Extraction of Monomethylhydrazine of Space Grade by Ternary Distillation: Modeling of Liquid/Vapor Equilibria

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Hydrazine and its alkylated derivatives are propellants used in aerospace and military industry (space shuttles, engines of midcourse adjustment of satellites, missiles).

In the case of monomethylhydrazine $H_3CN_2H_3$ (MMH), the existence of an azeotrope in the binary system MMH-H_2O prevents the extraction by simple distillation and limits the separation possibilities. An alternative, particularly judicious in the case of continuous flow production units, consists in exploiting another parameter by implementing distillations in overpressure or under reduced pressure. Unfortunately, the definition and the development of such processes imply the knowledge of a whole of experimental data which are very often lacking.

The modeling of the phenomena represents an advantageous alternative then since it allows the selection of the additives and an optimization of the conditions of extraction. The quasi ideal model developed by our team was applied to the predictive calculation of liquid/vapor equilibria of the system H_2O-Ethylenediamine (EDA) of formula $H_2NCH_2CH_2NH_2$. The phase diagram is characterized by the existence of an azeotrope which disappears under pressure. A perfect correlation is observed between the calculated results and those of the experiment for the five pressures of the binary system H_2O-EDA studied. This study highlights a limiting pressure, of 180 kPa, over which the azeotropy phenomenon is no more observed.

Then, we have calculated liquid-vapor equilibria of the ternary system H_2O-EDA-MMH. The phase diagram is characterized by the existence of a diazeotropic spindle whose projection in the compositions plane separates the system in two distinct distillation fields. This configuration is favorable to the extraction of anhydrous MMH from its azeotropic aqueous solution. Indeed, the continuous distillation of a mixture with a well defined composition leads to anhydrous MMH at the head of column and azeotrope H_2O-EDA at the column base. In practice, two flow charts can be proposed: in both cases, EDA is dehydrated by distillation under pressure and the anhydrous amine is recycled continuously.