	0.3414
<i>Ethanol</i> (1)– <i>n</i> -heptane			<i>Chloroform</i> (1)– <i>n</i> -hexane								
18.94	306.21	0.5631	57.98	330.53	0.6150	39.75	319.92	0.2645	101.40	344.28	0.3717
23.24	310.38	0.5725	70.66	335.28	0.6254	53.60	327.23	0.2958			
30.65	316.19	0.5847	85.69	340.09	0.6365	<i>1-Pentanol</i> (1)– <i>n</i> -heptane					
38.42	321.10	0.5957	101.33	344.44	0.6447	18.73	322.82	0.0280	50.35	349.16	0.0400
47.96	326.11	0.6064				22.99	327.72	0.0300	60.62	354.65	0.0440
<i>Ethanol</i> (1)–chloroform			<i>Acetone</i> (1)–methylacetate								
45.70	310.79	0.0959	89.67	328.89	0.1405	28.75	333.63	0.0320	73.30	360.39	0.0510
55.20	315.59	0.1072	100.39	332.18	0.1492	35.36	339.15	0.0350	88.95	366.74	0.0600
77.19	324.64	0.1290				42.14	344.01	0.0380	101.33	370.99	0.0690
<i>Ethanol</i> (1)–ethylacetate			<i>Methylacetate</i> (1)– <i>n</i> -hexane								
15.71	300.37	0.2948	66.35	333.54	0.4144	26.66	288.27	0.6248	66.66	311.02	0.6381
22.32	307.76	0.3206	87.98	341.05	0.4448	39.99	297.95	0.6302	99.99	315.97	0.6415
48.56	325.67	0.3839	101.07	344.87	0.4616	53.33	305.24	0.6351	101.32	322.78	0.6433
<i>Ethanol</i> (1)–benzene			<i>1-Propanol</i> (1)– <i>n</i> -hexane								
11.73	291.59	0.3230	79.67	334.50	0.4310	55.35	321.56	0.1175	85.00	333.28	0.1419
29.40	310.51	0.3660	91.63	338.20	0.4425	68.75	327.33	0.1297	101.33	338.55	0.1537
56.90	325.91	0.4056	101.33	340.95	0.4475	<i>1-Butanol</i> (1)– <i>n</i> -heptane					
<i>1-Propanol</i> (1)– <i>n</i> -hexane			<i>Methylacetate</i> (1)– <i>n</i> -hexane								
12.93	312.34	0.0984	48.78	345.21	0.1730	26.66	290.34	0.6461	66.66	312.74	0.6565
23.61	326.42	0.1274	74.47	357.58	0.1999	39.99	299.76	0.6464	79.99	317.94	0.6576
36.12	337.08	0.1518				53.33	306.94	0.6479	101.32	324.80	0.6655

Table 3  
Experimental data for ternary azeotropic systems, obtained at subatmospheric pressures

Systems	<i>P</i> /kPa	<i>T</i> /K	<i>x</i> <sub>1</sub>	<i>x</i> <sub>2</sub>	<i>P</i> /kPa	<i>T</i> /K	<i>x</i> <sub>1</sub>	<i>x</i> <sub>2</sub>
Methanol(1)–methylacetate(2)– <i>n</i> -heptane	26.66	288.40	0.2814	0.3214	66.66	309.59	0.3156	0.2986
	39.99	297.27	0.2920	0.3159	79.99	314.47	0.3201	0.2940
	53.33	304.03	0.3035	0.3088	101.32	320.48	0.3326	0.2885
Methanol(1)–Acetone(2)–methylacetate	26.66	293.33	0.1352	0.7319	66.66	315.63	0.2335	0.1876
	39.99	303.05	0.1733	0.4780	79.99	320.18	0.2606	0.1237
	53.33	309.91	0.2028	0.2940	101.32	326.52	0.3054	0.0632
Methanol(1)–Acetone(2)– <i>n</i> -heptane	26.66	287.96	0.1435	0.4874	66.66	309.69	0.2349	0.3801
	39.99	297.36	0.1808	0.4350	79.99	314.29	0.2630	0.3604
	53.33	303.95	0.2098	0.4136	101.32	320.59	0.3113	0.3346
Acetone(1)–methylacetate(2)– <i>n</i> -heptane	26.66	288.35	0.5879	0.0283	66.66	310.99	0.6029	0.0306
	39.99	297.93	0.5941	0.0284	79.99	315.97	0.6028	0.0342
	53.33	305.09	0.5944	0.0316	101.32	322.78	0.6063	0.0374
Benzene(1)– <i>n</i> -heptane(2)–ethanol	14.69	296.26	0.6241	0.0597	40.69	317.92	0.5809	0.0307
	21.18	303.46	0.6052	0.0516	47.09	321.27	0.5723	0.0290
	25.06	307.02	0.6012	0.0486	100.39	340.71	0.5316	0.0145
Benzene(1)–cyclohexane(2)–isopropanol	13.61	294.14	0.3090	0.5011	66.63	330.55	0.2130	0.4653
	26.64	307.76	0.2873	0.4701	80.02	335.42	0.2002	0.4642
	40.02	317.20	0.2753	0.4610	101.36	342.19	0.1467	0.4723
	53.37	324.72	0.2423	0.4701				
Benzene(1)–cyclohexane(2)– <i>t</i> -butanol	13.61	294.91	0.3288	0.5292	66.63	332.45	0.2065	0.5146
	26.64	309.55	0.2925	0.5059	80.02	337.73	0.1652	0.5144
	40.02	317.31	0.2573	0.5076	101.36	344.25	0.1182	0.5337
	53.37	326.88	0.2357	0.5144				

relative volatility of each component is unity. Thus the problem of predicting data for multicomponent azeotropes involves searching for a set of equilibrium vapor composition parameters that exactly equals those for the coexisting liquid. For ternary systems, three pairs of Wilson energy parameters can be obtained from the three corresponding binary azeotropes, and the activity coefficients of the three components can be calculated via the three-component Wilson equation. Thus the ternary azeotrope can be predicted. The predicted results are compared with experimental data in Table 4.

#### 4. Prediction of vapor–liquid equilibria and heat of vaporization

##### 4.1. Prediction of vapor–liquid equilibria

As described above (Section 3.2.), two parameters of the model can be determined from the azeotropic point of a binary system. The activity coefficients and

Table 4  
Predicted azeotropic data for ternary systems

Predicted					Deviations from experimental data			
<i>P</i> /kPa	<i>T</i> /K	<i>x</i> <sub>1</sub>	<i>x</i> <sub>2</sub>	<i>x</i> <sub>3</sub>	$\Delta T$	$\Delta x_1$	$\Delta x_2$	$\Delta x_3$
<i>Benzene</i> (1)– <i>n</i> - <i>heptane</i> (2)– <i>ethanol</i>								
14.69	295.87	0.6160	0.0499	0.3341	–0.39	–0.0081	–0.0098	0.0179
21.18	303.33	0.5944	0.0516	0.3540	–0.13	–0.0108	0.0000	0.0108
25.06	306.90	0.5940	0.0525	0.3535	–0.12	–0.0072	0.0039	0.0033
40.69	317.80	0.5843	0.0227	0.3930	–0.12	0.0034	–0.0080	0.0046
47.09	321.25	0.5792	0.0188	0.4020	–0.02	0.0069	–0.0102	0.0033
100.39	340.49	0.5292	0.0168	0.4540	–0.22	–0.0024	0.0023	0.0001
<i>Benzene</i> (1)– <i>cyclohexane</i> (2)– <i>isopropanol</i>								
13.61	294.08	0.3049	0.5045	0.1906	–0.06	–0.0041	0.0034	0.0007
26.64	307.94	0.2879	0.4766	0.2355	0.18	0.0006	0.0065	–0.0071
40.02	317.37	0.2661	0.4651	0.2688	0.17	–0.0092	0.0041	0.0051
53.37	324.56	0.2438	0.4604	0.2958	–0.16	0.0015	–0.0097	0.0082
66.63	330.42	0.2209	0.4599	0.3192	–0.13	0.0079	–0.0054	–0.0025
80.02	335.48	0.1969	0.4628	0.3403	0.06	–0.0033	–0.0014	0.0047
101.36	342.30	0.1559	0.4732	0.3709	0.11	0.0092	0.0009	–0.0101
<i>Benzene</i> (1)– <i>cyclohexane</i> (2)– <i>t</i> - <i>butanol</i>								
13.61	294.86	0.3332	0.5235	0.1434	–0.05	0.0044	–0.0057	0.0014
26.64	309.64	0.3007	0.5071	0.1922	0.09	0.0082	0.0012	–0.0094
40.02	319.42	0.2675	0.5033	0.2292	0.11	0.0102	–0.0043	–0.0059
53.37	326.73	0.2344	0.5054	0.2602	–0.15	–0.0013	–0.0090	0.0103
66.63	332.59	0.2011	0.5114	0.2875	0.14	–0.0054	–0.0032	0.0086
80.02	337.56	0.1666	0.5207	0.3127	–0.17	0.0014	0.0063	–0.0077
101.36	344.17	0.1086	0.5415	0.3499	–0.08	–0.0096	0.0078	0.0018

vapor–liquid equilibria for binary, ternary and other multicomponent systems can also be predicted via the activity coefficient model. In this work, the vapor–liquid equilibria for some relevant ternary systems were predicted by using the Wilson equation. The results obtained are compared with experimental data from the literature in Table 5.

#### 4.2. Prediction of the heat of vaporization

The differential heat of vaporization, the integral heat of vaporization, the isobaric and isothermal heats of vaporization and the differential heat of condensation of an azeotropic mixture all have the same value. Thus the heat of vaporization of an azeotrope has a special meaning in the study of the thermodynamic properties of solutions.

The Watson [10] equation, which is used to calculate the heat of vaporization of pure substances, can be extended to the azeotropic mixtures:

Table 5  
Predicted vapor–liquid equilibria for Ternary systems

Constant <i>T</i> or <i>P</i>	No. of points	<i>T</i> / <i>K</i> <i>P</i> / <i>kPa</i>	$\Delta P/\Delta T$	$\Delta y_1$	$\Delta y_2$	$\Delta y_3$	Ref.
<i>Ethanol</i> (1)– <i>benzene</i> (2)– <i>cyclohexane</i>							
<i>T</i>	19	278.15	1.69	0.0113	0.0103	0.0102	7
<i>P</i>	19	40.00	0.53	0.0154	0.0101	0.0101	7
<i>P</i>	19	101.33	0.68	0.0100	0.0071	0.0073	7
<i>P</i>	57	101.33	0.56	0.0151	0.0124	0.0134	7
<i>1-Propanol</i> (1)– <i>Benzene</i> (2)– <i>Cyclohexane</i>							
<i>P</i>	56	101.33	0.59	0.0054	0.0149	0.0200	8
<i>P</i>	26	101.33	1.10	0.0242	0.0060	0.0252	7
<i>Ethanol</i> (1)– <i>benzene</i> (2)– <i>n-heptane</i>							
<i>P</i>	54	24.00	1.07	0.0179	0.0173	0.0086	7
<i>P</i>	50	53.33	0.50	0.0161	0.0098	0.0111	7
<i>P</i>	47	101.33	0.39	0.0142	0.0074	0.0108	7
<i>P</i>	31	101.33	0.47	0.0080	0.0054	0.0119	9
<i>1-Propanol</i> (1)– <i>benzene</i> (2)– <i>n-heptane</i>							
<i>T</i>	77	348.15	1.19	0.0137	0.0152	0.0138	7
<i>Ethanol</i> (1)– <i>chloroform</i> (2)– <i>n-hexane</i>							
<i>T</i>	36	308.15	1.50	0.0108	0.0137	0.0202	7
<i>T</i>	45	318.15	0.84	0.0093	0.0185	0.0204	7
<i>T</i>	36	328.15	1.29	0.0077	0.0094	0.0112	7
<i>P</i>	36	101.33	1.57	0.0124	0.0107	0.0150	7

$$L_v = L'_v \left( \frac{1 - T_{rm}}{1 - T'_{rm}} \right)^K \quad (5)$$

where  $T_{rm}$  is the reduced temperature ( $T/T_c$ ) for the mixture, and the prime denotes the reference state. The critical temperature for the mixture can be calculated using Li's [11] mixing rule:

$$T_{cm} = \frac{\sum_{i=1}^m x_i v_{ci}^L}{\sum_{j=1}^m x_j v_{cj}^L} T_{ci}$$

where  $T_{ci}$  and  $V_{ci}$  are the critical temperature and the critical volume of component  $i$ ; these values were taken from the literature [12].

To calculate  $L_v$  using Eq. (5), it is necessary to know the heat of vaporization of the azeotrope at some other temperature ( $L'_v$ ). In the present work, the heat of vaporization of the azeotropic mixture at a pressure of 66.66 kPa was taken as the reference state to ensure that the pressure was within the experimental pressure range for all systems. The value of  $K$  in Eq. (5) was optimized by using the least-squares technique ( $K = 0.14$ ). The calculated results are presented in Table 6.



Table 6  
The heat of vaporization for azeotropic mixtures

<i>T</i> /K	$x_1$	$L_v$	<i>T</i> /K	$x_1$	$L_v$
<i>Ethanol</i> (1)– <i>n</i> -hexane			<i>n</i> -Propanol(1)– <i>n</i> -hexane		
308.15	0.2711	32.97	323.15	0.1208	31.19
313.15	0.2852	32.86	328.15	0.1314	31.07
318.15	0.2992	32.74	333.15	0.1420	30.95
323.15	0.3133	32.62	338.15	0.1526	30.83
328.15	0.3273	32.49	<i>n</i> -Pentanol(1)– <i>n</i> -heptane		
<i>Ethanol</i> (1)– <i>n</i> -heptane			323.15	0.0287	34.35
308.15	0.5676	37.95	328.15	0.0295	34.24
313.15	0.5783	37.83	333.15	0.0311	34.12
318.15	0.5889	37.71	338.15	0.0334	34.01
323.15	0.5996	37.59	343.15	0.0364	33.89
328.15	0.6103	37.46	348.15	0.0401	33.77
333.15	0.6210	37.33	353.15	0.0446	33.64
338.15	0.6317	37.20	358.15	0.0498	33.52
343.15	0.6424	37.06	363.15	0.0557	33.39
<i>n</i> -Propanol(1)– <i>n</i> -heptane			<i>Ethanol</i> (1)–ethylacetate		
318.15	0.3282	37.39	303.15	0.3043	35.84
323.15	0.3443	37.27	308.15	0.3211	35.73
328.15	0.3605	37.15	313.15	0.3384	35.61
333.15	0.3767	37.02	318.15	0.3563	35.49
338.15	0.3928	36.90	323.15	0.3748	35.36
343.15	0.4090	36.77	328.15	0.3937	35.24
348.15	0.4252	36.63	333.15	0.4132	35.11
353.15	0.4413	36.50	338.15	0.4332	34.98
<i>n</i> -Butanol(1)– <i>n</i> -hexane			343.15	0.4538	34.84
308.15	0.0184	30.53	<i>Ethanol</i> (1)–chloroform		
313.15	0.0214	30.43	313.15	0.1013	30.97
318.15	0.0245	30.32	318.15	0.1138	30.87
323.15	0.0275	30.20	323.15	0.1262	30.77
328.15	0.0305	30.09	328.15	0.1386	30.67
333.15	0.0335	29.97	333.15	0.1511	30.56
338.15	0.0366	29.85	<i>Chloroform</i> (1)– <i>n</i> -hexane		
<i>n</i> -Butanol(1)– <i>n</i> -heptane			318.15	0.7368	29.47
313.15	0.0989	35.72	323.15	0.7426	29.37
318.15	0.1103	35.61	328.15	0.7483	29.27
323.15	0.1217	35.50	333.15	0.7541	29.17
328.15	0.1330	35.38	<i>Ethanol</i> (1)–benzene		
333.15	0.1444	35.27	293.15	0.3267	34.60
338.15	0.1558	35.15	303.15	0.3488	34.42
343.15	0.1672	35.02	313.15	0.3728	34.22
348.15	0.1785	34.90	323.15	0.3986	34.02
353.15	0.1899	34.77	333.15	0.4262	33.80
			343.15	0.4557	33.57

## 5. Results and discussion

Azeotropic data were determined experimentally by using the apparatuses designed by ourselves for 11 binary systems at atmospheric pressure, and 20 binary and 7 ternary systems at subatmospheric pressures. In general, the variation of the azeotropic temperature with pressure can be correlated by using an Antoine-like equation, and the plot of azeotropic composition versus temperature is linear.

The Wilson activity coefficient model can be used to predict the azeotropic composition and vapor–liquid equilibria of multicomponent systems, using only the data for corresponding binary azeotropes.

The extended Watson equation can be used to calculate the heat of vaporization of the azeotropic mixtures.

Binary hydrocarbon–alcohol systems usually form a minimum boiling point azeotrope. This might be a special feature of these asymmetric systems. The highly polar molecules of the low molecular weight alcohols associate with each other via hydrogen bonding. When nonpolar or weakly polar hydrocarbons are added to the alcohols, the degree of association of the alcohols and the interactions between the molecules in the mixture are decreased. The molecules in the liquid are thus more readily evaporated. Therefore, a minimum boiling point azeotrope is easily formed for hydrocarbon–alcohol systems over a wide range of pressures.

The alcohol content of the azeotropic mixture increases as the pressure is raised (see Tables 1–3). The association interaction between alcohol molecules makes the heat of vaporization larger than that for hydrocarbons. Thus the rate of change in the boiling point of alcohols with the pressure is slower than that for hydrocarbons, and the alcohol content of the azeotropic mixture increases as the pressure is raised.

The alcohol content of the azeotropic mixture decreases as the number of carbon atoms is increased (at constant pressure). For example, at atmospheric pressure, the mole fractions of methanol, ethanol, 1-propanol and 1-butanol are 0.5018, 0.2639, 0.1537 and 0.0390, respectively, in the *n*-alcohol–*n*-hexane azeotropic mixtures. Under the same conditions, the amount of branched-chain alcohol in the azeotropic mixture is greater than the amount of straight-chain alcohol. For example, at normal pressure, the mole fraction of *t*-butanol in the *t*-butanol–cyclohexane azeotropic mixture is 0.3717, whilst the mole fraction of 1-butanol in the 1-butanol–cyclohexane azeotropic mixture is 0.0830.

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## References

- [1] D.R. Lide, CRC Handbook of Chemistry and Physics, CRC Press, Ann Arbor, Boca Raton, FL/Boston, 71st edn., 1990–1991.

- [2] L.H. Horsley, *Azeotropic Data*, Vols. I–III, American Chemical Society, Washington, DC, 1953, 1962, 1973.
- [3] W. Malesinski, *Azeotropy and Other Theoretic Problems of Vapor–Liquid Equilibrium*, Interscience, New York, 1965.
- [4] G.-H. Chen, Z.-H. Cao and S.-J. Han, *Acta Petrol. Sin.*, 10(2) (1994) 100.
- [5] Y.-Z. Liao, J.-B. Bao and S.-J. Han, *Petrochem. Technol. (China)*, 20 (1991) 171.
- [6] C. Tsionopoulos, *AIChE J.*, 20 (1974) 263.
- [7] J. Gmehling and U. Onken, *Vapor–Liquid Equilibrium Data Collection*, Vol. 1, Part 2a, DECHEMA, 1977.
- [8] T. Haiki, K. Tochiji and K. Kojima, *Fluid Phase Equil.*, 26 (1986) 83.
- [9] Q. Wang, G.-H. Chen and S.-J. Han, *Chem. J. Chinese Univ.*, 4 (1990) 389.
- [10] K.M. Watson, *I.E.C.*, 35 (1943) 398.
- [11] C.C. Li, *Can. J. Chem. Eng.*, 49 (1972) 709.
- [12] R.C. Reid, J.M. Prausnitz and T.K. Sherwood, *The Properties of Gases and Liquids*, McGraw-Hill, New York, 3rd edn., 1977.