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Binary Isobaric Vapor−Liquid Equilibria of Ethanolamines + Water

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Binary vapor−liquid equilibria for monoethanolamine + water at pressures of 101.33 kPa and 66.66 kPa and diethanolamine + water and monoethanolamine + diethanolamine at 6.66 kPa were measured. The modified UNIFAC model was used to calculate the results.

Introduction

Ethanolamines have been widely used in the chemical industry since the 1980s. Although new tube reaction technology has been applied in large scale chemical plants, the isobaric vapor−liquid equilibrium data of ethanolamine + water over the whole composition range have not appeared in the literature. Touhara et al. (1982) measured the vapor pressure of monoethanolamine + water at 298.15 K and 308.15 K by a static method. Nath et al. (1983) also determined isothermal vapor−liquid equilibria of monoethanolamine + water ($p-T-x$) by a static method.

The normal boiling points of ethanolamines are quite high, so experiments can often be operated in vaccum conditions. This work intended to determine the vapor−liquid equilibrium data of ethanolamine and water systems to meet the need of design and optimization of refined processes of ethanolamine products.

Experimental Apparatus and Results

The modified Rose−Williams still is shown in Figure 1. The mixtures in reboiler 1 are brought to boiling by an electric heater. The equilibrium vapor from chamber 2 is condensed in port 4 and dropped into 8; here, it is mixed with the equilibrium liquid from chamber 2 by a magnetic stirrer. Then, they go up to the reboiler again and complete the normal circulation of vapor and liquid in the still. The samples of vapor and liquid were taken from 5 and 7 simultaneously. The pressure of the system was controlled within ±133 Pa by a pressure regulator. The equilibrium temperature was measured with a calibrated mercury thermometer graduated in 0.1 K.

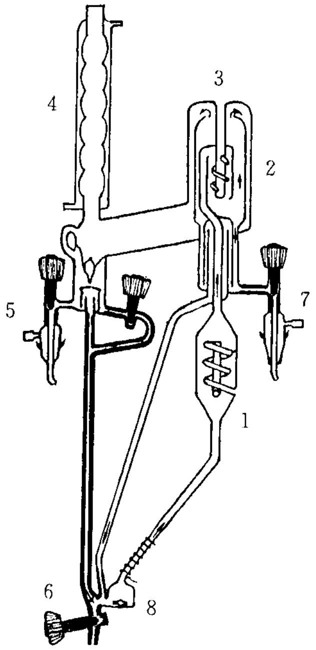

Figure 1. Equilibrium still; (1) reboiler; (2) equilibrium chamber; (3) thermometer well; (4) condenser; (5) vapor sampler; (6) exit valve; (7) liquid sampler; (8) mixing cell.

Table 1. Experimental Equilibrium Data for Ethanol (1) + Water (2) at 101.33 kPa[a]

this work		Stabnikov et al.[b]	
x_1	y_1	x_1	y_1
0.0043	0.0498	0.0040	0.0421
0.0497	0.3230	0.0500	0.3245
0.0983	0.4349	0.0950	0.4283
0.2546	0.5620	0.2500	0.5505
0.3210	0.5816	0.3200	0.5805
0.3971	0.6128	0.4000	0.6102
0.5706	0.6807	0.5700	0.6810
0.6729	0.7352	0.6700	0.7365
0.7112	0.7592	0.7100	0.7590
0.8390	0.8388	0.8400	0.8470
0.9106	0.9082	0.9100	0.9075

[a] x_1 and y_1 are mole fractions of ethanol. [b] Cited partly.

Table 2. Experimental and Calculated Data for Water (1) + MEA (2) at 101.33 kPa

T/K	x_1	y_1	ΔT[a]	Δy_1[b]
443.38	0.0000	0.0000	−0.17	0.0006
431.85	0.0736	0.3411	2.49	0.0001
424.76	0.1322	0.5129	2.89	−0.0075
420.42	0.1799	0.6252	2.45	−0.0193
415.92	0.2522	0.7344	−0.83	−0.0044
410.94	0.2948	0.7878	0.082	−0.0102
406.83	0.3322	0.8312	0.78	−0.0158
394.88	0.4694	0.9146	1.74	0.0024
393.25	0.5080	0.9293	0.72	0.0055
387.85	0.6125	0.9596	−0.22	−0.0005
378.37	0.8238	0.9883	0.01	−0.0003
376.88	0.8615	0.9914	0.24	0.0000
374.09	0.9517	0.9974	0.36	0.0003
373.15	1.0000	1.0000	0.01	0.0000
AAD			0.93	0.0048

[a] $\Delta T = T_{\mathrm{cal}} - T_{\mathrm{exp}}$; AAD of $T = (1/N)\sum_i^N|\Delta T_i|$. [b] $\Delta y_1 = y_{\mathrm{cal},1} - y_{\mathrm{exp},1}$; AAD of $y = (1/N)\sum_i^N|\Delta y_i|$.

The liquid and vapor compositions (x and y) were determined using the standard curve of refraction index vs mole fraction of the binary mixture at 20 °C. The maximum error in the composition measurement is 0.001 mole fraction.

The experimental apparatus was tested by measuring the vapor−liquid equilibria of ethanol + water at 101.33

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Table 3. Experimental and Calculated Data for Water (1) + MEA (2) at 66.66 kPa

T/K	x_1	y_1	ΔT	Δy_1
431.39	0.0000	0.0000	−0.13	0.0000
420.53	0.0967	0.3589	−0.28	0.0118
416.60	0.1332	0.4945	−0.66	0.0071
413.33	0.1695	0.5813	−1.71	0.0036
407.18	0.2107	0.6781	−0.35	−0.0035
403.30	0.2589	0.7537	−1.84	0.0016
395.37	0.3362	0.8425	−1.69	0.0000
391.37	0.3861	0.8848	−2.00	−0.0042
385.73	0.4477	0.9210	−0.52	−0.0052
380.82	0.5419	0.9542	−0.90	0.0000
375.17	0.6359	0.9732	0.00	−0.0001
367.96	0.8363	0.9921	−1.15	0.0004
365.60	0.8550	0.9937	0.55	−0.0001
362.81	0.9509	0.9982	0.29	0.0003
361.75	1.0000	1.0000	0.01	0.0000
AAD			0.81	0.0025

Table 4. Experimental and Calculated Data for Water (1) + DEA (2) at 6.66 kPa

T/K	x_1	y_1	ΔT	Δy_1
458.64	0.0000	0.0000	0.10	−0.0012
456.17	0.0102	0.2600	−0.67	0.0213
444.20	0.0221	0.4821	1.48	0.0049
424.32	0.0378	0.7792	−2.23	0.0413
414.40	0.0429	0.9122	−1.71	0.0019
399.23	0.0515	0.9732	1.25	−0.0232
360.20	0.1179	0.9908	1.48	0.0013
340.47	0.3010	0.9940	−0.62	0.0002
311.29	1.0000	1.0000	0.14	0.0006
AAD			1.08	0.011

Table 5. Experimental and Calculated Data for MEA (1) + DEA (2) at 6.66 kPa

T/K	x_1	y_1	ΔT	Δy_1
458.64	0.0000	0.0000	0.58	0.0012
456.68	0.0051	0.1321	0.36	−0.0253
448.56	0.0202	0.3222	2.17	0.0280
444.35	0.0393	0.5781	−0.95	−0.0352
431.17	0.0712	0.7250	2.05	−0.0069
419.07	0.1231	0.8306	2.83	0.0208
409.57	0.1893	0.9225	2.53	−0.0070
397.99	0.3503	0.9717	−0.48	0.0002
386.77	0.5145	0.9841	1.74	0.0038
376.64	0.7700	0.9932	2.74	0.0039
373.79	1.0000	1.0000	0.37	0.0001
AAD			1.53	0.012

Table 6. Thermodynamic Consistency Test for Experimental Data of Water (1) + MEA (2)

system	θ	T_{min}/K	D	J
101.33 kPa	70.23	373.15	1.24	28.22
66.66 kPa	69.64	361.75	13.84	28.88

kPa. The results are listed in Table 1. It can be seen that the present data agree well with those of Stabnikov et al. (cited from Gmehling and Onken, 1977).

MEA and DEA are products of Shanghai Third Chemical Reagent Co. and were purified further by distillation in our laboratory. The purity was more than 99.9%. Water used in this work was refined from nonionic water.

The isobaric vapor−liquid equilibria for water (1) + MEA (2) at pressures of 101.33 kPa and 66.66 kPa, water (1) + DEA (2) at 6.66 kPa, and MEA (1) + DEA (2) at 6.66 kPa were determined and listed in Tables 2−5.

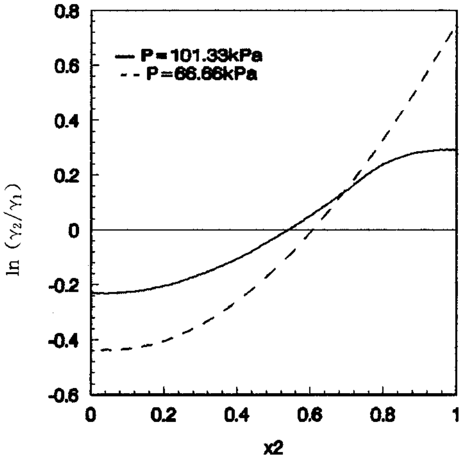

Figure 2. $\ln(\gamma_2/\gamma_1) \sim x_2$ diagram for the water (1) + MEA (2) system.

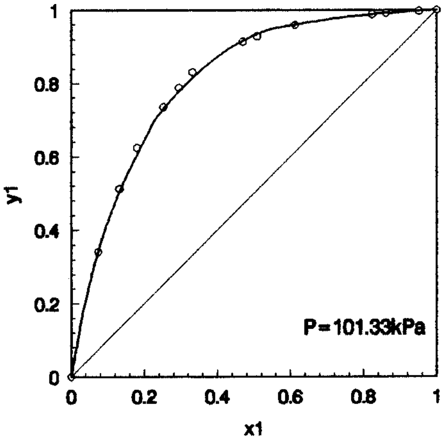

Figure 3. $y \sim x$ diagram for the water (1) + MEA (2) system at 101.33 kPa: (○) experimental; (—) calculated.

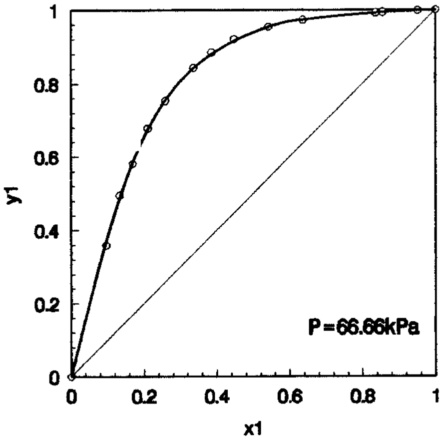

Figure 4. $y \sim$ x diagram for the water (1) + MEA (2) system at 66.66 kPa: (○) experimental; (—) calculated.

The thermodynamic consistency test for water (1) + MEA (2) was made using the area test for isobaric data described by Herington (1951). For these systems, the plots of $\ln(\gamma_2/\gamma_1)$ vs x_2 were shown in Figure 2. The results were listed in Table 6. The D and J values were calculated from the following equations:

$$D = \left|\int_{x_1=0}^{x_1=1} \ln(\gamma_1/\gamma_2)\, dx_1 \Big/ \int_{x_1=0}^{x=1} |\ln(\gamma_1/\gamma_2)\right| |dx_1| \times 100$$

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

θ is the difference between maximum and minimum boiling points, and T_{min} is the lowest boiling point in the whole composition range.

Since $D < J$ for the above experimental data, the data can then be considered to be thermodynamically consistent

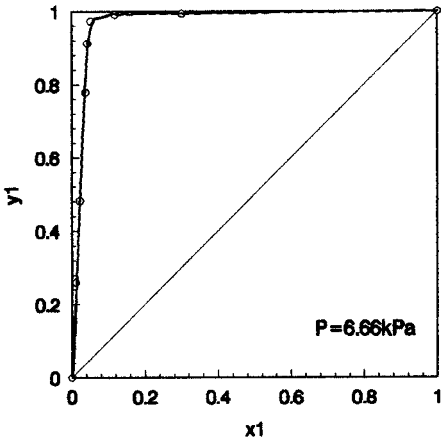

Figure 5. $y \sim x$ diagram for the water (1) + DEA (2) system at 6.66 kPa: (○) experimental; (—) calculated.

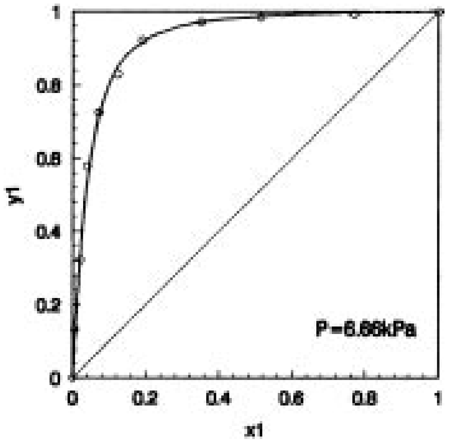

Figure 6. $y \sim x$ diagram for the MEA (1) + DEA (2) system at 6.66 kPa: (○) experimental; (—) calculated.

according to Herington's rule (1951). Because the vapor pressure of diethanolamine at the present temperature is quite small in the measurement range, the other data including DEA systems were not tested by Herington's method.

Data Correlation

The equilibrium relation between vapor and liquid phases can be expressed as

$$\hat{\Phi}_i^{v} y_i p = \gamma_i x_i p_i^{s} \Phi_i^{s} \exp[V_i^{L}(p - p_i^{s})/RT]$$

For low pressures, we can assume the Poynting term to equal 1.0. The liquid activity coefficient γ_i was calculated with the UNIFAC (Fredenslund et al., 1977) group contribution model modified by Larsen et al. (1987). The vapor fugacity coefficient $\hat{\Phi}_i^{v}$ was calculated by the generalized virial equation modified by Tsonopoulos (1975). The Antoine constants of monoethanolamine and diethanolamine were cited from the literature (Boublik et al., 1984).

The molecules were divided into groups as follows:

$$H_2O\text{: } 1H_2O$$

$$NH_2CH_2CH_2OH\text{: } 1NH_2,\ 2CH_2,\ 1OH$$

$$NH(CH_2CH_2OH)_2\text{: } 1NHCH_2,\ 3CH_2,\ 2OH$$

The required group parameters in the calculation of vapor–liquid equilibria were taken from Larsen's work.

The calculated y–x diagrams for ethanolamine systems are plotted in Figures 3–6. Their average absolute deviations (AAD) for vapor phase compositions are less than 0.012 and smaller for H_2O + MEA systems. AAD of T is more than that of y_1. It seems that the UNIFAC relations can be used to design the refined processes for ethanolamine production.

Pure ethanolamines easily absorb water in air, which can cause measurement deviation in weighing and refraction index analysis in the concentrated range. The measurement was made with an Abbe precision refractometer (with an accuracy of ±0.000 05), so the precision of 0.001 composition analysis can be obtained. Although the deviation 0.001 of liquid composition x can yield about 0.027 deviation of vapor y, especially under very low pressure, the smooth plots of experimental data show the reliability of the measurement.

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