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A comprehensive study on equilibrium and kinetics of morpholine extraction from aqueous stream with CA in toluene: Experimental evaluation, extraction model and parametric optimization employing desirability function

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ABSTRACT

The present study explores the equilibrium and kinetics for the reactive extraction of morpholine, an important industrial reagent from its aqueous stream using capric acid, CA (extractant) in toluene (diluent). An equilibrium model that employs the mass action law was also developed to evaluate the optimum apparent equilibrium constants (K_E), stoichiometric ratio (m) and physical constant (S). Equilibrium model was valid in representing the mechanism of morpholine extraction. Moreover, for the first time the study availed the simultaneous optimization of two significant response characteristics; extraction efficiency (%E) and loading ratio (Z) using Box–Behnken design (3^3) employing multivariate desirability function. The statistical models predicted %E of 80.2 and Z of 0.64 for the optimum combination of process parameters as follows: $C_{MO} = 5\%$, $C_{CAO} = 5\%$ and $T = 303.15$ K with the desirability of 0.947. Further, the intrinsic kinetics of the extraction model demonstrated that the reactions between morpholine and CA fall in regime 3 (fast chemical reaction in diffusion film), follows first order kinetics with respect to morpholine and displays exothermicity of the process as revealed from thermodynamic studies. The equilibrium and kinetic data is useful for the development, design and reliable scale-up of the extraction process.

1. Introduction

4-Methyl-1,3-dioxolan-2-one or morpholine has emerged as a commercially competent product having widespread applications in petrochemical plants, rubber industries, dye and resin industries, coking as well as in many other organic chemical industries. It has often been selected for temperature-dependent multi-component solvent system applications such as in hydroformylation reaction and used in fruit waxing (Behr et al., 2008; Lee et al., 2014; Kumari et al., 2017). It is also used as separating agent and implemented as a building block in the preparation of antibiotics and, anti-cancer agents (Lee et al., 2014; McGuire and Dimitrios, 1999). In this context, the separation of morpholine from aqueous waste streams is a statutory obligation. In the preparation of morpholine by the dehydration of diethanolamine with sulphuric acid or hydrochloric acid a reaction mixture is obtained which contains the morpholine as an acid salt

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dissolved in excess aqueous acid. An amount of alkali added renders the mixture strongly alkaline, which is generally separated by steam distillation. The concentration of aqueous morpholine so produced depends on the quantity of excess alkali present during steam distillation (George and Laemmle, 1957). The recovery of morpholine from the aqueous stream has not been in practice by distillation owing to its economical constraint. The prevalence of strong bonding between the amino functional group in morpholine and water yields a highly non-ideal mixture, making the separation difficult and requires a large and costly distillation column. Besides, morpholine boil at higher temperatures than water, the entire water needs to be vaporized by distillation. This introduces the use of vast amounts of heat, steam and cooling water (Somekh and Hawkes, 1969). To preclude the difficulties encountered in the distillation operation, some of the prior art work resorted the processes like utilization of concentrated NaOH solution to dewater an aqueous morpholine solution. To regenerate the concentrated NaOH solution necessitates evaporating the large amounts of water by distillation, as previously indicated, costly and undesirable. Another method utilizes ethyl ether as an extracting agent, which is again extremely inefficient and expensive due to high solvent losses (Somekh and Hawkes, 1969). Amidst the various intensified techniques, reactive extraction has emerged as a promising one that leads to the separation of close volatility or non-ideal mixtures with a substantial reduction in the overall cost as compared to other methods (Marti et al., 2011). In this context, reactive extraction technique was explored to avoid the above stated difficulties encountered during separation of morpholine from its aqueous stream. The extraction parameters such as initial concentration in the aqueous phase, extractant concentration, temperature, types of complexes formed, properties of diluents and extractants play a vital role in influencing the reactive extraction process (Kahya et al., 2001). In this study, capric acid (CA) has been selected as a complexion agent, which is immiscible in water and highly soluble in selected diluents (toluene).

Additionally, an equilibrium model employing mass action law with suitable assumptions was utilized to regress the stoichiometries in the reactive extraction. For an amine based aqueous solution, literature is found scarce given a model and correlation of apparent equilibrium constants. Further, Box–Behnken multivariate optimization based on desirability approach was employed to obtain the global optimum combination of design variables, where two dependant variables were selected as the response characteristics. In general trend, only one response characteristics i.e., distribution coefficient (K_D) or extraction efficiency (%*E*) has been investigated in the optimization of the reactive extraction process, although the loading ratio (*Z*) imparts a crucial role in the optimization since it decides the stoichiometry of the amine–acid complex formed. Therefore, in the present study two response characteristics, %*E* and *z* were simultaneously optimized in the multivariate process.

Fundamentally, overall extraction rate depends on two different models; interfacial and homogeneous reaction models (Steensma et al., 2007). In the kinetic study, a homogeneous reaction model was adopted owing to the limited solubility of morpholine in the organic phase. The Vantoff's expression was fitted to the thermodynamic data to obtain the enthalpy and entropy for extraction of morpholine.

2. Theoretical consideration

2.1. *Equilibrium models*

The equilibrium model is interpreted by mass action law proposed by Guldberg and Waage in 1864 describes the physical and chemical phenomena and also explains the interaction mechanism between the components (morpholine and water) of the aqueous phase and organic (CA and toluene) phase (Datta and Kumar, 2013). It is assumed that particular concentration of the components is proportional to the mass action law activities of the aqueous and organic phase species and the non-ideals coupled with the reactive system (Datta et al., 2014). Therefore, a mathematical model is developed using the apparent equilibrium constant for the reaction equilibrium. This model can be classified into two types (i) physical extraction and (ii) chemical extraction. The details of the physical and chemical equilibrium, Box–Behnken design, desirability functions and kinetic models (Table S1) are described in the supporting information under theoretical consideration.

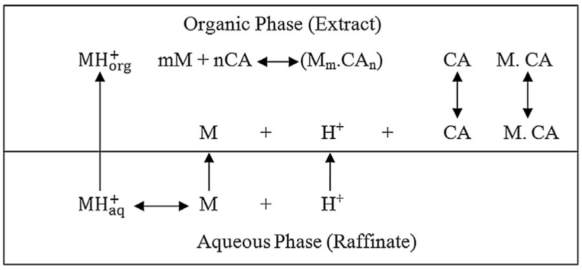

Fig. 1 – Mechanism of reactive extraction of morpholine with capric acid.

The interaction of amine-acid molecules in the chemical extraction happened through (i) hydrogen bonding of undissociated amine molecules (ii) by ion-pair formation. The mechanism of interfacial reactive extraction between morpholine with CA is displayed in Fig. 1.

The morpholine molecules protonated in the aqueous phase and forms HM^+ ions and moves towards organic phase. The reaction occurs at the interface between aqueous and organic phase and forms acid–amine complex, which stabilizes in the organic phase. In the present study, the reaction between morpholine and CA occurs mainly through H-bond formation because most of the morpholine is in the undissociated form in aqueous phase. The undissociated form of morpholine in the aqueous phase transferred (diffuse) to the interface, CA diffuses through the organic phase and moves to the interface, where amine-acid associates through H-bonding and the complex dissolves in the bulk organic phase.

3. Experimental section

3.1. *Chemicals*

All the chemicals used were of analytical grade. The morpholine (purity ≥ 99.0%) procured from Sigma–Aldrich was stored in desiccators to prevent from moisture attack and dust contamination. Toluene (purity ≥ 99.5%) was acquired from s–d fine chemical Ltd., Mumbai, India and stored in a segregated and approved area. CA (purity ≥ 99%) was supplied from Alfa-Aesar, Heysham, England and stored away from extreme heat. Sodium 1,2-naphthoquinone-4-sulfonate (purity ≥ 97%) was provided by Alfa-Aesar, Heysham, England. Distilled water was used for the experimentation to prepare required concentrations of aqueous solutions.

3.2. *Instruments*

The mixtures were prepared using a high precision Sartorius CP224S electronic balance with an accuracy of ±0.0001 g. The equilibrium studies were carried out using a shaking incubator (Model No.-LSI4018R) provided by Daihan Labtech India Pvt., Ltd., capable of maintaining the temperature within ±0.1 K. A Polyscience refrigerating and heating thermostat model 9702 with a digital temperature controller was used to circulate hot water through the jacketed reactor for maintaining the