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

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ABSTRACT

The quantum chemical parameters of fluorinated octanol, such as charge distribution, molecular electrostatic potential and frontier molecular orbital have been investigated through quantum chemistry calculation by DFT method using the B3LYP level with the standard 6-311++G(d,p) basis set. In first step the natural population analysis (NPA) and molecular electrostatic potential (MEP) methods were applied to determine the reactive site of fluorinated octanol. In second step comparative analysis of frontier molecular orbital energy gaps of fluorinated octanol and benzoic acid was used to investigate the effect of fluorinated substitutional degree on benzoic acid extraction behavior of fluorinated octanol. The calculated results suggested that the reactive site is localized on the oxygen atom and the electron donor strength of the oxygen atom decreases with the increase of the fluorinated substitional degree due to the electron-withdrawing of fluorous group. 1H,1H,2H,2H-perfluoro-1-octanol and 5,5,6,6,7,7,8,8-nonafluoro-1-octanol were selected as the extractants to testify the proposed theory. According to the prediction, the extraction capability on benzoic acid by 1H,1H,2H,2H-perfluoro-1-octanol is lower than that of 5,5,6,6,7,7,8,8-nonafluoro-1-octanol at room temperature. The experimental results are in agreement with the corresponding theoretical data.

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1. Introduction

Many processes including precipitation, distillation, adsorption, membrane separation, ion exchange and solvent extraction, are proposed to recover carboxylic acids from their dilute aqueous solution [1–8]. Among them, solvent extraction is an economical and easy scaling-up method for separation of carboxylic acids from their dilute aqueous solutions [9–11]. Unfortunately, even some non-ionized extractants as ketones or alcohols, have been proved to be loss in the feed solution significantly as secondary waste, which was intorlerated by the environment [3,12–15]. Hence, to solve extractant loss is of great value.

Recent studies have shown that entrainment and dissolution of extractant in aqueous discharge streams are essential reasons for extractant loss [13]. Hatton showed that in some cases conventional extractant can be tailored to modify their physical properties while retaining their chemical functionalities. As one example of nOTE (n-octyl tetrahydrofurfuryl ether) replaces for THF (tetrahydrofuran) to reduce its water solubility significantly while retaining its chemical functionalities [16]. Baker et al. reported that substituting fluorine into the chelating agent of ScCO$_2$, such as perfluorinated phosphine oxide, perfluorinated phenols and perfluorinated ketone, increased the solubility in the supercritical phase by up to three orders of magnitude and the distribution ratios of extraction process for perfluorinated compounds are generally similar to that for the non-flourinated compounds [17–20]. In our previous work, we disclosed the extraction of benzoic acid from its dilute aqueous solution by using 1H,1H,2H,2H-perfluoro-1-octano as extractant. The results showed that the residual of 1H, 1H, 2H, 2H-perfluoro-1-octanol in aqueous phase was quite low compared to octanol, which indicates that 1H,1H,2H,2H-perfluoro-1-octanol has a high hydrophobicity [21].

Nomenclature

E	extraction efficiency
C_{HA_0}	the initial carboxylic acid concentration in the aqueous phase
C_{HA}	the total (dissociated and undissociated) concentration in the aqueous phase at equilibrium

Table 1
Property-summery of Chemicals.

Chemicals	Molecular structure	Molar mass	Density (kg/m³)
Benzoic acid	C_6H_5COOH	122.12	1266
5,5,6,6,7,7,8,8-nonafluoro-1-octanol	$C_8H_8F_9OH$	292.15	–
1H,1H,2H,2H-perfluoro-1-octanol	$C_8H_4F_{13}OH$	364.10	1651

However, the distribution ratio, load ratio and extraction efficiency for fluorinated octanol, 1H,1H,2H,2H-perfluoro-1-octanol, were generally less than that of the non-flourinated octanol. It indicates that the fluorous group of flourinated octanol has a certain effect on the extraction behavior of fluorinated octanol.

Quantum chemical calculations involves electronic properties and chemical reactivity [22–24]. In fact, extractant interacts with target acid through electronic transfer [25]. The density functional theory (DFT) provides an adequate treatment of the correlation between the motions of the electrons within a molecular system and the results are in great agreement with the experimental results [26–30].

In this paper, density function theory (DFT) calculation methods were carried out to study the effect of fluorinated substitional degree on benzoic acid extraction behavior of fluorinated octanol. First of all, the atom charge distribution and electrostatic surface potential of fluorinated octanol were calculated to determine the reactive site. Next, comparative analysis of molecular orbital energy gaps of fluorinated octanol was used to investigate the effect of fluorinated substitutional degree. In addition, 1H,1H,2H,2H-perfluoro-1-octanol and 5,5,6,6,7,7,8,8-nonafluoro-1-octanol were selected as the extractant. The extraction equilibrium on benzoic acid by 1H,1H,2H,2H-perfluoro-1-octanol and 5,5,6,6,7,7,8,8-nonafluoro-1-octanol were studied to verify the theoretical calculations. Through the above work, predicting the best fluorinated extractant is of theoretical and practical significance.
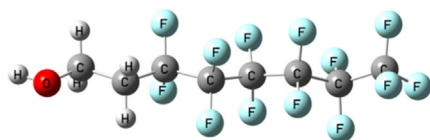
2. Materials and methodology

2.1. Materials

1H,1H,2H,2H-perfluoro-1-octanol and 5,5,6,6,7,7,8,8-nonafluoro-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 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.
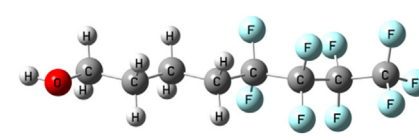
2.2. Methodology

2.2.1. Computational details

The theoretical calculations were performed at the density functional level of theory (DFT, B3LYP functional) [31–33],

employing the Gaussian 03 suite of programs [34]. In the first step of our calculation, the 6-31G(d,p) basis set were chosen for the optimized geometries of fluorinated octanol and benzoic acid. In the second step, the quantum chemical parameters calculations (frontier molecular orbital, charge distribution analysis, molecular electrostatic potential) of the molecule were performed using a large basis set 6-311++G(d,p) in the case of solvation with water. These analysis have been used to study for illuminating the electronic effects (Fig. 1).

2.2.2. Experimental details

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 1H,1H,2H,2H-perfluoro-1-octanol and 5,5,6,6,7,7,8,8-nonafluoro-1-octanol, phase ratio was assumed to be constant) [23].

The extraction efficiency is defined as

$$E(\%) = \frac{(C_{HA_0} - C_{HA})}{C_{HA_0}} \times 100$$

3. Results and discussion

3.1. Charge distribution analysis

The calculation of atomic charges plays an important role in the application of quantum mechanical calculations to molecular systems. The natural population analysis (NPA) provides an efficient method for predicting the reactive site of molecules [35]. The charge distributions over the atoms suggest the formation of donor and acceptor pairs involving the charge transfer in chemical reactions [36]. The atomic charge distribution in n-octanol molecule was calculated and collected in Fig. 2.

(i) 1H,1H,2H,2H-Perfluoro-1-octanol   (ii) 5,5,6,6,7,7,8,8-Nonafluoro-1-octanol

Fig. 1. The construction of fluorinated octanol.