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Efficiency of fluorinated alcohol for extraction of organic acid from its dilute aqueous solution: A model study

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ABSTRACT

1H,1H,2H,2H-Perfluoro-1-octanol, octanol and benzoic acid were selected as model extractant and target acid to investigate extraction behaviors of fluorinated n-alcohol. According to experimental results, the extraction capacity of 1H,1H,2H,2H-perfluoro-1-octanol is acceptable with distribution ratio (D) of 13. The extraction efficiency reaches 98.0% after three stage continuous countercurrent extraction under the conditions of pH 2.55–3.16 and temperature 20–25 °C at oil to water (V_o/V_w) ratio of 1. The residual of 1H,1H,2H,2H-perfluoro-1-octanol in aqueous phase was quite low, which was less than 2 ppm. The back-extraction of 1H,1H,2H,2H-perfluoro-1-octanol by NaOH was demonstrated to be feasible, which is up to 100% with single stage.

1. Introduction

Carboxylic acids are a species of popular organics presented as reagents, mediums, products or by-products. Aqueous streams containing some carboxylic acids at relatively low concentration are often discharged by many industries, which often cause the environmental pollution. Recovery of these carboxylic acids from the dilute aqueous solutions has received increasing attention [1–8].

Many processes which include precipitation, distillation, adsorption, membrane separation, ion exchange or solvent extraction are proposed to recover carboxylic acids from their dilute aqueous solution. Among them, solvent extraction is taken as a kind of important separation method for its high efficiency, economy and maturity to isolate carboxylic acids from dilute aqueous solutions [9–18].

For a successful solvent extraction implementation, a proper extractant needs to be identified. Organics used for the extraction of carboxylic acids are categorized as: (i) oxygen-bearing and hydrocarbon extractants; (ii) organophosphorus compounds; and (iii) high molecular weight aliphatic amines [1]. Since amines provides higher distribution ratio, a lot of work about the

extraction of carboxylic acids using amines has been reported [19,20]. However, the amines could interact with protons of carboxylic acids to form ammonium salts in extraction process. Such ammonium salts have the similar characteristics of ionic surfactants and are prone to form emulsion phases, which decrease the extraction efficiencies or even ruin the whole operation [21,22]. In addition, the high affinity of amines to carboxylic acid brings about difficulty of back-extraction. Therefore, oxygen-bearing and organophosphorus compounds like octanol, tri-n-butyl phosphate (TBP) are attempted as extractants for carboxylic acids recovery [23]. Unfortunately, the residual of extractant in the feed solution is significant and often called second contamination [11,24–26]. Hence, to solve extractant loss is of great value.

The solubility of extractant in aqueous phase is one of essential reasons for extractant loss [27]. Thus strong hydrophobic groups for an excellent extractant are absolutely necessary. The traditional hydrophobic groups are categorized according to the sequence of their hydrophobic strength, as: perfluorocarbon > mixed hydrocarbon > aromatic hydrocarbon > hydrocarbon with weak hydrophilic group. Baker et al. have introduced the perfluorinated analogues of TOPO ($\{CF_3(CF_2)_5CH_2CH_2\}_3P = O$), perfluorinated phenols (C_6F_5OH) and perfluorinated ketone($\{CF_3(CF_2)_5CH_2CH_2\}_2C = O$ to investigate the extraction of a number of metals and radioisotopes from water [28–31]. The distribution ratios of extraction process for perfluorinated compounds are generally similar to

Fig. 1. The construction of 1*H*,1*H*,2*H*,2*H*-perfluoro-1-octanol.

Table 1
Property-summary of chemicals.

Chemicals	Molecular structure	Molar mass	Density (kg/m³)
Benzoic acid	C_6H_5COOH	122.12	1266
Octanol	$C_8H_{17}OH$	130.23	830
1*H*,1*H*,2*H*,2*H*-Perfluoro-1-octanol	$C_8H_4F_{13}OH$	364.10	1651

that for the non-flourinated compounds, indicating that the electron withdrawing fluorous groups do not significantly influence the donor strength of the extractant. Hence, it is feasible to use perfluorinated analogues of extractant to decrease the residual of extractant in aqueous phase.

1*H*,1*H*,2*H*,2*H*-Perfluoro-1-octanol is a unique molecule containing a group with high affinity for carboxylic acids and a strong hydrophobic fluorocarbon group, its structure is shown in Fig. 1 [32]. It is possible to be applied as a novel extractant not only with reasonable extraction ability, but also with sufficiently low solubility in aqueous phase due to its high hydrophobicity. Hence, 1*H*,1*H*,2*H*,2*H*-perfluoro-1-octanol, octanol and benzoic acid were selected as the model extractant, opponent and target acid to investigate their extraction and residual behaviors.

2. Materials and experimental

2.1. Materials

Octanol with purity of 99% and 1*H*,1*H*,2*H*,2*H*-perfluoro-1-octanol with purity of 97% were purchased from Sigma Aldrich, Germany. Benzoic acid with purity of 99.5%, analytical grade hydrochloric acid and sodium hydroxide all were produced by Beijing chemical factory, China. The deionized water was produced in the Laboratory Centre of University of Science and Technology Beijing, China. The properties of chemicals are summarized in Table 1.

2.2. Experimental

2.2.1. Extraction section

Due to the maximum solubility of benzoic acid of 0.35 g in water at 25 °C, the aqueous acidic solutions with initial concentrations ranges from 0.1 to 0.35%(w/w) (0.008 to 0.028 mol/L) were prepared by dissolving stoichiometric benzoic acid in deionized water.

All extraction experiments were carried out with total 20 mL mixtures of different volume ratios of the aqueous and organic solutions in Erlenmeyer flasks of 100 mL and shaken at 250 rpm in a temperature-controlled reciprocal shaker water bath. The pH of the extraction system was adjusted by 1% (weight) hydrochloric acid or sodium hydroxide aqueous solutions. The operation time was set as 2 h which was proved sufficient for equilibration by preliminary tests. Then the mixtures were kept in the bath for phase separation. After the two phases were separated, the pH
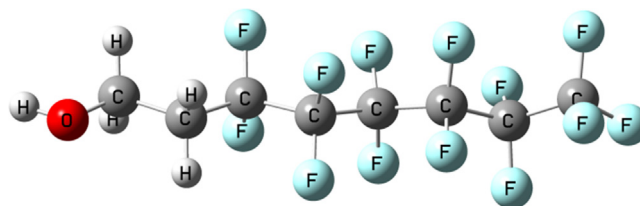
value of aqueous solution was measured by a digital pH meter (pH211, HANNA, Italy). The benzoic acid concentrations in aqueous phase were determined through UV–vis absorption spectra (TU-1901, UV–vis spectrophotometer, China) at 270 nm. The acid concentrations in the organic phase were calculated by mass balance(due to the high hydrophobicity of 1*H*,1*H*,2*H*,2*H*-perfluoro-1-octanol, phase ratio was assumed to be constant).

The extraction efficiency is defined as $E(\%)$

$$= \frac{(C_{HA0} - C_{HA})}{C_{HA0}} \times 100 \tag{1}$$

The distribution ratio is defined as $\quad D = \dfrac{C_{HA^*}}{C_{HA}} \tag{2}$

The experiment value of the loading factor is defined as $\quad Z$

$$= \frac{N_{HA^*}}{N_{extractant}} \tag{3}$$

The three-stage simulated continuous counter-current extraction was carried out as follows [33]. The fresh organic phase (org 0) was well mixed with the fresh aqueous phase (aq 0) with the O/A ratio of 1. After the mixture was settled down, the aqueous phase was discarded. The acquired preloaded organic phase a1 was well mixed with the fresh aqueous phase (aq 0) with the O/A ratio of 1. After the mixture was settled down, the organic phase (a2) of the first stage of the three-stage simulated continuous counter-current extraction was ready. The discharged aqueous phase (b1) was well mixed with the fresh organic phase (org 0) with the O/A ratio of 1. After the mixture was settled down, the aqueous phase was discarded. The organic phase (c1) of the second stage of the three-stage simulated continuous counter-current extraction was ready. The third stage of the three-stage simulated continuous counter-current extraction was the fresh organic phase. The fresh aqueous phase was well mixed with the prepared first stage organic phase with the O/A ratio of 1. After the mixture was settled down, the aqueous phase was transferred to the second stage and well mixed with the prepared second stage organic phase. In this way, the three-stage continuous counter-current extraction was simulated. The whole process was described in Fig. 2.

2.2.2. Back extraction/extractant regeneration

In back-extraction process, the loaded organic phase mentioned above was mixed with equal volumes of various concentrations of NaOH aqueous solutions.