Experimental Determination of Liquid-Liquid Equilibria under Pressure in an Amine-Water-NaOH Ternary System: Application to the Extraction Process

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In the present paper an experimental apparatus and sampling method were developed for the study of a amine – NaOH – H_2O ternary system with vapor pressures from 1 up to 13 bars. The results are important to design new process for the recovery of amine from aqueous mixture by leaching with sodium hydroxide. Three isothermal sections were determined at 298 K, 313 K and 343 K. The compositions of the liquids (miscibility curves, ternary invariant liquids) and the critical points were respectively determined by chemical titration and by the generalized diameter method (Labarthe *et al.*, 2009). Tie line data were also correlated by the Othmer – Tobias method on a mass-fraction basis (Othmer and Tobias, 1942). Experimental results show the existence of a miscibility gap in the amine – NaOH – H_2O system. Further study of these data suggests that it is possible to obtain an organic phase containing more than 95%w of the amine compound.

1. Introduction

Numerous chemical process require ternary equilibrium data (liquid-liquid extraction, distillation, selective crystallization...), hence the study of liquid-liquid equilibria is still of great interest during extraction by demixing (Prausnitz *et al.*, 1986). Although equilibrium data on a large number of ternary systems are available, the study of systems with high vapor pressures always presents a challenge by its experimental approach. In this paper, we developed an experimental apparatus and sampling technique to investigate these systems. The work was then applied to determine isotherms of a amine – NaOH – H_2O ternary system at 298 K, 313 K and 343 K.

2. Experimental

2.1 Materials

40%w aqueous solutions of amine were supplied by Acros and used without any further purification. Sodium hydroxide was use in solid form and provided by Acros. 0.1N and 1N standard hydrochloric acid solutions were supplied by Acros. Deionised water was filtered and used throughout all experiments.

2.2 Apparatus

Because of the volatility of the amine and high vapor pressure of the mixture, all experiments were carried out in a closed system. For this purpose a Parr Instrument 5100 low pressure reactor system was used. A Pyrex Parr 5101 jacketed glass reactor able to withstand an internal pressure up to 10 bars was implemented as containing vessel. The glass provided direct observation of mixing actions and changes of state, a feature which more than compensated for its fragility (Ayres, 1944). For experiments where the vapor pressure exceeded 9 bars, a Parr 4566B stainless steel fixed-head reactor was used. The apparatus was constructed as shown in the schematic diagram (Figure 1).
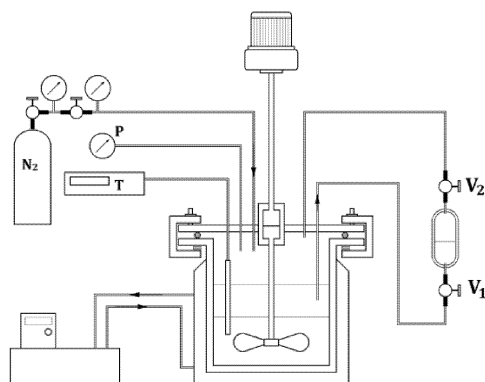

Figure 1: Schematic diagram of the apparatus.

The cover plate provided accesses to the inside of the vessel. These accesses were for pressure gage P, thermometer T, phase sampling tubes, security valve, nitrogen pressurization and stirring. Valve and piping system were supplied by Swagelok. The temperature was read by means of a thermometer dip in the liquid phases inside the vessel and was controlled to within 0.3 K of the desired value by mean of a liquid thermostat. Stirring and agitation were carried out by means of a magnetic drive with a 45° pitched four-blade impeller.

2.3 Preparation

The aqueous amine solution was pre-cooled at -10 °C and a known amount is added to the vessel. Weighted amounts of solid sodium hydroxide were added next. The system

was then sealed and brought to desired temperature with slightly increasing agitation. The agitation should be carried out in a way that no material stayed on the lid or the side of the vessel and was continued at the experiment temperature for at least 1h if only liquid phases were present. In case of important proportion of sodium hydroxide, where equilibrium mixtures could consist of liquid and solid phases, the temperature was brought to higher value and allowed to slowly return to the desired temperature. As soon as stirring was stopped, a slight stream of nitrogen is flushed from the sampling cylinder through the branch V_1 to the vessel in order to eliminate unmixed liquid in the tube. The system was then allowed to settle overnight with slight agitation (5 to 10 rpm). With valve V_2 opened so that the vapor pressure was uniform inside the whole system.

As leakage might occur, the apparatus is tested with nitrogen to 9 bars and 20 bars respectively for the glass and steel vessel. During the experiment, a piece of pH paper was placed near the cover plate to verify whether there was any leak. In case of serious leakage, the sample cylinder was unmounted and materials were flushed directly in large amount of water.

2.4 Sampling and analysis of samples

The sampling manipulations were carried out by closing both V_1 and V_2, then the pressure in the vessel was increased by means of nitrogen such that the total pressure was 2-3 bars higher than the equilibrium pressure. V_1 was then opened, the liquid followed the V_1 branch and came into the sampling cylinder. V_1 and V_2 were then closed and the sampling cylinder was unmounted from the apparatus. It was desirable to slightly open then close the V_1 valve in order to depressurize the sampling cylinder. Sample was cooled down to -5 °C and added to a known amount of water. The solution was then ready for analysis. Samples with high concentration of sodium hydroxide were directly added to known amount of water without any cooling down. After each experiment, the vessel, valves and piping system were washed 4 to 5 times with deionized water and dried by means of compressed air for at least 2h. Samples were analyzed for the total alkalinity and sodium hydroxide contents. The total alkaline content was determined by direct titration of the sample solution by standard 1N hydrochloric acid. Sodium hydroxide content was determined by vaporizing the sample solution under reduced pressure and titrating of the residuum with standard 0.1N hydrochloric acid. Sample quantities were calculated on a mass basis which allowed the determination of the mass composition of the sample.

3. Results

Experimental results are gathered in tables 1, 2 and 3, in which x_{ij} denotes the mass fraction of the j-compound in the i-phase. When the quantity is below the limit of detection of the analysis methods, x_{ij} is noted by ε. The most fruitful source of errors was probably the sampling operations but the experimental errors were not important enough to shift the points by more than 1 percentage point of their real positions on the diagram. Results from all the runs were systematically verified by material balances.

Table 1: Experimental tie lie data at 298 K.

Organic phase (mass fraction)			Aqueous phase (mass fraction)			Total relative
H_2O x_{11}	Amine x_{12}	NaOH x_{13}	H_2O x_{21}	Amine x_{22}	NaOH x_{23}	P bars
0.6123	0.3127	0.0750	0.6990	0.0912	0.2099	0.50
0.5061	0.4610	0.0329	0.6756	0.0345	0.2899	0.60
0.4199	0.5556	0.0245	0.6384	0.0205	0.3411	0.65
0.3351	0.6542	0.0108	0.6013	0.0096	0.3891	0.80
0.2766	0.7216	0.0018	0.5661	0.0037	0.4302	0.95
0.2152	0.7837	0.0011	0.5380	ε	0.4620	1.10
0.1021	0.8976	0.0003	0.5007	ε	0.4993	1.60

Table 2: Experimental tie lie data at 313 K.

Organic phase (mass fraction)			Aqueous phase (mass fraction)			Total relative
H_2O x_{11}	Amine x_{12}	NaOH x_{13}	H_2O x_{21}	Amine x_{22}	NaOH x_{23}	P bars
0.5177	0.4545	0.0278	0.6738	0.0457	0.2805	1.10
0.4457	0.5412	0.0131	0.6432	0.0114	0.3453	1.40
0.3362	0.6582	0.0056	0.6032	0.0040	0.3928	1.90
0.2824	0.7129	0.0047	0.5680	0.0035	0.4285	2.80
0.1672	0.8322	0.0005	0.5010	0.0005	0.4986	3.45
0.1142	0.8856	0.0002	0.4626	0.0041	0.5334	3.75

Table 3: Experimental tie lie data at 343 K.

| Organic phase (mass fraction)			Aqueous phase (mass fraction)			Total relative
H_2O x_{11}	Amine x_{12}	NaOH x_{13}	H_2O x_{21}	Amine x_{22}	NaOH x_{23}	P bars
0.4967	0.4753	0.0280	0.6770	0.0164	0.3066	3.45
0.4015	0.5777	0.0208	0.6438	0.0166	0.3396	4.25
0.2039	0.7942	0.0019	0.5433	0.0129	0.4438	7.05
0.1602	0.8391	0.0007	0.4998	0.0006	0.4996	8.30
0.1049	0.8936	0.0015	0.4555	ε	0.5445	10.10
0.0736	0.9247	0.0017	0.4121	ε	0.5879	10.95
0.0408	0.9592	ε	0.3402	ε	0.6598	11.80
0.0190	0.9810	ε	0.2940	ε	0.7060	12.90
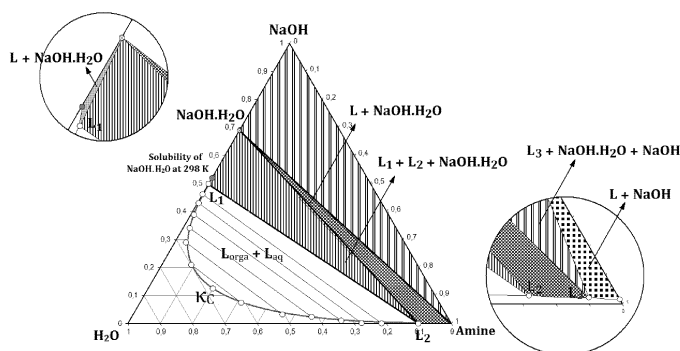
Figure 2: Isotherm of the amine – NaOH – H₂O ternary system at 298 K (the isotherm at 313 K is similar and is not shown).
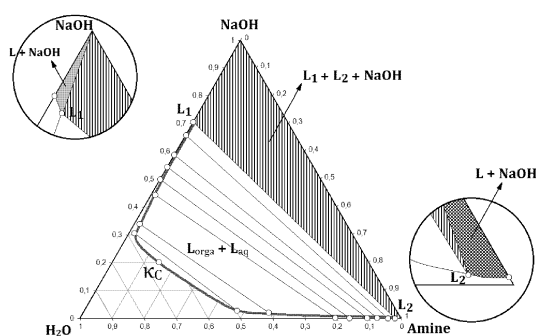

Figure 3: Isotherm of the amine – NaOH – H₂O ternary system at 343 K.

The isotherms show a miscibility gap L_1KL_2. It should be noticed that the two invariant liquids L_1 and L_2 cannot fall directly on the H_2O – NaOH and H_2O – Amine binary axes but as shown in the two zoom windows the solubility of amine in aqueous phase and sodium hydroxide in organic phase were below the limit of detection. The critical point κ_C is determined by the generalized diameter method (Labarthe *et al.*, 2009). Mosaic zones are theoretically drawn. Investigations show that at 298 K and 313 K, by adding sodium hydroxide in an aqueous amine solution, the organic phase can have a maximum mass content of amine lower than 90%w but at 343 K, the composition of the organic phase can reach 98%w. This enrichment in amine content of the organic phase can be explained by the fact that at 343 K, the solubility of sodium hydroxide is clearly greater. Saturated solution of sodium hydroxide at 343 K has 75% mass content of the compound and there is no more formation of the monohydrate of sodium hydroxide (Chretien *et al.*, 1966). This miscibility gap provides an alternative way of purification. Particular cases are the purification of amine and hydrazine in aqueous solutions, instead of a serie of distillation and crystallization, the mixture can be mixed to sodium

hydroxide to give after demixing a concentrated organic phase with negligible inorganic content (sodium salts and hydroxide). The reliability of the experimental tie line data was confirmed by the Othmer – Tobias correlation for ternary systems on a mass fraction basis (Othmer and Tobias, 1942):

$$\ln(\frac{1-x_{12}}{x_{12}}) = A + B \cdot \ln(\frac{1-x_{23}}{x_{23}})$$ (1)

where A and B are constants, x_{12} is the mass fraction of the amine in the organic phase and x_{23} is the mass fraction of sodium hydroxide in the aqueous phase. The linearity of the plot, represented by the correlation coefficient R^2, indicates the degree of consistency of the experimental data. The parameters of the correlation are shown in table 4.

Table 4: Othmer – Tobias correlation constants for tie line data at various temperatures.

Temperature	A	B	R^2
298 K	0.826	0.597	0.995
313 K	0.767	0.467	0.978
343 K	0.452	0.791	0.989

4. Conclusions

An apparatus and sampling technique suitable for phase-rule investigation of system with high vapor pressure up to 9 and 20 bars were developed. Equilibrium data for the amine – water – NaOH ternary system were determined at 298 K, 313 K and 343 K. Miscibility gaps in the amine – NaOH – H_2O ternary system were determined, they present an interesting way for the concentration of amine. It can be concluded that adding NaOH to the reaction mixture may serve as an adequate way for the purification process of amines. Starting from diluted aqueous solutions, this method of salting-out is highly recommended before the distillation operation for industrial transposition.

References

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