Vapor-Liquid Equlibria in Water-Alkanolamine Solutions

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Conclusion/Summary

Isothermal vapour-liquid equilibria for the aqueous solutions of monoethanolamine (MEA), N-methyl-diethanolamine (MDEA), 3-(Methylamino)propylamine (MAPA) and MDEA-MAPA-H_2O mixtures was measured in a modified Swietoslawski ebulliometer (Fig.1) at 40 (MEA), 60, 80 and 100ºC.

The ebulliometer enables very accurate determination of the vapour-liquid equilibrium of pure components and mixtures. The accuracy of the results obtained is limited only by the purity of the substances used and by the precision of the analytical methods used for the sample analyses.

The experimental data were used for regression of binary interaction parameters for the Wilson equation (Table 1), using Modfit, an in-house Matlab program for parameter estimation.

Experimental activity coefficients were calculated using equation (1).

$$\gamma_i = \frac{y_i P}{x_i P_i^{sat}} \quad (1)$$

Table 1. Wilson parameters for MEA, MDEA and MAPA

Amine	λ_{12}	λ_{21}
MEA	3020	-5882
MDEA	63197	-23758
MAPA	1984	-2601

Table 2. Vapour-liquid equlibrium data for MDEA-MAPA-H_2O mixtures at 60, 80 and 100ºC

T (ºC)	P (mbar)	γ_{Am} Am = MDEA	Am = MAPA	Am = H_2O
25 wt% MDEA - 10 wt % MAPA				
59.913	183.7	4.1089	0.0850	0.9942
80.027	435.8	3.2710	0.1529	0.9888
99.999	934.8	4.2323	0.2738	1.0049
25 wt% MDEA - 15 wt % MAPA				
59.972	179.8	0.0000	0.0902	0.9853
59.96	178.7	0.0000	0.0916	0.9798
80.027	425.8	2.7913	0.1872	0.9890
99.999	916	8.2473	0.3209	0.9945
25 wt% MDEA - 20 wt % MAPA				
60.007	174.8	2.2680	0.1114	0.9836
79.998	419.8	1.6210	0.1672	1.0027
80.040	414.9	1.4032	0.1753	0.9968
80.022	421.9	2.3889	0.1713	0.9983
99.999	905.0	1.4664	0.2730	1.0037
100.001	908.3	5.2623	0.3365	1.0021
99.992	888.9	2.7311	0.3223	1.0038

Table 3. Activity coefficients, γ, of MDEA and MAPA in mixtures

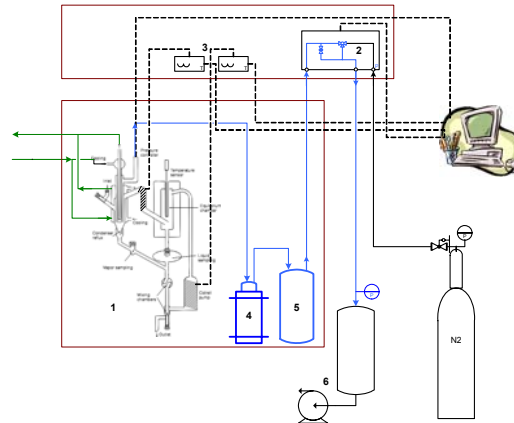| T (ºC)	P (mbar)	γ_{Am} Am = MDEA	Am = MAPA	Am = H_2O
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Experimental

Figure 1. 1 – ebulliometer; 2 – pressure controller; 3 – temperature controllers; 4 – cold trap; 5 – buffer vessel; 6 – vacuum pump with a buffer vessel

Swietoslawski ebulliometer:
- total volume ~200 cm^3
- pressure range < 1atm
- temperature < 200°C

Materials:
MEA (99% pure), MDEA (99+% pure) and MAPA (99% pure) were purchased from ACROS Organics and distilled water was used without any further purification.

Experimental procedure:
The initial solution (80-100mL) was charged into the ebulliometer which was preliminary flushed with nitrogen and evacuated. The liquid in the ebulliometer was heated by an electric heater and partially evaporated. The stream of overhead liquid and vapour obtained was pumped by a Cottrell pump and passed to a thermometer placed inside the equilibrium chamber. The measured temperature corresponds to the equilibrium conditions established by the total pressure and the equilibrium composition of the liquid and vapour phases. The apparatus enables the withdrawal of samples of both vapour condensate and liquid phase. Gradual change of the composition of the solution in the apparatus was made by introducing known quantities of one of the pure components. The samples were analyzed by titration with 0.01-0.1M H_2SO_4 and by gas chromatography.

Results and discussion

Isothermal P-x-y measurements for different alkanolamine-water mixtures were performed at 40 (MEA), 60, 80 and 100ºC. The results for MEA and MDEA-MAPA mixtures are presented in Fig. 2 and Table 2 correspondingly. Fig. 3 and Table 3 also present the activity coefficients of water and amines calculated using eqn. (1). The results for MEA are compared with published data from Nath and Bender (1983). Calculations show that scatter in the values of the activity coefficients is very sensitive to the accuracy of y-values. For example, Δy=0.002 mol/mol (MEA, 60ºC) gives outliers in the activity coefficient scale (Fig.3).

It confirms that accurate analysis of the vapour phase is crucial in the calculation of the experimental activity coefficients. Thermodynamic consistency of the experimental data was done using the method of Van Ness et al., 1973. According to them, the experimental data are considered consistent if the average deviation in the vapour phase mole fraction (Δy) is smaller than 0.01 and in the total pressure (ΔP_{tot}) is within ± 2 mmHg (~0.3kPa)
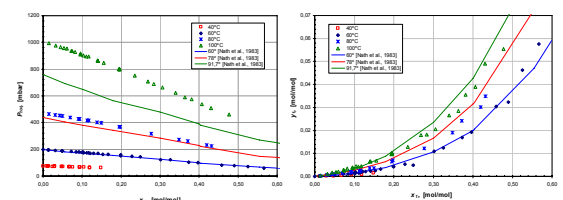

Figure 2. Experimental xy- and Px-data for MEA-H_2O system compared with literature data (Nath et al., 1980).
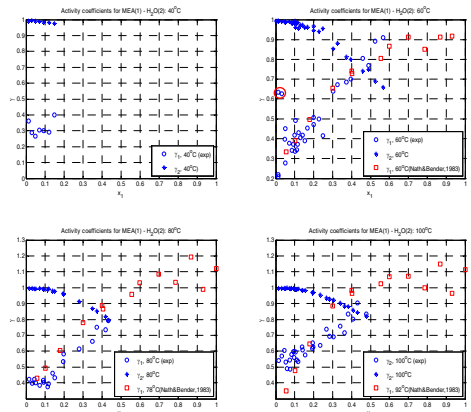

Figure 3. Experimental activity coefficients for MEA-H_2O compared with literature data (Nath et al., 1980).

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