Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Yao, Bingjia and Yang, Li(2009) 'Cloud Point Extraction of Acetic Acid from Aqueous Solution', Separation Science and Technology, 44: 2, 476 — 490
To link to this Article: DOI: 10.1080/01496390802437198
URL: http://dx.doi.org/10.1080/01496390802437198

Separation Science and Technology, 44: 476–490, 2009

ISSN: 0149-6395 print/1520-5754 online
DOI: 10.1080/01496390802437198

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Cloud Point Extraction of Acetic Acid from Aqueous Solution

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Abstract: A new acetic acid separation method was developed through a successful combination of cloud point extraction and complex extraction technology (CPE-SE), where an acetic acid complex compound formed and was solubilized in a surfactant micelle solution, instead of an organic solvent, and then concentrated into one phase by a phase separation process of the CPE technology. Since no organic solvent diluents were used, the new process was environmentally friendly and with a lower cost; meanwhile, the high selectivity of the complex extraction based on chemical complexation and high efficiency of CPE were also inherited as advantages over conventional solvent extraction process. In consideration of the compatibility and the related CPE characteristics, tributyl phosphate and PEG/PPG-18/18 Dimethicone were selected as complexing agent and surfactant of the CPE-SE system, respectively, and the extraction system was optimized by studying the effect of the main process parameters, including surfactant and complexing agent concentration, temperatures for the stirring and incubation steps, on the recovery and the distribution coefficient. A relative high recovery of 71.4% and a distribution coefficient of 1.4 were achieved simultaneously with the optimized process in the treatment of 0.1 M acetic acid solution. Based on its competitive extractability, high efficiency, low-cost, and environment friendlyness, the CPE-SE process was expected to be a potential separation method for a dilute acetic acid solution.

Keywords: Acetic acid, cloud point extraction, silicone surfactant, solvent extraction, TBP, water treatment

Received 22 February 2008; accepted 4 June 2008.

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INTRODUCTION

Acetic acid (AA) is widely used as solvent or raw material in chemical synthesis, medicinal chemistry, and food, printing and dyeing industries. As a result, most of their waste waters contain AA (1–3). AA can be produced from petrochemical feed stocks or renewable source such as corn or biomass by fermentation, however, the concentration of AA obtained was usually below 60%, and even lower than 20% by the fermentation method (2,4,5). Thus the enrichment and recovery of AA from its aqueous solution, especially the dilute one, were important to both its production and application. Owing to high energy consumption, conventional industrial separation technologies including azotropic distillation and precipitation were mainly used in the treatment of the AA solution with a high concentration; while a common solvent extraction with organic solvents, e.g., ethyl acetate or diethyl ketone, also showed a low economic efficiency facing a dilute AA solution lower than 3 wt% (3,6,7).

Although several new separation technologies, including the aqueous-phase system, have been developed, solvent extraction based on reversible chemical complexation (SE, also known as complex extraction, and the term complex extraction was used in this paper to differentiate from the conventional solvent extraction), is recognized as a high efficient separation technology for many extractable species, including recovering AA from a dilute solution (8–13). The most commonly used complexing agents in the SE process of AA were phosphate and amine, i.e., tributyl phosphate (TBP) and tri-n-octyl/decylamines (TOA), and in order to facilitate the phase separation efficiency, it is necessary to mix them with some organic solvent, namely a diluent (3,6). A variety of organic solvents, such as kerosene, benzene, cyclohexane, and methyl isobutyl ketone (MIBK) were reported to be used as the diluents in the SE process of AA, and their effects on the performance has also been compared (8). In addition to its phase separation efficiency, the performance of diluents were mainly focused on their ability to solvate complex compound and stabilize the complex compound (14). However, the usage of organic solvent led to a high production cost and environment pressure; moreover, the toxicity of solvents to bacteria, yeast, or cultures made the technology unavailable to the AA production with the fermentation method (1).

Recently, J. Causse et al. reported that TBP was able to be solubilized into surfactant micelles at a temperature higher than a critical value, so-called solubilization minimum temperature (SMT). Both SMT and solubilization amount of TBP can be adjusted by changing the hydrophobicity or structure of the surfactant (15,16). Although only one kind of surfactant, Pluronic (a PEO-PPO polyether nonionic surfactant), was researched in their works, the successful solubilization showed a good potential for surfactant micelle

solution to be used as the diluent, instead of organic solvents, in complex extraction. Meanwhile, a separation technology which is based on surfactant solubilization, cloud point extraction (CPE), has been reported as a promising method in recovering and enriching various species, including metal ions, protein, and organic species(17–19). Depending on the phase separation technology of CPE, the solubilized species were able to be separated along with micelles out of water, and concentrated into one phase, namely the surfactant-rich phase. Due to there being no organic solvent appearing in the whole process, CPE offered a cost-saving, environment-friendly separation method for the species which were able to be solubilized.

In this study, a cloud point extraction process combined with the complex extraction (CPE-SE) was used to recover AA from a dilute solution. In the new process, AA and the complexing agent formed complex compounds, which was solubilized with nonionic surfactants micelle solution, and then concentrated along with micelles into a surfactant-rich phase by phase separation after an incubation over cloud point. The combination of the two separation methods would endow the surfactant micelle solution with comparable phase separation and solubilization performance to that of organic solvents. Thus, employing micelle solution as diluent to substitute organic solvents, the new process would be environment friendly and with a lower cost.

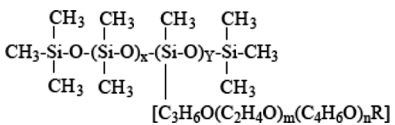
Different CPE and complex extraction systems were attempted to establish a compatible combination by finding a suitable complexing agent and surfactant, and the extraction system was optimized by studying the influence of many process parameters including the concentration of the surfactant and the complexing agent, and the temperature for the stirring and incubation step on the extractability, which was evaluated with recovery and the distribution coefficient. And then the suitability of the optimized system was also investigated in the acetic acid solution with different initial concentrations.

EXPERIMENTAL

Reagents

Dow Corning DC-190 (PEG/PPG-18/18 Dimethicone) (INCI), also known as silicone-ethylene oxide/propylene oxide copolymer, was supplied by Dow Corning (USA). Unfortunately, no information on the detailed molecular structure, i.e., the values of x, y, m, n, and the molecular weight of the compounds were available from the manufacturer; Triton X-114 (TX-114) and Tergitol TMN-6 (90% active ingredients) were obtained from Fluka (USA). Cloud point, SMT, and the structure

Table 1. Characteristic of surfactants used in this study

	Triton X-114	DC-190	Tergitol TMN-6
Cloud point (°C)*	68°C	38°C	60°C
SMT (°C)**	75°C	50°C	/
Structure	t-Oct-C_6H_4-$(OC_2H_4)_x$ OH, x = 7–8		$(CH_3)_3C(CH_2)_8(OC_2H_4)_xOH$ average of x = 6

*Surfactant concentration used in the cloud point determination is 40 wt%.

**Surfactant concentration used in the SMT determination: 50 wt%; complexing agent concentration: TBP, 2 wt%; AA concentration: 0.1 M.

of the three surfactants were listed in Table 1. TBP (99%) and TOA (98%) were purchased from Acros Organics. Deionized water was with a resistivity of 18.2 MΩ · cm. All the other reagents were of analytical grade, purchased from Sinopharm Group Chemical Reagent, and used without further treatment.

Procedure

AA aqueous solution with a prescribed concentration (0.1 M, except indicated) was prepared by diluting acetic acid with deionized water, and the concentration was determined by the titration with sodium hydroxide aqueous solution with a known concentration. A certain amount of complexing agent, surfactant, and AA solution with a fixed 10 ml total volume were contained into a 15 ml graduated glass test tube with a stopper and mixed with magnetic stirring apparatus in a water bath at a certain temperature, namely stirring temperature (ST, 60°C, except indicated). After 1 h of stirring (previous study showed that this time is sufficient to attain equilibrium), the test tube was transferred into another water bath and settled for 30 min at a certain temperature, namely incubation temperature (IT, 60°C, except indicated), and then treated by a centrifugation at a 4000 rpm for 15 min.

Analytical Procedure

After the centrifugation operation, the mixed solution was separated into two phases, aqueous phase (on the top) and surfactant-rich phase (in the bottom), and the volume of the two phases (V_a and V_s, respectively) were obtained by observing the graduation of the test tube. The AA concentration of the two phases (C_a and C_s, respectively) were determined by titration with sodium hydroxide aqueous solution with a known concentration, where the surfactant-rich phase was diluted with deionized water in a certain proportion before the titration. The recovery (R) and distribution coefficient (K_d) were calculated with following equations:

$$R = (C_s^* V_s)/(C_s^* V_s + C_a^* V_a) \tag{1}$$

$$K_d = (C_s/C_a) \tag{2}$$

The solubilization minimum temperature (SMT) was determined as the lowest temperature at which the phase separation of surfactant micelle solution occurred with the present of AA and complexing agent.

RESULTS AND DISCUSSION

Selection of Complexing Agent and Surfactant

Although TBP has been reported to be solvated in surfactant micelles, no study showed that the solubilization was available to its complex compound or occurred in AA solution. So, based on their structures and CPE performances, three nonionic surfactants were selected as the candidates for the CPE system to match with SE process. Good CPE performances were all achieved with the three surfactants in our previous studies. Among them, Tergitol TMN-6 possessed a similar polyether structure as the surfactant used in J. Causse's study; Triton X-114 was the most widely used surfactant in CPE studies, covering the extraction of metal ionic (with hydrophobic ligand) and organic species with a low molecular weight, e.g., polycyclic aromatic hydrocarbons (PAHs); DC-190 is a polyether silicone surfactant possessing a flexing chain structure, with which a lower water content in the surfactant-rich phase and a resulting lower V_s was achieved, and the low values were able to be persisted in a high surfactant concentration, thus a very high corresponding K_d was obtained in our previous CPE of PAHs research with DC-190 (20–23). According to J. Causse's study, a high surfactant concentration (>20 wt%) was necessary for a successful solubilization of TBP due to its big molecular volume, so a compact surfactant-rich phase is very important to a high K_d, considering the increasing V_s with surfactant concentration. Thus the lower V_s in a high surfactant concentration would be a big advantage to DC-190 to be used in the CPE-SE process of TBP, if it was able to offer a good solubilization for the complex compound.

As previously mentioned, TBP and TOA were well-known representatives of the two main kinds of AA complexing agents, phosphate and amine, respectively. Here, the CPE with the above three surfactants were attempted to match the SE processes with the two complexing agents respectively; results were shown in Table 2. Neither of the Tergitol TMN-6 CPE-SE system with the two complexing agents achieved a phase separation in the AA solution, regardless of adjusting the surfactant concentration or the incubation temperature. Although a good phase separation was achieved in the process with TX-114 or DC-190, both of the two CPE-SE systems offered a very low recovery (< 5%) of AA when TOA was employed as complexing agent. Different from TBP, TOA did not solvate its AA complex compound, so the corresponding extractability is more dependent on the solubility of diluents. The low extractability in Table 2 indicated that the surfactant aqueous solution environment was not suitable to the SE process with TOA, where few TOA-AA complex compounds were generated

Table 2. Extractability of CPE-SE process with different surfactants and complexing agents

Complexing agent		TX-114	DC-190	Tergitol TMN-6
TBP	R(%)	69	62	/
	K_d	1.0	1.1	/
TOA	R(%)	/	/	/
	K_d	/	/	/

AA initial concentration: 0.1 M; surfactant concentration: 40 wt%; complexing agent concentration: 2 wt%; stirring and incubation temperature: 80°C, 60°C, 75°C for TX-114, DC-190 and Tergitol TMN-6 respectively; '/': data obtained were very low or not able to be obtained.

or solubilized into the micelles. In the case of TBP, TX-114 and DC-190 CPE-SE systems both obtained relative high extractabilities, and the data of recovery and K_d with the two surfactants were both close. The decreasing extractability with the increasing of TBP concentration (the trend of DC-190 was shown in Fig. 2, TX-114 system has a similar trend, although the data were not given) proved that the solubilization of TBP-AA complex compound occurred in both two surfactant solutions. However, comparing with DC-190, TX-114 has a higher cloud point and solubilization minimum temperature (SMT, referring to Table 1), and the surfactants containing aromatic structure, including TX-114, were prohibited from using in many countries or groups including Europe union. Thus in the consideration of energy cost and the potential application, DC-190 was a better selection as the surfactant for the CPE-SE process with TBP as the complexing agent, and the following optimization study was also focused in DC-190 –TBP system.

Effect of Process Parameters on the CPE-SE Performance

Surfactant Concentration

Both the recovery and K_d increased with surfactant concentration ranged from 20 wt% to 50 wt% (Fig. 1), where a relative high recovery (70.65%) and K_d (1.24) were obtained simultaneously at 50 wt% in the CPE-SE system with 4 wt% TBP at 60°C ST and 60°C IT. The direct proportion trend of recovery to the surfactant concentration confirmed that the solubilization of TBP-AA complex compound required a high surfactant concentration, and the concentration of 50 wt% still did not offer a total solubilization of the whole complex compound (TBP

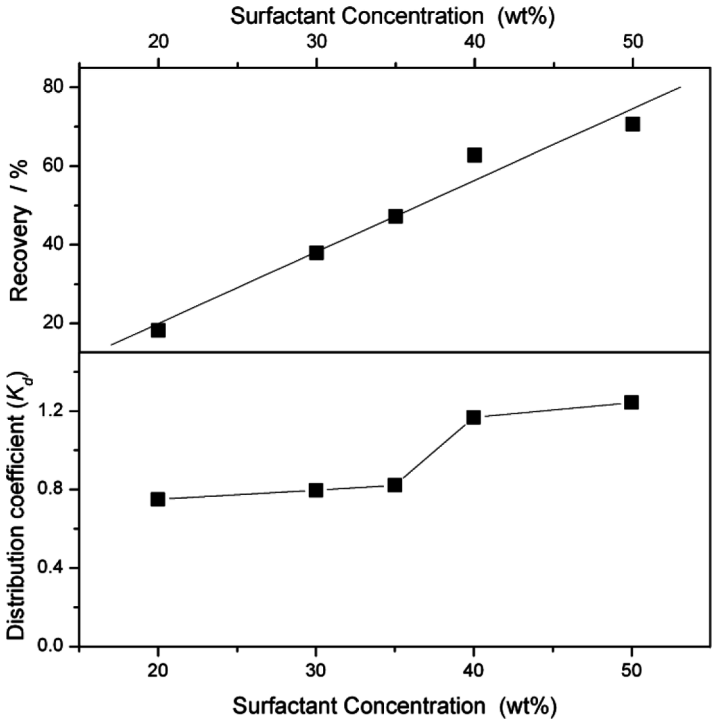


Figure 1. Effect of surfactant concentration on the recovery and distribution coefficient of acetic acid in the CPE-SE process (TBP concentration: 4wt%; ST: 60°C; IT: 60°C; AA concentration: 0.1 M).

concentration: 4 wt%), supposing that all AA molecules formed complex compound with TBP. Lower water content in the surfactant-rich phase was one of the important advantages of the DC-190 CPE process, comparing with the one with conventional surfactants, especially in the condition of high surfactant concentration. The detailed experiment results of the surfactant distribution after the phase separation were reported in our previous CPE research and equilibrium study, where the surfactant concentration in the surfactant-rich phase were close to 50 wt%, which was already a very high value, comparing with the commonly around 20 wt% value in the process with traditional surfactants, including Triton X-114 (21,24). In this study, we also determined the DC-190 concentration in the surfactant-rich phase by the same method (Because DC-190 has no UV absorbance, the spectrometry method was not able to be used to in the determination of its concentration in the phase. So in our previous study, the surfactant-rich phase was evaporated at 120°C for

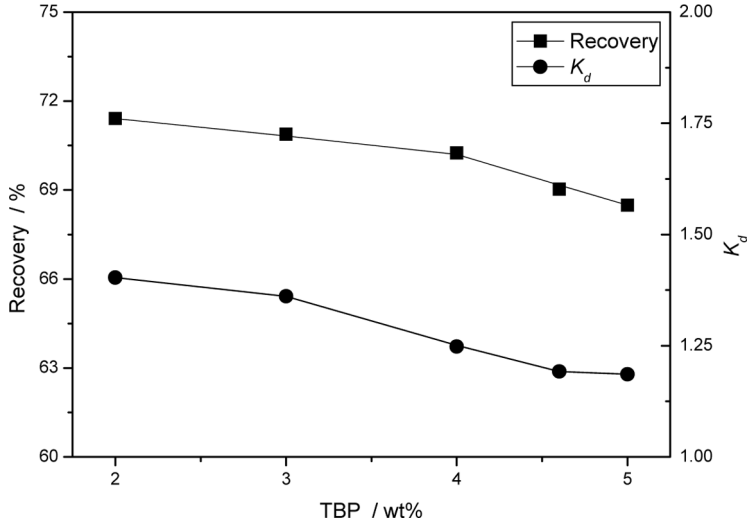


Figure 2. Effect of complexing agent concentration on the recovery and distribution coefficient of acetic acid in the CPE-SE process (Surfactant concentration: 50wt%; ST: 60°C; IT: 60°C; AA concentration: 0.1 M).

24 hr to totally remove the water, and the surfactant concentration was calculated by the difference of the phase weight before and after the evaporation) (21,24,25). When the initial surfactant concentration was 50 wt%, a surfactant concentration of 42.5% in the surfactant-rich phase was still able to be obtained, which means DC-190 successfully compressed the increasing V_s with surfactant concentration even at the initial surfactant concentration as high as 50 wt%; and cooperating with the quick increasing recovery, an increasing trend of corresponding K_d was obtained with surfactant concentration.

Although the complex ratio of TBP to acetic acid was mostly reported to (1:1), the molar ratios of TBP to AA in the feeds were usually much higher than 1 in common SE processes. In this experiment, their molar ratio in the feed was 1.5, which was a very low value in the SE process of AA with TBP, even in the presence of the organic solvent as the diluent. Together with the relatively high recovery, the good extractability proved that the surfactant micelle solution offered a comparable, even better environment for TBP to form a complex compound with AA efficiently and ensured its stability, than the one provided by TBP itself or its mixture with organic solvents, which increased the utilization rate of TBP and saved the cost. In a blank contrast experiment, where the same AA solution was treated with only the CPE process without TBP, a very low extractability

was obtained, which proved that the extractability of the current CPE-SE system was not sourced from the solubilization of micelles to AA, but to the TBP-AA complex compound. In the consideration of cost, 50 wt% was selected as the surfactant concentration for the following discussions.

Complexing Agent Concentration

Contrast to the effect of surfactant concentration, increasing concentration of complexing agent led to a decreasing trend in both recovery and K_d (Fig. 2). In common SE processes with the organic solvent, the extractability usually increased with the TBP concentration, where TBP acted as both complexing agent and extractant, due to its good solubility of TBP-AA complex compound, thus the higher TBP concentration increased the extractability of AA in both two ways. However, in the case of CPE-SE process, with a fixed surfactant concentration, micelle solution could only provide a limited solubilization capability, some of which might be taken up by the redundant free TBP, leading to a decrease of extractability for the complex compound. Although the redundant TBP could also solvate the complex compound, due to their large volumes, they could not be solubilized by micelles together with the complex compound. Meanwhile, the difference from the usual SE process also indicated that TBP only acted as the complexing agent in the current CPE-SE system, and the redundant TBP would lead to a drop of extractability, which was shown more conspicuously in the effect on K_d. The highest recovery and K_d were obtained simultaneously at 2 wt% TBP in the current CPE-SE system (at a lower TBP concentration, very low extractability was obtained), where the molar ratio of TBP to acetic acid in the feed was a lower value, 0.75, which also confirmed that the micelle environment was suitable for the complex extraction. Thus, 2 wt% was set as the optimal TBP concentration to be used in the following discussions.

Operation Temperature

To accelerate the formation of TBP-AA complex compound, the mixture of TBP, DC-190 and AA solution was stirred for 1 hr prior to the phase separation, but it would affect the increase of micelle volume and disturb the solubilization. So, after the stirring operation, the system was settled for another 30 min before sent to the centrifuge. Both of the two steps required incubation, and their temperatures were thought to affect the system in different ways: in the former, the effect on the formation of a complex compound was more important, while the growing of micelle volume and separating out of water was the main effect in the incubation

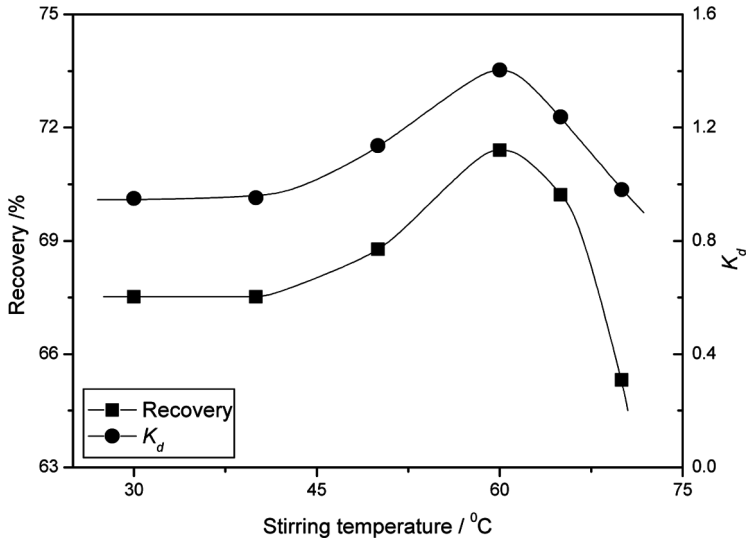


Figure 3. Effect of stirring temperature on the recovery and distribution coefficient of acetic acid in the CPE-SE process (Surfactant concentration: 50 wt%; TBP concentration: 2 wt%; IT: 60°C; AA concentration: 0.1 M).

step. Thus the effects of temperature on the two steps were discussed respectively in this study.

In the stirring step, both the recovery and K_d increased with temperature, achieving a maximum at 60°C, and decreased quickly at a higher temperature (Fig. 3). Based on the exothermic effect of forming a hydrogen-bond and the decrease of entropy during the complexation reaction, the increase of temperature was reported to have a negative effect on the formation of the complex compound; however, J. Causse's study showed that the solubility of the micelle to TBP increased with temperature, due to the increase of the hydrophobic character of PEO and PPO chain. The competition between the two inverse effects led to a critical temperature, 60°C, below which the solubilization has a bigger effect, while the dominant one belongs to the negative effect of complexation reaction at a higher temperature.

In incubation step, DC-190 CPE-SE system achieved a phase separation only at a temperature higher than 50°C (SMT of DC-190), and over 55°C the temperature has little effect on both recovery and K_d (Fig. 4), which means that 55°C was high enough in the incubation step. And in the consideration of energy cost, the temperature should be decreased from 60°C (ST) to 55°C (IT) when the system was transferred from the stirring step to the incubation step.

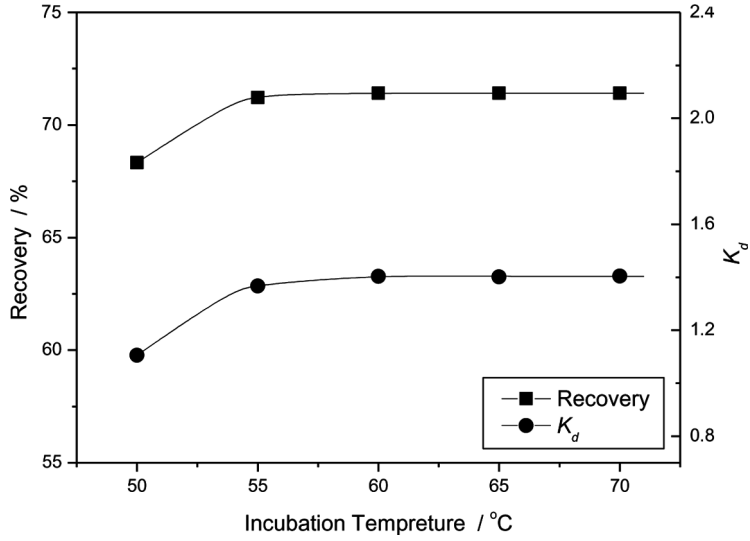


Figure 4. Effect of incubation temperature on the recovery and distribution coefficient of acetic acid in the CPE-SE process (Surfactant concentration: 50 wt%; TBP concentration: 2 wt%; ST: 60°C; AA concentration: 0.1 M).

Performance of the System at Different Initial Acetic Acid Concentrations

Based on the above discussions of the effects of different process parameters, an optimal CPE-SE process was selected, where 50 wt% DC-190 and 2 wt% TBP solution were used and the temperature for stirring and incubation were set at 60°C and 55°C respectively. The optimal

Table 3. Treatment results of the CPE-SE system at different initial AA concentrations

Acetic acid initial concentration (M)	Phase separation result after the centrifugation operation
0.05	phase interface is not clear, and aqueous phase volume is very low
0.1	phase interface is very clear
0.2	phase interface is not clear, and aqueous phase volume is very low
0.3	monophase

Surfactant concentration: 50 wt%; TBP concentration: 2 wt%; stirring temperature: 60°C; incubation temperature: 55°C.

process was applied to remove AA from its solution with different initial concentrations in the range of 0.05 M to 0.3 M, and the results were shown in Table 3. Unfortunately, it was hard to achieve a good phase separation for all the AA concentrations except 0.1 M, and the phase separation result turned worse with the increase of the deviation of AA concentration from 0.1 M, which indicated that the mechanism of the CPE-SE process was complicated, and the phase separation performance was influenced by AA concentration to a great extent. Thus the optimal condition under a certain condition was not able to be applied simply to other AA concentrations.

CONCLUSION

In this study, a new acetic acid separation technology combining cloud point extraction and complex extraction (CPE-SE process) was developed, where the organic solvent diluent used in conventional complex extraction was substituted by surfactant micelle solution to solubilize the complex compound of acetic acid and complexing agent, the complexed acetic acid was enriched in a surfactant-rich phase by a centrifugation operation after a incubation over cloud point. TBP and DC-190 were selected as the complexing agent and surfactant of the CPE-SE system, respectively. The investigation showed that the recovery and the distribution coefficient varied in a similar trend all along. The extractability increased with surfactant concentration, while a negative effect was observed with the increase of TBP concentration. In the case of operation temperature, the extractability increased with stirring temperature, achieving the maximum at 60°C, and then decreasing quickly at a higher stirring temperature; while a relatively high extractability was persisted with a incubating temperature over 55°C. The optimum conditions were: 50 wt% DC-190 and 2 wt% TBP, and the temperature for stirring and incubation were set as 60°C and 55°C respectively. A relative high recovery of 71.4% and a distribution coefficient of 1.4 were able to be achieved simultaneously with the optimal process in the treatment of 0.1 M acetic acid solution.

The CPE-SE process was totally free from the organic solvent, resulting in it being environment-friendly and at a lower cost; adding the high selectivity and quick process derived from the complex extraction and cloud point extraction respectively, the CPE-SE process was thought to be an efficient and feasible separation method for a dilute acetic acid solution.

ACKNOWLEDGEMENTS

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