

# Recovery of Acetonitrile from Aqueous Solutions by Extractive Distillation—Effect of Entrainer

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**Abstract**—The aim of this work was to apply extractive distillation for acetonitrile removal from water solutions, to validate thermodynamic criterion based on excess Gibbs energy to entrainer selection process for acetonitrile – water mixture separation and show its potential efficiency at isothermal conditions as well as at isobaric (conditions of real distillation process), to simulate and analyze an extractive distillation process with chosen entrainers: optimize amount of trays and feeds, entrainer/original mixture and reflux ratios. Equimolar composition of the feed stream was chosen for the process, comparison of the energy consumptions was carried out. Glycerol was suggested as the most energetically and ecologically suitable entrainer.

**Keywords**—Acetonitrile, entrainer, extractive distillation, water.

## I. INTRODUCTION

ACETONITRILE is an important organic solvent extensively employed in organic synthesis [1], pharmaceutical [2], liquid chromatography [3], and as photosensitive material [4]. It is a by-product of the manufacture of acrylonitrile with catalytic ammoxidation of propylene, also known as the Sohio process, but can additionally be obtained by reaction of acetic acid in the excess of ammonia. Since aqueous solution of acetonitrile (ACN) is encountered in many chemical processes, the purification of acetonitrile from water is needed, which is complicated by the presence of a minimum azeotrope in the acetonitrile – water system containing 0.676 mole fraction ACN at 76.8°C and ambient pressure [5]. Different unconventional methods to separate this mixture were reported in the literature, such as combined method of solvent extraction with butyl acetate and batch distillation [6], pressure swing distillation [7], extractive distillation with dimethylsulfoxide (DMSO) [8] and 1,2-ethandiol [9], membrane separation [10], etc.

Extractive distillation (ED) is a topic of great industrial interest as a proven successful technique to separate azeotropic systems. It involves the addition of a separating agent (entrainer) which interacts differently with the components of the original mixture and alters their volatilities. Successful entrainer selection is one of the most important steps as it determines capital and energy costs of the whole process. At present, this step is mostly carried out by using specialized data banks [11] and empirical rules, based on

general physical and chemical criteria such as chemical inactivity, selective influence to relative volatility, ecological and economic factors, low corrosion, easy regeneration and etc. Furthermore, in the last decades, unconventional substances, such as hyperbranched polymers, and ionic liquids, have started to play a crucial role in distillation processes, though no data were encountered in published literature on their application for acetonitrile – water mixture separation.

Previously, acrylonitrile – water constituent of industrial mixture acrylonitrile – acetonitrile – water was investigated [12]. The objective of our present research is not only to select a suitable solvent for the most effective and economically viable design of ED in acetonitrile – water mixture separation, but also to prove its effectiveness with simulation and analysis of ED and energy consumptions via Aspen Plus 7.3 simulator. A methodology for the selection of various potential entrainers was based on thermodynamic criterion described elsewhere [13], [14].

## II. RESULTS AND DISCUSSION

### A. Entrainer Selection

Entrainer selection is the key step for the extractive distillation technique. General requirements for entrainers as well as commonly used methods of their selection are listed in [15]. Thermodynamic criterion used for the selection establishes the connection between the difference in excess Gibbs energy values  $\Delta(\Delta gE)$  in binary systems “component of original mixture (1 or 2) – entrainer” and values of relative volatility under separation conditions. When  $\Delta(\Delta gE) \sim 1000$  J/mol than the relative volatility of original mixture compounds in the presence of entrainer is sufficient for extractive effect. Inclusion of this step in the selection process provides a decrease in the amount of selective compounds, usually adopted in traditional procedure, which in turn allows for faster calculations. It should also be noted that this criterion can be applied over the whole range of compositions of original mixture.

In this section, entrainers which were found suitable using thermodynamic criterion are reported. Out of 6 substances listed in Table I DMSO, 1,2-Ethandiol, DMF and Glycerol form no new azeotropes and possess the highest Vaporization heat in the system ACN – water – entrainer. Moreover, according to used thermodynamic criterion, DMF provides difference in excess Gibbs energy values  $\Delta(\Delta gE)$  of only about 500 J/mol, which, although indicating presence of extractive effect, is not enough for successful separation at low energy consumption.

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TABLE I  
POSSIBLE ENTRAINERS CHOSEN USING THERMODYNAMIC CRITERION

Entrainer	BP, K	$\Delta H_{\text{vap}}^{\circ}$ , kJ/mol	Azeotrope
DMSO	464.0	52.7	No
1,2-Ethandiol	470.5	63.9	No
DMF <sup>a</sup>	426.0	47.57	No
Glycerol	560.0	90.43	No
Butyl Acetate	399.0	43.89	Yes (Water)
Pyridine	388.5	40.15	Yes (water)

<sup>a</sup>dimethyl formamide

It should be also mentioned that the last 2 substances, butyl acetate and pyridine, not only alter the volatility in the system but also create heterogeneous region and new azeotrope (in case of pyridine heterogeneous region is formed under high pressure), a process referred to as heteroazeotropic extractive distillation (HAED), whose definition is given in the literature [16].

Glycerol, DMF, butyl acetate and pyridine were considered as entrainers for ED and HAED for the first time. Other substances previously published were taken for thermodynamic criterion validation, as well as comparison and selection of the best entrainer [8], [9].

According to Fig. 1 relative volilities in the presence of entrainers are sufficient for DMSO, 1,2-Ethandiol and Glycerol. In this case the larger the amount of the entrainer added, the higher the relative volatility is going to be.

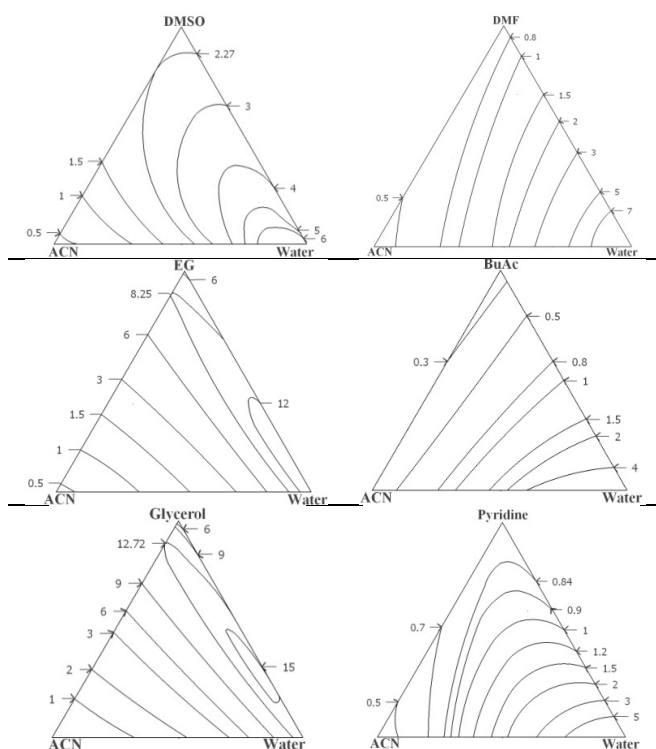


Fig. 1 Relative volilities in original mixtures in presence of selected entrainers

The different situation is observed for DMF, butyl acetate and pyridine. Volatility lines are not favorable for ACN

separation at the top of the ED column. In case of butyl acetate and pyridine, complications arise due to the Vaporization heats of entrainers, as both exhibit middle vaporization heats in the system ACN – water – entrainer (laying between  $\Delta H_{\text{vap}}^{\circ}(\text{ACN})=33.45$  and  $\Delta H_{\text{vap}}^{\circ}(\text{Water})=43.99$ ).

Results of entrainer evaluation using thermodynamic criterion at 298.15 K (isothermal) and at 760 mmHg (isobaric, real distillation process) are shown in Figs. 2 and 3.

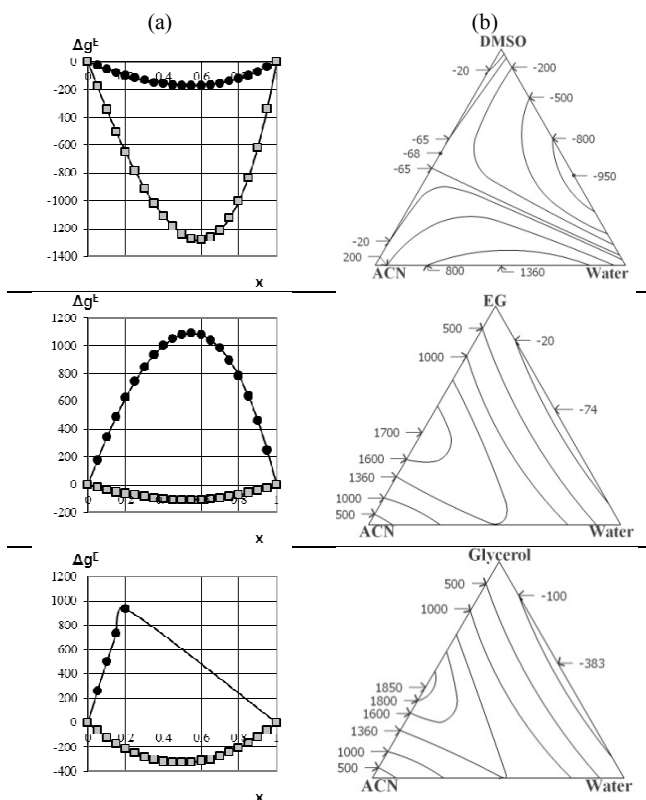


Fig. 2 Feasibility of thermodynamic criterion – values of excess Gibbs energy (J/mol) of ACN and water solutions with DMSO, 1,2-ethandiol (EG) and Glycerol in binary systems (a) at 298.15 K and (b) in ternary systems under 101.3 kPa ● ● ● ACN – entrainer, ◆ ◆ ◆ water – entrainer. In Figs. 2, 3:  $x$  is the concentration of ACN and water in mole fractions

It is well seen that potentially all compounds except for DMF will provide an increase in relative volatility as  $\Delta(\Delta G^E) \sim 1000$  J/mol is achieved, therefore we could pass on to the next step – calculations of ED and HAED and evaluation of energy costs.

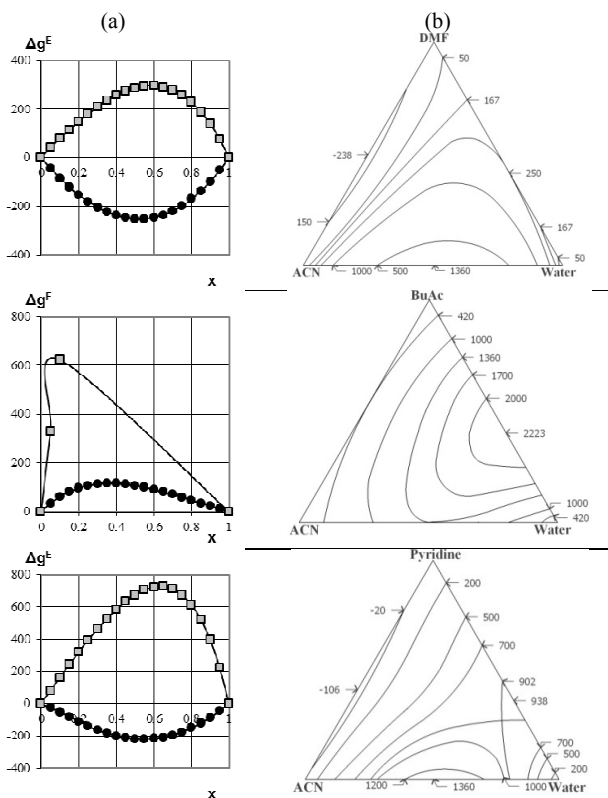


Fig. 3 Feasibility of thermodynamic criterion – values of excess Gibbs energy (J/mol) of ACN and water solutions with DMF, Butyl Acetate and Pyridine in binary systems (a) at 298.15 K and (b) in ternary systems under 101.3 kPa ● ● ACN – entrainer, ◆ ◆ ◆ water – entrainer

### B. Distillation and Energy Consumptions

Flowsheet on Fig. 4 was proposed for the ACN – water separation with selected entrainers. Stages for original ACN – water mixture and the entrainer feed into the extractive distillation column were optimized. ED column contains three sections: rectifying, extractive and stripping. Regeneration column is a column of ordinary distillation with one feed and two sections: rectifying and stripping.

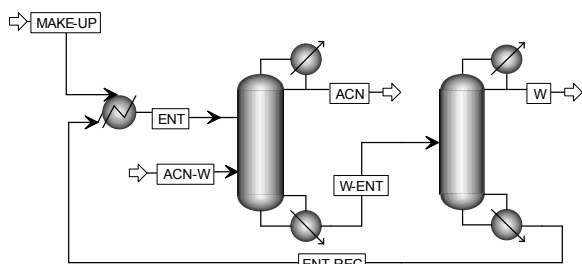


Fig. 4 Flowsheet for ACN separation process

Calculation of vapor liquid equilibrium of acetonitrile – water – entrainer was performed using the NRTL-RK model, and binary interaction parameters were regressed using

experimental data. The nonrandom two-liquid (NRTL) model was applied to correlate the binary and ternary VLE data.

The solvent to feed molar ratio, reflux molar ratio, feed stage, feed solvent stage, and feed solvent temperature, were determined and their effects on the separation and the energy consumption in the two columns were investigated.

Tables II-III represent data and initial conditions for ED and regeneration columns for DMSO, EG and Glycerol.

TABLE II  
RESULTS OF COMPARISON FOR ED COLUMN

Parameter	DMSO	1,2-Ethandiol	Glycerol
ACN Purity, %	0.9990	0.9990	0.9990
ED Reboiler Duty, kW	790.7	965.5	815.0
Ent/Feed, kmol/hr	32:100	60:100	15:100
R	0.8	1	0.87
Total No. of trays	40	40	35
Ent/Feed stage	6:33	4:35	2:32

TABLE III  
RESULTS OF COMPARISON FOR REGENERATION COLUMN

Parameter	DMSO	1,2-Ethandiol	Glycerol
Water Purity, %	0.9990	0.9990	0.9990
Regeneration Column Reboiler Duty, kW	871.7	946.0	739.2
R	0.3	0.3	0.01
Total No. of trays	12	10	8
Ent/Feed stage	5	6	4

Simulation results showed many advantages when using glycerol as entrainer, such as lower capital costs for the 5 theoretical stages, lower flow of entrainer needed, lower reflux ratio and less stages for regeneration compared to DMSO and 1,2-Ethandiol. Furthermore, glycerol has been shown to be the most suitable entrainer in relation to increasing concern regarding environmental issues, and for its versatility in support of greener technologies to conventional ED process.

Calculations for DMF, Butyl Acetate and pyridine were carried out and no suitable purity was reached by extractive distillation. The underlying reason for butyl acetate and pyridine can be found in the relation between the Vaporization Heats of these entrainers with the Vaporization heats of original mixture components, as each entrainer has to provide not only the maximum boiling temperature in the system, but also maximal Vaporization heat under real distillation process conditions to be efficient. For DMF, thermodynamic criterion showed that values of excess Gibbs energy were not high enough for effective separation at low energy costs, and its accuracy was proven by ED calculations.

### III. CONCLUSIONS AND FUTURE WORK

Several conclusions can be drawn from this work. First of all, to overcome azeotropy during ACN removal from water mixtures, extractive distillation was proposed as the best available technique. Column consequences were simulated respectively on the basis of NRTL model with Aspen Plus software. The effects of various parameters like entrainer flow, number of trays, their position and reflux ratio were

investigated. The results of the design led to the conclusion that the new process with glycerol as entrainer provides energy savings in reboiler of 6.5% and 13.0% to DMSO and 1,2-ethandiol, respectively. Furthermore, DMF, butyl acetate and pyridine entrainers have shown much higher energy consumptions and would not be suitable entrainers. Secondly, thermodynamic criterion for entrainer selection was validated both for isobaric and isothermal data, and could therefore be applied in both forms.

Future work will focus on ternary industrial mixtures separation, containing acetonitrile – water constituent by means of extractive distillation.

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