DISTILLATION OF WATER – *N*–METHYLIMIDAZOLE SYSTEM[#]

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[#]This paper is dedicated to Professor Roman Modic at the occasion of his 90th Birthday

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Abstract

N-Methylimidazole is used in the synthesis of various organic materials as a catalyst and in some cases as a solvent. In the industrial processes where the large quantities of *N*-methylimidazole are used the need for the regeneration and recycling is obvious because of its high price and ecological requirements.

In this work a method for solvent recovery from water - *N*-methylimidazole system is proposed. For this purpose the vapour-liquid equilibrium diagram was determined and refractometry was used as a convenient physico-chemical method for the determination of water content in the mixture.

Introduction

N-Methylimidazole has been extensively used as a catalyst in the reaction of acetylation of some polymers and other organic materials,[1-3] while its use as a solvent is rare. During the development of a new synthetic procedure for the preparation of certain chemical and pharmaceutical products *N*-methylimidazole is used as a solvent. Afer this synthetic procedure the mixture of solvent and water is obtained, which is useless for further process without purification. Due to the cost of *N*-methylimidazole and green technology demands the necessity of recycling the solvent of appropriate quality has become evident.

The choice of the adequate separation method depends mainly on the amount and composition of the mixture, its physico-chemical properties and the required final purity of the solvent.[5]

Batch rectification has been found to be an efficient environment-friendly method of solvent recovery in pharmaceutical industry as well as in chemical, food and cosmetic

industries for separation of smaller amounts of solvents.[4,5] This method could be used also for the separation of water - *N*-methylimidazole mixture ensuring highly concentrated solvent with minimal water content as well as distillate – mostly composed of water - acceptable corresponding to the ecological criteria. Batch rectification column can be run in three different modes: with constant reflux ratio, constant overhead composition and as time optimal batch rectification. It was shown[6] that the operation with constant overhead composition is closer to the optimal than to constant reflux technique and also easier to control than the optimal batch rectification. In order to maintain constant overhead composition, the reflux ratio should be increased continuously. When variable reflux control is to be used and determined in advance, the shortest time operation can be achieved.

To our knowledge, equilibrium data for water - *N*-methylimidazole system have not been published yet. They are essential for the selection and design of the separation method. The aim of this work is therefore (i) to develop a simple and efficient method to establish the composition on the basis of known refractive indexes for pure components; (ii) to determine the boiling diagram for water - *N*-methylimidazole mixture, which serves as the basis for equilibrium diagram, appropriate for a process calculation; and (iii) to establish the necessary data for batch rectification computation, i.e. the data for the solution of Bogart's integral.

Materials and methods

Materials

N-Methylimidazole was supplied by Aldrich with the purity greater than 99 % and was redistilled. The water used was distilled. The purity of *N*-methylimidazole was checked by refractometry and gas chromatography.

(i) Measurement of Refractive Index

Since the refractive indexes of pure water and pure *N*-methylimidazole are 1.333 and 1.497 respectively, we assumed that the refractometry would be an useful tool for the determination of water content in the mixture. For this purpose, the digital apparatus Reichert-Jung, Abbe Mark II (Cambridge Instruments, Inc., Buffalo, USA) was used.

Refractive indexes were measured at 20 °C. Low water contents were determined by coulometric Karl Fischer titration (Metrohm 684 KF Coulometer, cell without diaphragm) accurate to 0.002% (wt). The solutions were prepared by using a Mettler balance (Model AT 261) and air-tight stoppered bottles.

When the values of refractive index versus weight fraction of water (*w*) in the mixture with *N*-methylimidazole are plotted, linear correlation is obtained, which is practical for use (Chart 1).

In distillation molar units are common. Conversion between weight fractions and molar fractions can be easily done using molar weights of both components, which are 18 $gmol^{-1}$ for water and 82 $gmol^{-1}$ for *N*-methylimidazole respectively. The composition of the mixture is expressed by molar fraction *x* of the more volatile component, in this case water.

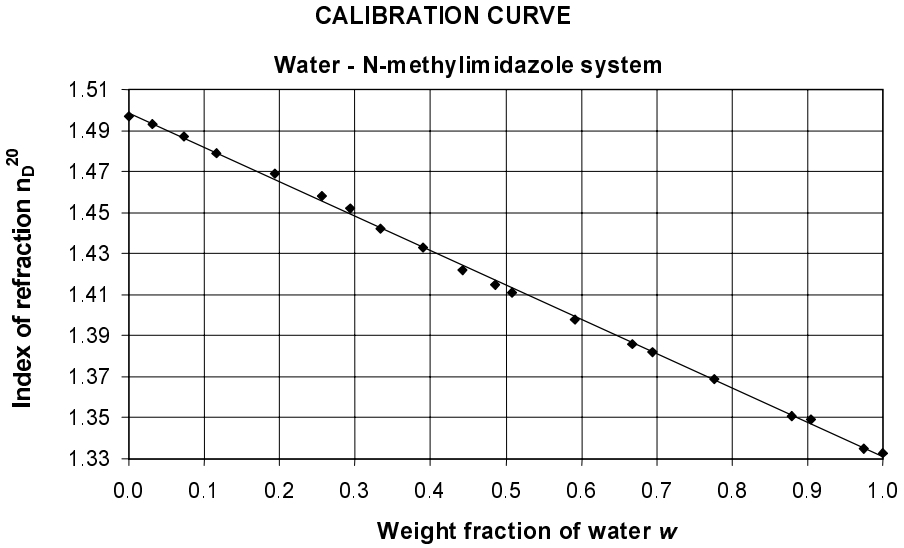

Chart 1. Dependence of refractive index on the composition of the mixture

(ii) Determination of boiling diagram

The vapour-liquid equilibrium was measured using modified dynamic phase equilibrium apparatus Labodest 602 (Fischer, Germany). The temperature range of the operation is up to 250 °C, the pressure range from 1 bar to 2,5 mbar**.** The approximate amount of mixture loaded in the cell is 85 cm^3. The temperature was detected with a digital precision platinum resistance thermometer (Hart Scientific, Model 1506), calibrated according to the MIL-STD-45662-A standard with the resolution of 0.0001 K

and the accuracy of ± 0.005 K. A pressure transducer VKH 300, calibrated against an MKS Baratron type 170 M System, was employed to measure the pressure. The pressure was maintained at its set point with an electric pressure controller within ± 1 mbar.

The vapour-liquid equilibrium measurements were performed over the entire concentration range at 100 mbar. After each experiment, the mixture from the cell was removed and the cell was rinsed several times with acetone, kept under vacuum for a while and dried.

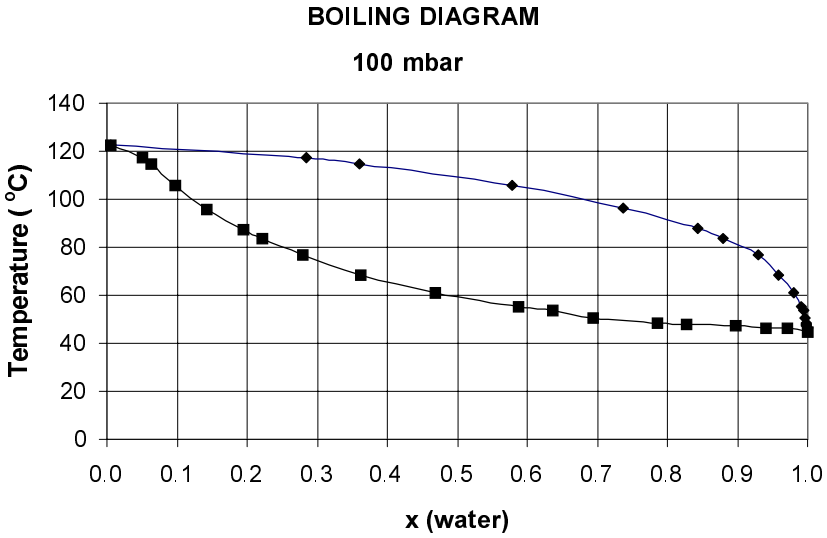

Chart 2. Boiling diagram of water - *N*-methylimidazole mixture at 100 mbar

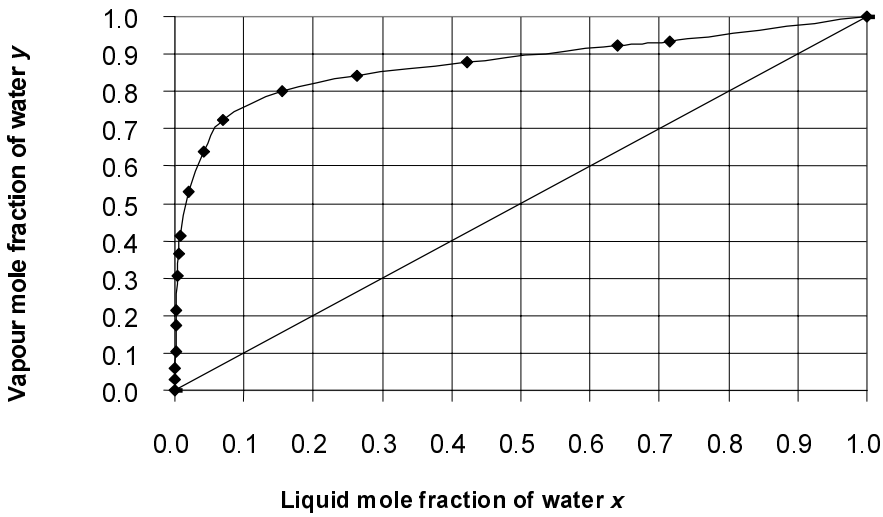

Chart 3. Equilibrium diagram of water - *N*-methylimidazole mixture at 100 mbar

(iii) Reflux ratio dependence on liquid composition

By standard method described in literature[7-9] the reflux ratio R dependence on bottom composition x_B can be found by graphical method for the construction of operating lines at different reflux ratios in the equilibrium diagram (Chart 3), taking into account the values similar to those in the industrial process: the initial molar bottom composition $x_{B0} = 0.1$, the required molar bottom composition $x_B = 0.0045$, the distillate composition $x_D = 0.95$ and the number of theoretical stages $n_t = 4$ as an acceptable starting technical solution.

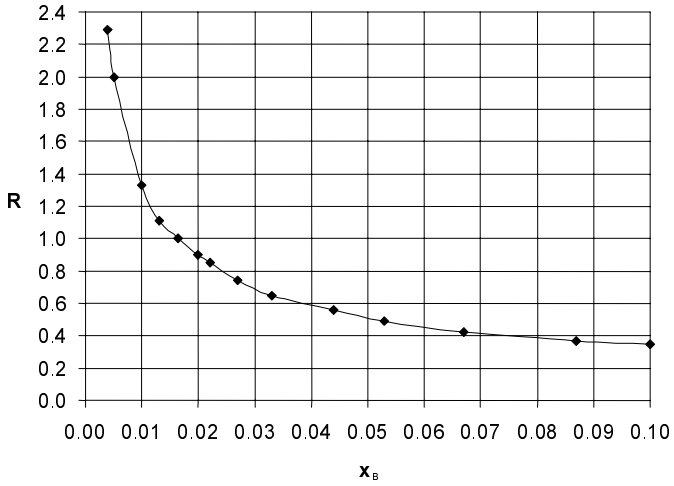

Chart 4. Reflux ratio (R) as a function of bottom composition (x_B)

For the mixture under consideration $R = a \cdot x_B^b$ is an useful expression for the solution of Bogart's integral,[10] which describes the time dependency on bottom composition:

$$t = \frac{B_0 \cdot (x_D - x_{B0})}{V} \cdot \int_{x_{B0}}^{x_B} \frac{(R(x_B)+1)dx_B}{(x_D - x_B)^2}, \qquad \textbf{(1)}$$

where B_0 is the initial molar amount of the mixture in the still and V is vapour flow rate in moles s^{-1}, kept constant throughout the distillation.

Using data from Chart 4, coefficients a and b were calculated and the relationship between reflux ratio R and bottom composition x_B is following:

$$R = 0.09 \cdot x_B^{-0.6} \qquad \textbf{(2)}$$

Correlation (**2**) enables the analytical solution of Bogart's integral (**1**), taking into account specific technical data like heat flux and vapour flow.

This study can present an useful basis for technology development of a separation unit as a part of drug production equipment.

Conclusions

In this paper equilibrium data for the system water - *N*-methylimidazole have been presented. Further research is still in progress and final results will be used for the separation of mixture obtained from the industrial process.

Notes

n_D^{20}...index of refraction
w.....weight fraction of water
x.....mole fraction of the more volatile component (water) in the liquid phase
y.....vapour mole fraction of water
B_0.....amount of the mixture in the still at t = 0 (*moles*)
x_{B0}..... bottom composition (mole fraction of water) at t=0
x_B..... bottom composition (mole fraction of water)
V ….. vapour flow rate (*moles* s^{-1})
x_D..... distillate composition (mole fraction of water)
R..... reflux ratio

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Povzetek

N-Metilimidazol uporabljajo v sintezi različnih organskih materialov kot katalizator pri nekaterih reakcijah aciliranja, v nekaterih primerih pa služi tudi kot topilo. Pri uporabi večjih količin ga je zaradi visoke cene smiselno regenerirati in vračati v sintezni postopek.
V članku so predstavljeni ravnotežni podatki tekoče-para za sistem voda - N-metilimidazol, ki doslej še niso bili znani. Ugotovili smo, da je sestavo zmesi možno spremljati z merjenjem lomnega količnika, kar je enostavna in v praksi zelo uporabna metoda. Na podlagi meritev smo izbrali šaržno rektifikacijo kot najprimernejšo metodo za ločitev zmesi voda – N-metilimidazol. Predstavljeni podatki bodo služili za načrtovanje in praktično izvedbo ločevanja zmesi iz industrijskega postopka.