

A new combination process of distillation with salt extraction for separating organic solvent-water azeotropes

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Abstract: A novel process which can purify the organic solvents from their azeotropes with water is proposed. In this process, water can be drained off both from bottom and overhead of tower at the same time, and the organic solvent is concentrated in the tower and accumulated in the middle vessel at last. So the progress is time-shortened and energy-saving. The product purity is 99.8% and the product yield is more than 99.5%. Simulation of liquid-liquid equilibrium (LLE) and the equipment operation data agree well with the experiment.

Key words: azeotrope; separation; bath distillation; salt extraction

For the system that is either impossible (due to the existence of an azeotrope) or uneconomical (due to excessively low relative volatility) to separate by normal fractional distillation, several kinds of special distillation techniques can be employed. They are extractive distillation, salt-containing distillation^[1] and salt-containing extractive distillation^[2].

Accounting for the fact that salt has the effect on altering the mutual solubility of a solution components^[3], salting out one component of a solution and causing phase separation, a new salt effect separation process is promising, especially for organic solvents and water azeotropes. We call it "salt extraction", that is, only salt is used as the extraction agent and the salt-out effect makes the miserable systems separate into two phases. Most organic solvents can be salted out into the organic layer while water is salted in into the water layer.

1 Liquid-Liquid Equilibrium Experiment

Take a water-acetonitrile system as an example. According to the electronic theory, bivalent salt has a stronger effect on liquid-liquid equilibrium (LLE) than the monovalent salt does, so we chose CaCl_2 as a salt-out agent. The salt used was an analyzed reagent and was dried over 200 °C for six hours. Highly purified acetonitrile and distilled water were used in all of the experiment work.

The LLE data for water-acetonitrile- CaCl_2 system were determined at 25 °C and 0.1 MPa. In addition, the equilibrium was reached and maintained in a water bath thermostatically controlled at $(25 \pm 0.05)^\circ\text{C}$.

Magnetic agitation was operated to increase the rate of mass transfer and hasten the status to equilibrium. The gas chromatography was used in the determination of the solution composition.

The result shows that the concentration of acetonitrile in upper layer increased as the concentration of CaCl_2 increased. When it reached saturated concentration, $w(\text{CH}_3\text{CN}) = 96.6\%$ in upper layer.

2 Correlation of LLE Data

The liquid-liquid phase equilibrium is described using nonrandom two-liquid (NRTL) model^[4] developed for electrolytic system. It provides an accurate and thermodynamically consistent framework for representation of both the vapor-liquid equilibrium (VLE) and LLE of mixed-solvent electrolyte systems in the entire salt/solvent composition range with a single set of binary parameters. The model explicitly accounts for solvent-solvent, ion-ion, ion-solvent interaction in the liquid phase. The expression for the activity coefficient of solvent species in binary-solvent electrolyte system can be written as

$$\ln \gamma_1 = \frac{x_2 G_{21} \tau_{21} + 2x_3 G_{31} \tau_{31}}{x_1 + x_2 G_{21} + 2x_3 G_{31}} - \frac{x_1 (x_2 G_{21} \tau_{21} + 2x_3 G_{31} \tau_{31})}{(x_1 + x_2 G_{21} + 2x_3 G_{31})^2} + \frac{x_2 G_{12} [x_2 \tau_{12} + 2x_3 G_{32} (\tau_{12} - \tau_{32})]}{(x_1 G_{21} + x_2 + 2x_3 G_{32})^2} + \frac{2x_3 G_{13} [x_2 G_{23} (\tau_{13} - \tau_{23}) + x_3 \tau_{13}]}{(x_1 G_{13} + x_2 G_{23} + x_3)^2}$$

where $G_{12} = \exp(-\alpha_{12} \tau_{12})$, $G_{21} = \exp(-\alpha_{21} \tau_{21})$, $\alpha_{12} = \alpha_{21}$, $\tau_{12} \neq \tau_{21}$, and $x_1 + x_2 + 2x_3 = 1$. α is the nonrandom factor, τ is the energy parameter. For this

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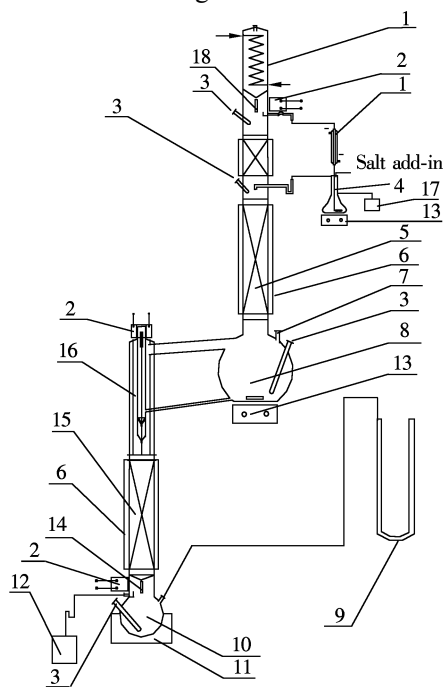
system of water-acetonitrile- CaCl_2 $\alpha = 0.12$, $\tau_{12} = 0.8865$, $\tau_{21} = 0.5268$.

The expression of γ_2 is similar with γ_1 , except interchange the footnotes 2 and 1.

Both the results of data correlation and the experimental data are compared in the ternary diagram of the system. It demonstrates that the electrolyte NRTL model gives an excellent representation of the system.

3 Process Combined

According to the experiment above, the pure acetonitrile product cannot be obtained by only salt extraction operation. It must be combined with fraction distillation, which removes the residual water in the organic layer after phase separation. The apparatus is shown in Fig.1.



1—Condenser; 2—Electromagnetic circuit; 3—Thermometric tube; 4—Salt extractor; 5—Distillation column; 6—Thermostatic glass jacket; 7—Feed tube of middle vessel; 8—Middle vessel; 9—Pressure gauge; 10—Reboiler; 11—Electronic furnace; 12—Acceptor; 13—Thermostatic magnetic stirrer; 14—Reboiling ratio controller; 15—Stripping column; 16—Reflux controller of middle vessel; 17—Salt-water storage tank; 18—Reflux ratio controller

Fig.1 Apparatus of distillation-salt extraction

The apparatus included three parts: distillation tower, salt extractor, and middle vessel.

The feed of any composition was added into the middle vessel and flowed slowly into the reboiler. The flow rate was controlled to maintain the storage of the boiler constant. The stripping column removed almost one half of water contained in the feed from the bottom of tower at a fixed reboiler ratio (that is the ratio of reflux and the efflux of the reboiler).

The azeotrope was formed at overhead of tower and condensed reflux flowed into the salt extractor, where enough CaCl_2 was put in advance, which made the azeotrope separate into two phases. Upper layer with high concentrate acetonitrile flowed back into the tower and low layer of salt aqueous was moved away.

As the distillation proceeded, the water was removed both from the bottom and the overhead of tower step by step, and the concentration of acetonitrile in the tower became higher and higher. When most of the water was moved away and in the middle vessel $w(\text{CH}_3\text{CN}) = 99.8\%$, stopped the operation.

The salt can be recovered by vaporization, then be used again in the salt extraction.

The feed in which $w(\text{CH}_3\text{CN}) = 40\%$ and $w(\text{water}) = 60\%$ was 2 000 mL and the operation time was 7.5 h. The amount of product was 780 mL and $w(\text{CH}_3\text{CN}) = 99.5\%$, with a yield 97.5%.

Compared with the normal distillation, the size of the bottom in this combined process was smaller and the energy consumed for boiling the feed was reduced greatly. Moreover, since water was removed from both the top and the bottom of the tower, the operation time was saved nearly a half.

4 Simulation of the Process

Compared with the normal distillation simulation, the salt extractor was a reflux ratio producer. Three different reflux ratios were: R_1 was the total reflux ratio, $R_{1,1}$ was the organic solvent reflux ratio and $R_{1,2}$ was the water reflux ratio. They were defined as the ratio of the amount of reflux with the efflux and determined by the electrolyte NRTL model referenced above. Ref. [5] described the simulation process in details. The result of simulation and the experiment were plotted in Fig.2.

It can be concluded that the simulation result agrees very well with the experiment.

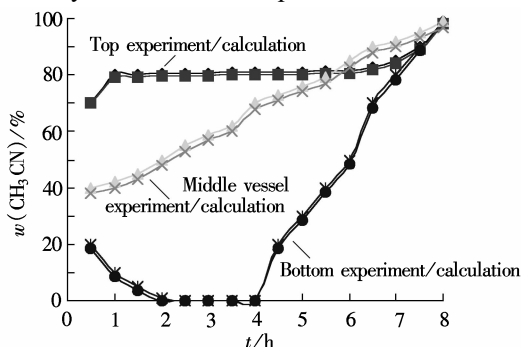


Fig.2 Composition profiles vs. time in top, middle, and bottom of the tower

5 Conclusions

In this paper, a new distillation-salt effect extraction combined process was proposed and simulated. The result proved the new process was efficient in purifying organic solvent from its azeotrope with water. In conclusion, the advantages of this process are:

1) It combines the fraction distillation and salt extraction together as one combination process, which can get the pure organic solvent product at last for some organic solvent-water mixture no matter what the original composite is;

2) With the middle vessel, not only the size of the bottom and energy consumed are greatly reduced, but also water can be removed from both the bottom of the tower and the overhead of the tower at the same time, so the operating time is greatly shortened;

3) Since salt extraction is conducted at the atmosphere pressure and room temperature, it is consumed nearly no energy in this step, which causes the whole process an energy-saving one compared with other special distillations.

The electrolyte NRTL model was fitful in describing the LLE of the water-acetonitrile- CaCl_2 system. And the mathematical simulation of the combined process agreed well with the experiment.

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利用分批精馏和盐效萃取分离有机溶剂-水共沸物的新工艺

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摘要: 建立了一种带有中间储罐的间歇精馏-盐效萃取联合装置. 通过塔顶盐效萃取器和中间罐的作用, 使原料中的水既能从塔顶除去, 又能从塔釜除去. 缩短了操作时间, 节约了塔釜加热量. 单批操作产品的质量浓度达 99.8% 以上, 收率达 99.5%. 对盐效萃取器中的液液平衡进行了实验研究和模型关联, 并在此基础上对整个装置进行了数学模拟, 模型计算结果与实验数据吻合良好.

关键词: 共沸物; 分离; 分批精馏; 盐效萃取

中图分类号: TQ26.3