Experimental and theoretical research on N-methyl-2-pyrrolidone concentration by vacuum membrane distillation using polypropylene hollow fiber membrane

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ABSTRACT

In this work, N-methyl-2-pyrrolidone (NMP) aqueous solution was concentrated by means of vacuum membrane distillation (VMD) using polypropylene (PP) hollow fiber hydrophobic membrane. The effects of operating variables including feed concentration, feed temperature and vacuum degree on VMD performance were studied experimentally and theoretically. The results indicated that higher feed temperature and/or higher vacuum pressure could lead to an enhancement in H_2O removal and no change in NMP rejection. The permeation flux of 9.5 L/m^2 h and the rejection 98% can be achieved at the feed temperature of 80 °C and vacuum degree of 0.09 MPa. Higher feed concentration leads to a decrease in H_2O flux and an increase in NMP flux and NMP molar fraction in permeate side. It proved that the Knudsen-viscous flow diffusion dominated the mass transform of H_2O/NMP vapor in our experiment condition. Furthermore, "Dusty-Gas" model was used to predict membrane properties and Wilson equation method was used for predicting γ of the NMP aqueous solution. The theoretical data fitted well with the experimental data in our experiment conditions.

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1. Introduction

Membrane distillation (MD) uses hydrophobic membrane such as polypropylene (PP), poly-tetrafluoroethylene (PTFE), polyethylene (PE) and polyvinylidene fluoride (PVDF) membranes as a physical barrier to prevent the feed solution passing through. In MD process components, gas evaporates in the heat side of the membrane and transports through the membrane pores under pressure gradient which caused by temperature gradient or by vacuum degree in permeate side, and then condenses in the cold side. Compared with many other membrane separations, the membrane itself does not interfere with MD performance but only provide a vapor–liquid interface. In contrast with the conventional distillation, MD has three advantages: firstly it takes place at low operating temperatures enabling separation of temperature-sensitive substances [1]; secondly the large membrane surface area increases the vapor–liquid contact area; thirdly it can reduce the heat loss and improve separation performance. Although most of MD can only be carried out in laboratory stage; MD is regarded as a promising membrane separation direction in the near future.

MD can be divided into four types in accordance with the condensation methods: direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), gas membrane distillation (SGMD), and vacuum membrane distillation (VMD). DCMD is usually used in desalination, crystallization, concentrating fruit juices and treatment of waste water; SGMD has been applied at laboratory scale for the treatment of aqueous solutions containing non-volatile solutes such as salts (NaCl) as well as volatile solutes such as ammonia, alcohols (ethanol, isopropanol) and acetone; AGMD is used in desalination, solar units, food processing, treatment of aqueous alcohol solutions, breaking of azeotropic mixtures and extraction of volatile organic compounds [2]. VMD has been found to be a suitable process for the removal of trace amount of contaminants form dilute aqueous solutions such as chloroform removal from aqueous solutions [3], removal of 1,1,1-trichloroethane from water using a polyvinylidene fluoride hollow fiber membrane module [4] and recovery of volatile aroma compounds from black currant juice by vacuum membrane distillation [5].

NMP is organic solvent that is widely used in preparation of membranes. Polymer was dissolved in the solvent at the first time to make a dope, then the dope was extruded into a coagulation bath of water though a spinneret to form a hollow fiber membrane or through a split die to a plan one. In the bath, bilateral diffusion

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occurred. Organic solvent form dope (or membrane) into water and water into membrane while polymer precipitated to form membrane. At the same time, a large amount of dilute organic aqueous solution formed in the bath. It would pollute the environment if the waste solution were discharged directly, and NMP was identified as a reproductive toxicant by California in 2001 and then by the European Commission in 2003. For environmental friendliness, the waste water could be concentrated to produce pure NMP to reuse. Generally speaking, the aqueous solution is concentrated to a certain concentration by MD and then reproduces pure NMP after common distillation, which will reduce energy consumption.

Concentration of organic solvents usually uses traditional distillation method [6,7] which commonly needs a high temperature and large energy consumption. Recently, membrane pervaporation is used [8–12]. The concentration and dehydration of NMP aqueous solution using membrane pervaporation with PAN and up-scaled high-silica CHA-type zeolite membranes were reported [13,14]. In this paper, NMP aqueous solution was concentrated by VMD technology with PP hollow fiber membrane prepared by melt-spinning and stretching method. PP membrane is a cheap membrane with good solvent resistance, high packing density and good mechanical strength. The effects of the operating variables of feed concentration, feed temperature and vacuum degree on VMD performance were studied both theoretically and experimentally. The mathematical model Knudsen-viscous Flow Diffusion together with Wilson equation method for γ of mixed solution was used to predict membrane properties.

2. Theoretical principle and correlation equations

The mechanism types of gas mass transfer mainly include Knudsen flow diffusion, viscous flow diffusion and Knudsen-viscous flow diffusion. There are two basic models for all possible transport mechanisms, "Dusty-Gas" model and "Schofield's" model. The main advantage of using "Dusty-Gas" model is the fact that they are parameters dependent only on membrane geometry and interactions of the membrane and the gas particle, yet independent of the temperature, which can be much briefer, whereas "Schofield's" model depends on the temperature and the gas used. The other disadvantage of "Schofield's" model is that the experimental error of some parameters can be fairly large [15]. In order to select a suitable mechanism, the relationship between the mean free path of the molecules λ and the size of the micropores r should be concerned. When $r \leq 0.05\lambda$, Knudsen flow diffusion should be selected, and when $0.05\lambda \leq r \leq 50\lambda$, Knudsen-viscous flow diffusion dominates the mass transfer through the membrane [16].

Eq. (1) indicates that the mass flux N of component i in Knudsen flow diffusion, is linearly related to the pressure gradient (ΔP) across the membrane as follows [17]:

$$N_i = -K_m \sqrt{M_i} \Delta P_i \qquad (1)$$

N_i is the mass flux, M_i is the molar mass. K_m is the transmembrane mass coefficient which only depends on membrane geometry, structure and temperature and has nothing to do with the types of the gas going through the membrane.

When viscous contribution is taken into account, "Dusty-Gas" model [18] provides the mass calculation shown in Eq. (2).

$$N = -\frac{M}{RT}\left[K_0\overline{V} + \frac{P_{avg}B_0}{\mu}\right]\frac{\Delta P}{\delta} \qquad (2)$$

$$\overline{V} = \sqrt{\frac{8RT}{\pi M}} \qquad (3)$$

where μ is the gas viscosity, K_0 and B_0 the parameters characteristic of the Knudsen and viscous flows, respectively, R the gas constant, T the thermodynamic temperature, P_{avg} the average of the pressure at both membrane sides, δ the membrane thickness, $\overline{V}$ the gas's mean molecular speed calculated by Eq. (3). B_0 is a constant characteristic of the medium alone, and K_0 is related in first approximation to a geometric constant characteristic of the dust particles and also a quantity. The main advantage of using K_0 and B_0 is the fact that they are parameters dependent only on membrane geometry and interactions of the membrane, but independent of the temperature.

Eq. (2) may be rearranged as follows:

$$\frac{NRT\delta}{\Delta PM\overline{V}} = K_0 + B_0\frac{P_{avg}}{\mu\overline{V}}$$

i.e.

$$Z = K_0 + B_0 X \qquad (4)$$

where $Z = NRT/\Delta P\overline{V}$ and $X = P_{avg}/\mu\overline{V}$, which is more suitable in order to obtain the parameters characteristic of the transport mechanisms (K_0 and B_0) from the linear fit of the experimental data (Z versus X).

Eq. (5) is used to calculate the transmembrane flux for mixed solution. P_1Y_{i1} and P_2Y_{i2} are respectively the partial pressure of component i in the heat side and in the vacuum side, and $P_1Y_{i1} = P_i = P_i^*\gamma_i X_i$. Y_{i2} is measured by the experimental test, γ_i is the activity coefficient of i.

$$N_i = K_m\sqrt{M_i}(P_1Y_{i1} - P_2Y_{i2}) \qquad (5)$$

There are three methods to calculate activity coefficient γ: Wilson equation, NRTL equation and UNIFAC group contribution method. Wilson equation is relatively simple, and its parameters are not appreciably affected by temperature, so we chose Wilson equation to estimate γ_i. Wu et al. [19] studied the NMP concentration using distillation, and obtained Antoine equation to calculate the saturation vapor pressure of pure NMP, shown in Eq. (6).

$$\lg PV = 6.882 - 2196.6434/(243.7 + t) \qquad (6)$$

Eqs. (7)–(12) are Wilson equation expressions, Wu et al. also obtained binary interaction parameters of the Wilson equation, and proved that the test results of thermodynamic consistency meet the Herington thermodynamic consistency requirements.

$$\ln\gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1}\right) \qquad (7)$$

$$\ln\gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) + x_1\left(\frac{\Lambda_{21}}{x_2 + \Lambda_{21}x_1} - \frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2}\right) \qquad (8)$$

$$\Lambda_{12} = \frac{V_2}{V_1}\exp[-(g_{12} - g_{11})/RT] \qquad (9)$$

$$\Lambda_{21} = \frac{V_1}{V_2}\exp[-(g_{21} - g_{22})/RT] \qquad (10)$$

$$(g_{12} - g_{11}) = 2447.16\,J/mol \qquad (11)$$

$$(g_{21} - g_{22}) = 1417.85\,J/mol \qquad (12)$$

3. Experimental

3.1. Membranes and chemicals

In this work, different mass fraction aqueous solutions of NMP (0–40 wt%) were employed. NMP purchased from Tianjin Kermel Chemical Reagent Co., Ltd was of AR grade and water content