

An efficient and cost-effective solvent extraction for recovery of phenol and its hydroxy derivatives from aqueous medium

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(Received 2 March 2010 • accepted 28 May 2010)

Abstract—A cost-effective solvent extraction process for recovery of phenol and its hydroxy derivatives from aqueous medium was developed. Four different solvents—Tributyl phosphate (TBP), Triphenyl phosphate (TPP), Methyl isobutyl ketone (MIBK) and Oleic acid (OA)—selected based on their miscibility with water. The extraction efficiency (EE) of the selected solvents was studied. A reversed-phase HPLC system connected to an RP, C18 column was used to analyze the aqueous medium to evaluate the performance of the selected solvents. TBP exhibited the best extraction performance, while TPP and MIBK proved to be good when large amount of solvent was used. However, OA was found to be inefficient to extract the solutes under investigation. Interestingly, a different solvation property was observed and elucidated using the solvation theory.

Key words: Solvent Extraction, Extraction Efficiency, Cost-effective, Phenol Hydroxylation Solvation Theory, Aqueous Medium

INTRODUCTION

Hydroxylation of phenol (PhOH) is an industrially important process wherein the products such as catechol (CAT), hydroquinone (HQ) and benzoquinone (BQ) have large-scale applications such as photographic film developers, antioxidants, polymerization inhibitors, drugs and pharmaceuticals [1-3]. The increasing demand for these products has been the driving force for developing new technologies for their production. A number of processes based on hydroxylation of phenol to produce catechol and hydroquinone were reported [2-6]. Among the heterogeneous catalysts, TS-1 and acid clays were used with organic solvents such as methanol and acetone [2,3]. However, it is well known that TS-1 is an expensive catalyst and also the organic solvents are difficult to recycle. In an attempt to replace TS-1 as well as the organic solvents, zeolites were tried with clean oxidants like H_2O_2 in aqueous medium [4-6]. This process gives good yield of the products of phenol dissolved in water. To maximize yield and minimize the environmental impact of waste water streams, it is important to recover as much of the phenol and its derivatives from the aqueous medium as possible. Phenol-containing aqueous streams are also generated from a number of sources of oil refining, petrochemical, coke and coal gasification industries. Thus an additional separation and purification process to recover phenol and its hydroxyl derivatives from aqueous medium has become highly inevitable. Usually, fractional distillation has been used to separate the components having different boiling points. Since the boiling point of water (373 K) is lower than that of phenol (455 K), water requires a high vaporization enthalpy of 539 cal·g⁻¹ because of its high specific capacity compared to phenol (117 cal·g⁻¹) [7]. Thus removing large quantity of water from the reaction mixture consumes more energy and gives rise to high process cost. From

literature, it has been noted that phenols could be extracted from waste water by using organic solvents [8-11]. Hence, it is worthwhile to develop a solvent extraction method by investigating suitable solvents for recovery of phenol and its derivatives. Another advantage of the method is that the water could be recycled for hydroxylation reaction after solvent extraction.

The present manuscript describes the selection of a suitable solvent for optimum recovery of phenol and its hydroxy derivatives from aqueous medium. The extraction efficiency of different solvents was examined and the most suitable solvent was presented.

The solvation properties were also elucidated theoretically.

EXPERIMENTAL

1. Simulated Phenol Solution (SPS)

A typical reaction product of hydroxylation of phenol using zeolite as a catalyst was simulated by preparing an aqueous solution containing phenol, catechol, hydroquinone and benzoquinone dissolved in distilled water in the weight ratio of water/PhOH/CAT/HQ/BQ=500/77/14/5.4/0.8 (w/v).

2. Solvent Selection

Initially, commercial grade solvents (tributyl phosphate (TBP), triphenyl phosphate (TPP), methyl isobutyl ketone (MIBK), n-butyl carbinol (NBC), tetraethylene glycol (TEG), oleic acid (OA) and NMP (n-methyl-2-pyrrolidone)) were chosen for extraction of PhOH and its hydroxy derivatives from water. Preliminarily, experiments were carried out to check their miscibility with water. Here, 10 g of water was mixed vigorously with each solvent and centrifuged at 3,000 rpm for 10 min. As shown in Table 1, the organic layers of TBP, TPP, MIBK and OA were separated from water and these four solvents were selected for further experiments.

3. Solvent Extraction

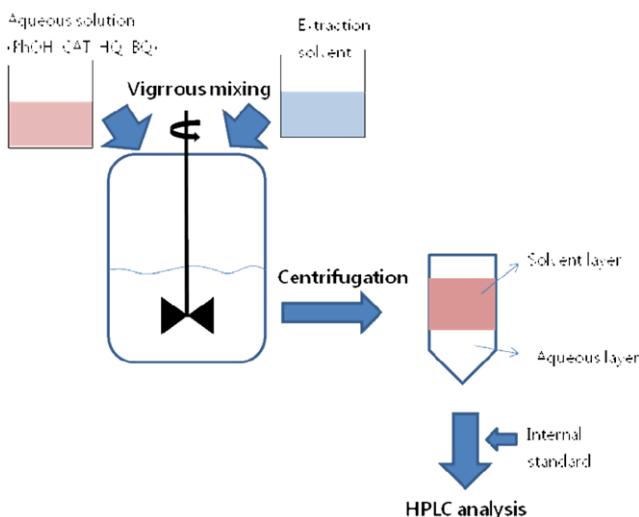
The selected solvents were added to 10 g of SPS to extract phenol and its derivatives from water. The amount of added solvent varied

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Table 1. Fundamental physical characteristics of the investigated solvents

Solvent	TBP	TPP	MIBK	OA
Boiling point (°C)	289	370	117	360
Melting point (°C)	-80	47-53	-84.7	13
Specific density (g/cc)	0.973	1.184	0.802	0.895
Dipole moment (μ (D))	3.07	N. F.	1.22	2.5
Solubility δ (J/mol) ^{0.5}	15.3	N. F.	17.7	15.95
Permittivity (ϵ_r)	8.1	N. F.	13.1	2.03

N.F: Not found

**Fig. 1. Schematic explanation of solvent extraction. Notice that solvent layer and aqueous one can be changed according to their density difference.**

from 10 g to 50 g. The solution was stirred vigorously with a mechanical stirrer at 500 rpm for 30 min. Later, it was centrifuged at 3,000 rpm for 10 min. Clear separation between water and solvent layers was observed. Samples were collected from each layer. The water layer was analyzed by a high-performance liquid chromatograph. All the experimental procedures are shown in Fig. 1 schematically.

4. HPLC Analysis

HPLC (Shimadzu, LC-10ADVP) equipped with a UV/Vis detector (ICL, LC1200) was used for analysis. A reversed-phase RP, C18 column with a mobile phase containing water: methanol (95 : 5 v/v)

at a flow rate of 1.5 ml/min and 2,000 psi pressure was used for separation. The detection was carried out at 254 nm of UV light. 4-Fluorophenol (f-PhOH) was used as an internal standard (IS). Methanol was used as a diluent. A clear separation between the peaks corresponding to HQ, BQ, CAT, HQ, PhOH and f-PhOH was obtained. For quantitative analysis for PhOH and its derivatives, calibration curves of individual compounds with respect to f-PhOH were plotted for pre-determined molar ratio vs. peak areas. The linear relationship obtained from the calibration curve was used for estimation of concentration of phenol and its derivatives before and after extraction.

RESULTS AND DISCUSSION

1. Suitable Solvent Selection

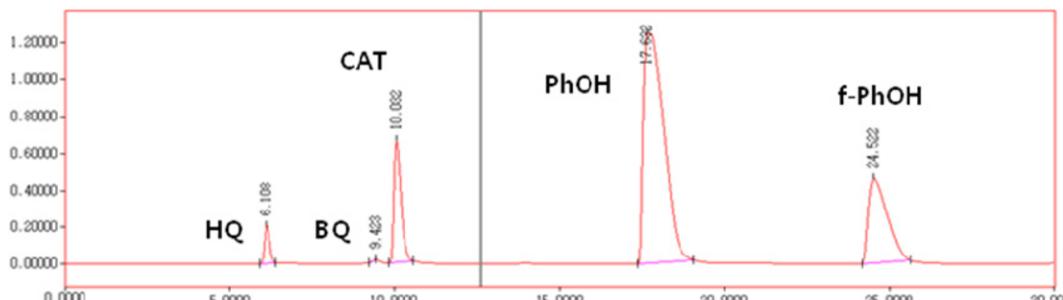
To extract all the solutes of PhOH and its derivatives from the reaction mixture, an extraction solvent immiscible with water, which produces phase separation, is required. Since TEG, NMP and NBC were found to be miscible with water, they were excluded and not considered as suitable solvents for extraction. In contrast, TBP, TPP, MIBK and OA were immiscible with water and a very good phase separation was observed. These four solvents were selected as suitable for extracting PhOH and its hydroxy derivatives from SPS. Table 1 gives the boiling points and other physical characteristics of the selected solvents which were considered later for developing an economical process.

2. HPLC Analysis of SPS before Solvent Extraction

Fig. 2 shows the HPLC chromatogram of the simulated solution of phenol and its derivatives (SPS). Fig. 2 shows that all the solutes were well separated from each other, confirming the suitability of the conditions used for separation and quantitative determination of PhOH and its derivatives. Also, no distinct peaks associated with the selected solvents of TBP, TPP, MIBK and OA were observed. The quantitative estimations were carried out from the peak area comparison between the individual solutes and f-PhOH used as an internal standard (IS).

3. HPLC Analysis of SPS after Solvent Extraction

Fig. 3 shows the HPLC chromatograms of the aqueous layer after extraction with (a) 10 g, (b) 20 g, (c) 30 g and (d) 40 g of TBP. When 10 g of TBP was used, small peaks associated with PhOH and its derivatives were seen in the chromatogram. Note that the retention time of internal standard varied little because of the fluctuation of high pressure from 2,000 to 1,500 psi. Above 20 g of TBP, no significant peaks corresponding to PhOH and its derivatives were observed in the chromatogram (Figs. 3(c) and (d)). Trace amount of

**Fig. 2. HPLC data for the simulated phenol-containing solution (SPS).**

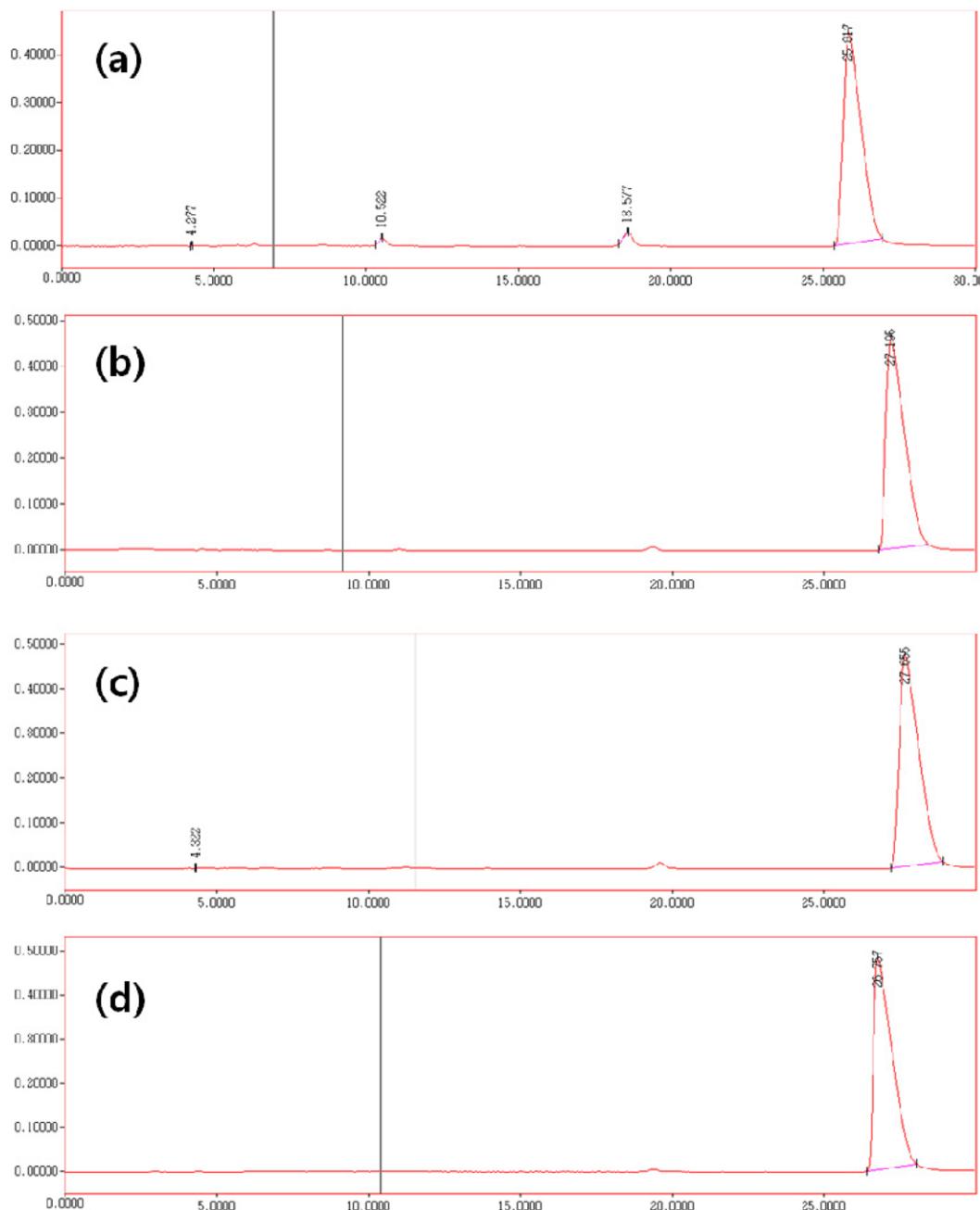


Fig. 3. HPLC data for the water layer after extraction of tributyl phosphate (TBP) with a change of TBP added amount. (a) 10 g, (b) 20 g, (c) 30 g and (d) 40 g.

PhOH exists until the addition of 40 g of TBP. Thus, the extraction of PhOH and its derivatives using TBP was found to be highly efficient. Fig. 4 displays the solvent extraction results using MIBK as a solvent. Here, small peaks were observed until 20 g. After an addition of 40 g of MIBK, only the peak corresponding to PhOH remained in a small amount and other peaks almost disappeared. Hence, MIBK exhibited a less efficient extraction performance than TBP. Similarly, the solvent extraction results using OA are shown in Fig. 5. In this case, large amount of PhOH and its derivatives still remained after extraction even with 40 g of solvent, indicative of a very poor extraction. To use an extraction solvent of high boiling point, TPP was tried and the results are shown in Fig. 6. Since the melting point of

TPP (47-53 °C) is higher than the ambient temperature, the extraction was carried out at 70 °C [7]. Fig. 6 shows HPLC chromatograms of SPS after extraction with different amounts of TPP. As seen, most of the PhOH and its derivatives were extracted when 10 g TPP was added. With an increase of solvent, peak heights became smaller but traces of solutes still remained even when 40 g of TPP was added.

The concentration of PhOH and its derivatives was calculated from the areas of the peaks seen in Figs. 3-6. The calibration curves between molar ratio and peak areas were obtained preliminarily and the relative response factors were calculated. The concentration of the remaining PhOH and its derivatives after extraction was esti-

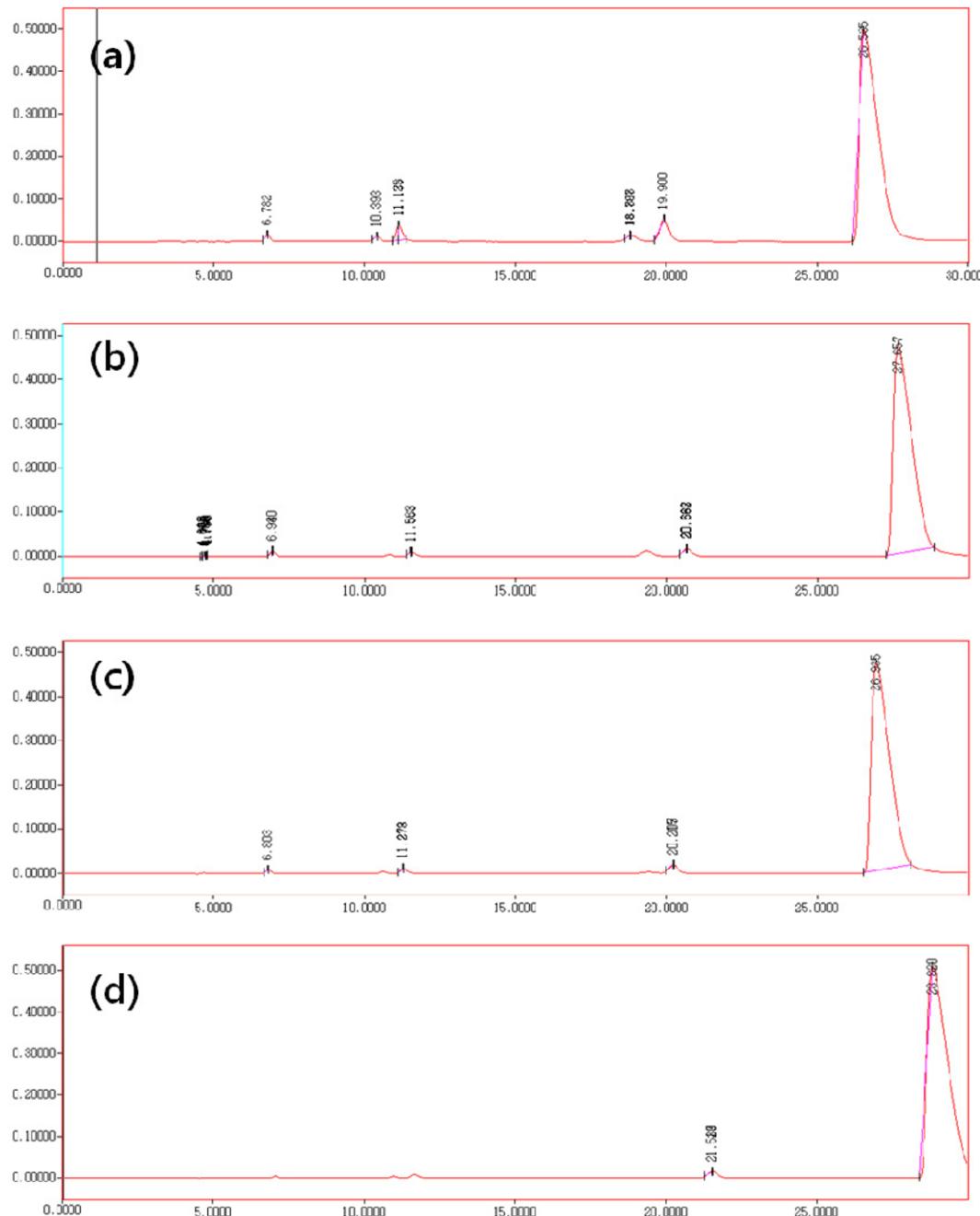


Fig. 4. HPLC data for the water layer after extraction of methyl isobutyl ketone (MIBK) with a change of TBP added amount. (a) 10 g, (b) 20 g, (c) 30 g and (d) 40 g.

mated. The determined concentrations of PhOH and its derivatives were plotted against the amount of added solvents and shown in Fig. 7. These results were utilized for determination of the extraction efficiency (EE) of each solvent.

4. Estimation of Extraction Efficiency

The extraction efficiency (EE) was calculated by using the following equation:

$$EE = \left(\frac{C_i - C_f}{C_i} \right) \times 100 \quad (1)$$

where C_i and C_f are the concentrations of an individual chemical

before and after extraction [9]. C_i was determined as initial concentration of PhOH and its derivatives before extraction. The values of C_f obtained from Fig. 7 were used. From Fig. 8(a), it can be seen that all of the dissolved species in water were recovered above 96% when 10 g of TBP was used. By adding 20 g, the efficiency became as high as 99.5%, which indicated that TBP was an efficient extraction solvent for PhOH and its derivatives. In case of MIBK as shown in Fig. 8(b), the extraction efficiency was much less compared to TBP. When 30 g MIBK was added, the EE was more than 95% for PhOH, HQ and CAT. However, BQ was not extracted above 90% even with 30 g of MIBK. Fig. 8(c) shows the EE of OA used

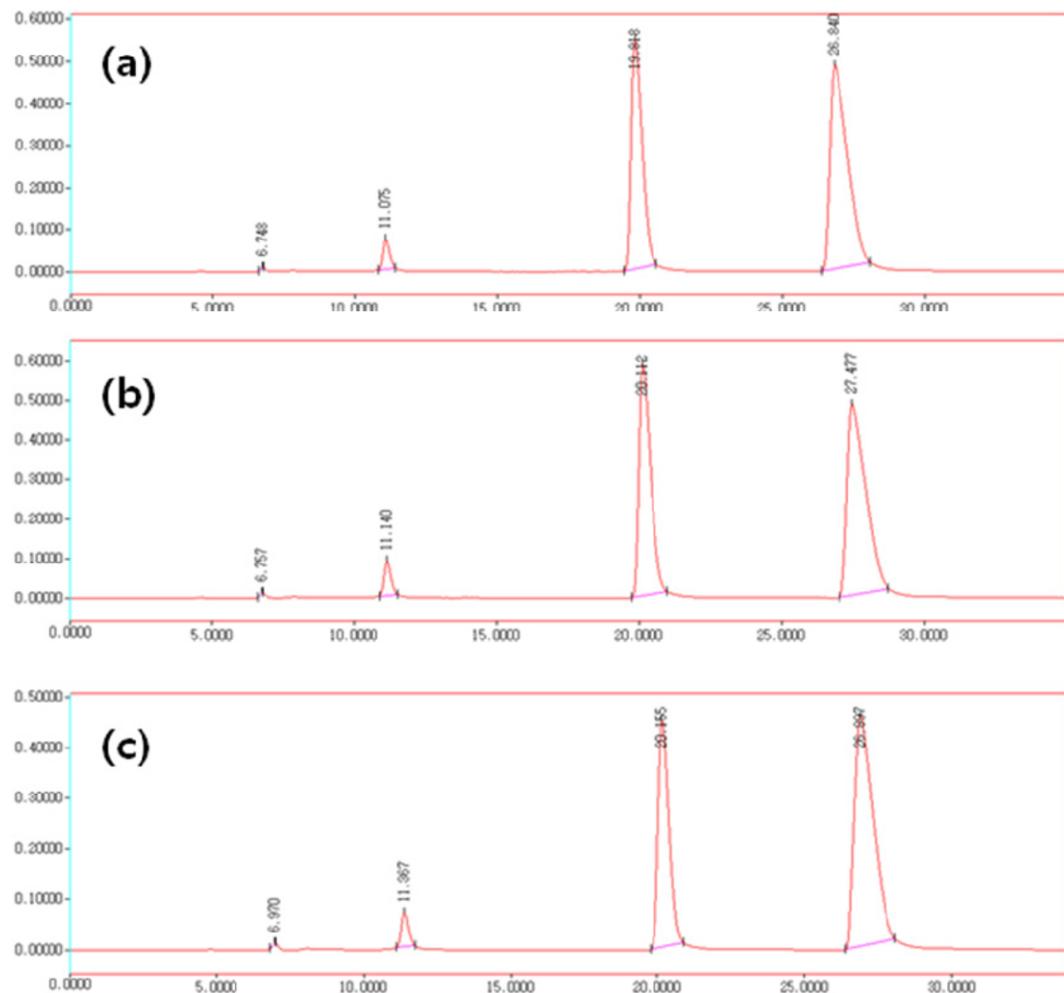


Fig. 5. HPLC data for the water layer after extraction of oleic acid (OA) with a change of TBP added amount. (a) 20 g, (b) 30 g and (c) 40 g.

as a solvent. As seen from Fig. 8, EE of OA for total solutes did not exceed 90% even when 40 g of solvent was added, indicating inefficient extraction. Interestingly, BQ was extracted better by OA than MIBK. Although less extraction performance was observed in case of TPP compared to TBP as shown in Fig. 8(d), its EE values for HQ, CAT, PhOH were above 95% when 40 g of solvent was used. However, its EE was around 90% for BQ. Fig. 9 gives the comparison of the EEs when 20 g solvent was used for all the four solvents. Initially, TBP exhibited an excellent solvent extraction behavior, but EEs of the solutes became lower when TPP was used. This low performance of TPP was probably due to its high viscosity associated with high melting point. CAT, PhOH were better extracted with MIBK than HQ and BQ. In contrast, HQ and BQ were better dissolved in OA than CAT and PhOH. This contradictory trend was explained based on solvation theory.

5. Elucidation of Solvent Behavior

The observed behavior of the four solvents in extraction of phenol and its derivatives from water can be explained theoretically as follows. In general, the interaction between solute and solvent is called the solvation of the solute in that particular solvent. The solvation process is related to the energy, volume, fluidity and electrical conductivity [12]. If an ideal gaseous particle solute (B) is introduced into a solvent (A) at a given temperature and pressure, the solute-

solvent interaction can be expressed by Gibbs free energy of solvation ($\Delta G_{B,solv}$). It is the summation of three Gibbs free energy components as follows:

$$\Delta G_{B,solv} = \Delta G_{dis} + \Delta G_{H-bond} + \Delta G_{cav} \quad (2)$$

Here, ΔG_{dis} , ΔG_{H-bond} and ΔG_{cav} are the dispersion, hydrogen bonding and the cavity formation energies respectively. The solute-solvent interaction by dispersion (ΔG_{dis}), is proportional to the product of polarities of the solute and solvent but decreases strongly with an increase in distance between them. Hence, it can be related to the dipole moment (μ), relative permittivity (ϵ_r) and molar volume of the solute-solvent system. Also, ΔG_{H-bond} is due to the hydrogen bonding between solute and the solvent. The last term, ΔG_{cav} , is the formation energy of a small cavity between solvents when solute is introduced and proportional to the square of solubility parameter (δ). When hydrogen bonding is not strong, ΔG_{dis} and ΔG_{cav} become dominant in the solvation process of hydrocarbon molecules [12]. For the purpose of ΔG_{dis} comparison, the dipole moments of solute and solvent were investigated initially. Since the dipole moments of CAT, PhOH and HQ are 2.62, 1.7 and 1.4 D, respectively, CAT and PhOH are more polar than HQ [13]. Also, the molar volume of the four solutes is similar considering their similarity in the molecular structures [13]. Table 1 gives the fundamental physical proper-

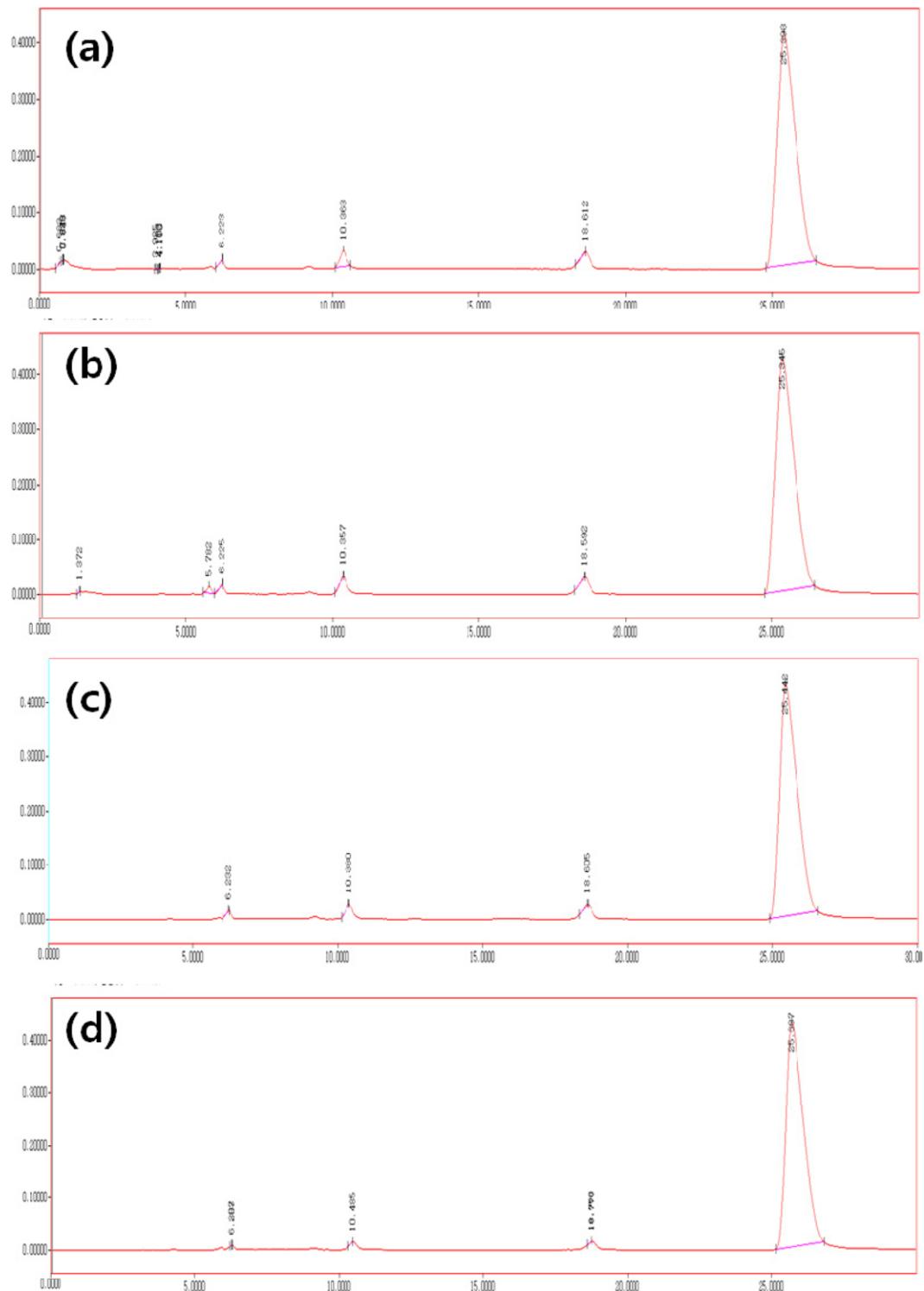


Fig. 6. HPLC data for the water layer after extraction of triphenyl phosphate (TPP) with a change of TBP added amount. (a) 10 g, (b) 20 g, (c) 30 g and (d) 40 g.

ties of various solvents investigated in this work. In the case of TBP, all the factors were high, indicative of an excellent ability of solvation irrespective of solvent polarity [14,15]. Therefore, it is natural that an excellent extraction performance of TBP was observed. Although the physical parameters of TPP were not included in Table 1, it is expected that the solvation using TPP could be reduced because

of its high melting point and large bulky benzene moiety of the molecule. Along this line, the extraction performance as shown in Fig. 9 was probably reduced. The contradictory behavior of MIBK and OA was also explained based on the same principles. In MIBK, polar solutes (CAT and PhOH) were dissolved more than less polar HQ and BQ, which is attributable to high dispersion energy induced

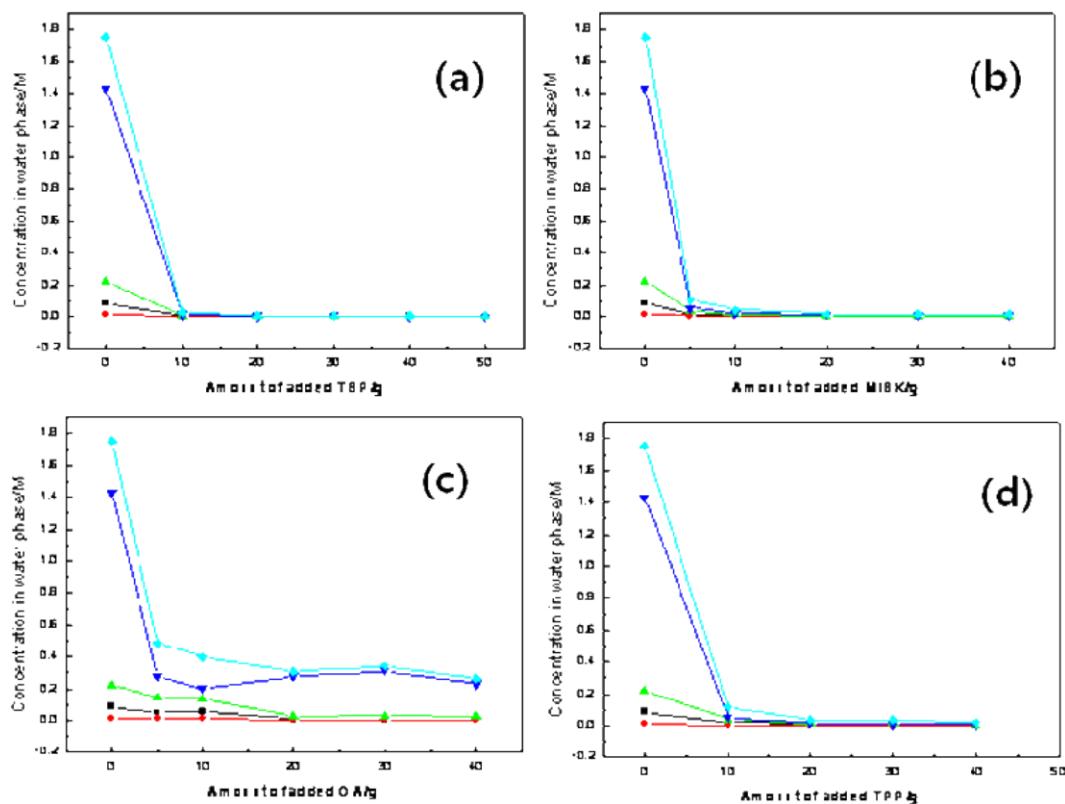


Fig. 7. Concentration of solutes after solvent extraction from quantitative analysis of HPLC spectra. Rectangle, circle, triangle, inverse-triangle and diamond are HQ, BQ, CAT, PhOH and Total solute, respectively. (a) TBP, (b) MIBK, (c) OA, (d) TPP.

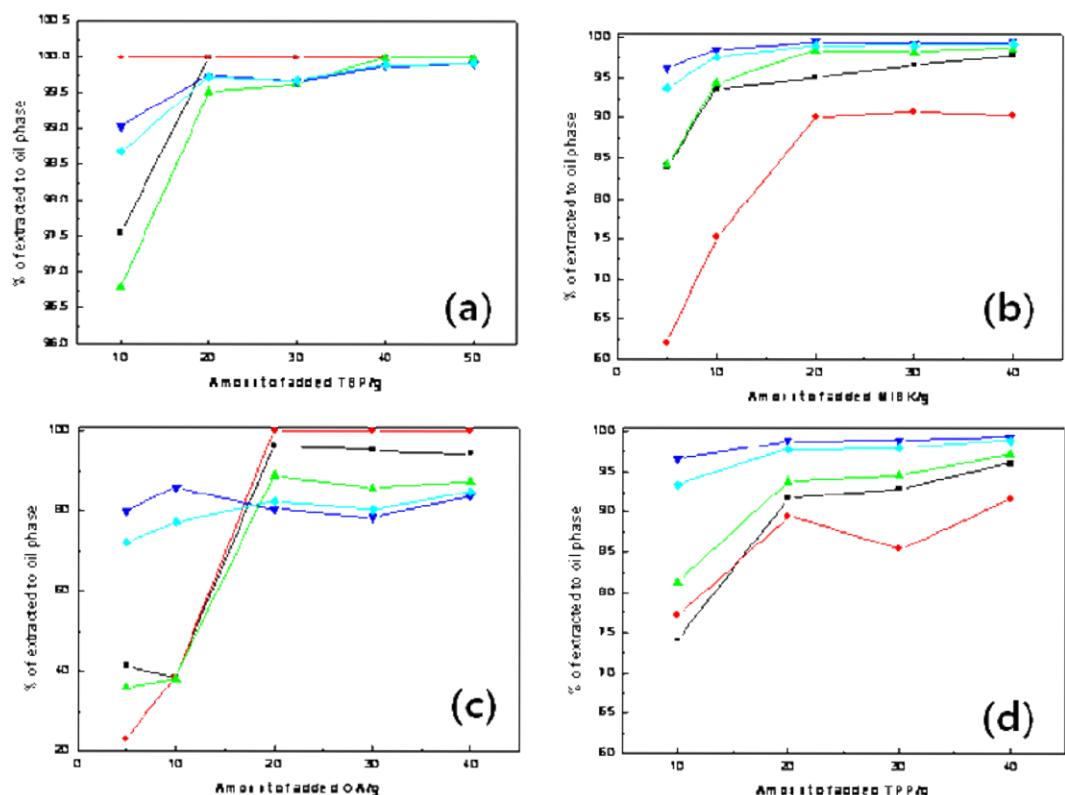


Fig. 8. Extraction efficiency of individual solutes according to solvent. Rectangle, circle, triangle, inverse-triangle and diamond are HQ, BQ, CAT, PhOH and Total solute, respectively. (a) TBP, (b) MIBK, (c) OA, (d) TPP.

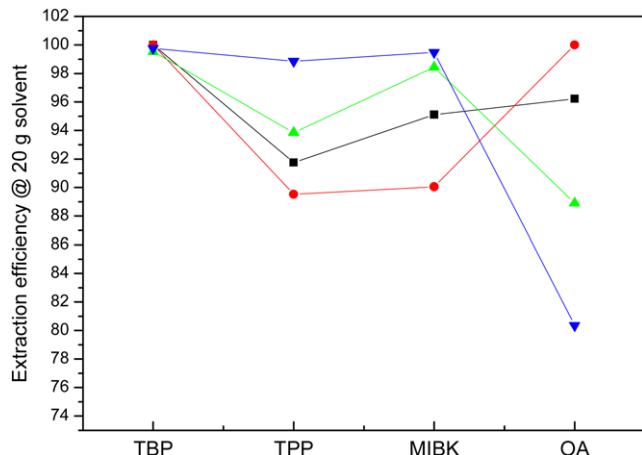


Fig. 9. Comparison of extraction efficiency when 20 g solvent was used. Rectangle, circle, triangle and inverse-triangle are HQ, BQ, CAT and PhOH, respectively.

by high permittivity of MIBK ($\epsilon_r=13.1$) although it has low dipole moment [13]. In OA case, however, very low EE was observed for polar solutes but higher extraction for less polar solutes. This phenomenon is certainly due to low dispersion energy from low polarizability and polarity, which is relevant to low permittivity ($\epsilon_r=2.03$) of OA as listed in Table 1 [14]. Also, the large size of the OA molecule can reduce dispersion energy, which resulted in poor total extraction efficiency.

The selection of an economical solvent for recovery of PhOH and its derivatives was based not only on its cost but also environmentally-benign, high efficiency and a suitable boiling point [12,16]. Although one can select a highly efficient solvent such as TBP, the afterward process should also be economical for industrial production. After the extraction of PhOH and its hydroxy species from water, a further step of separation is required for their purification. Since the boiling points of PhOH, HQ, BQ and CAT are 181.7, 285, 293 and 245 °C, respectively, fractional distillation is usually employed for obtaining pure components. The boiling point of TBP is around 289 °C, which is very similar to that of HQ and BQ. Since, distillation of TBP with hydroxy compounds is inevitable, it results in a high process cost for boiling off the used TBP. Hence, it could be more economical to use a solvent of much higher boiling point such as TPP or OA. In the case of OA, very poor extraction property was observed as shown in Fig. 9. Hence, TPP could be a more suitable solvent for extraction of PhOH and its hydroxy derivatives from aqueous medium.

CONCLUSIONS

From the present investigation, it could be concluded that tribu-

tyl phosphate (TBP) showed the best extraction performance and high suitability for extraction of PhOH and its hydroxy derivatives from water. Using the Gibbs free energy of solvation, the extraction results for the employed solvents were elucidated. Due to the high values of dipole moment, solubility and permittivity of TBP, it was reasonable to observe a high extraction efficiency. For economical extraction, however, trphenyl phosphate (TPP) having a high boiling point was recommended. The extraction performance of Methyl-isobutyl ketone (MIBK) and oleic acid (OA), was not satisfactory but their extraction tendency was elucidated according to the solute polarity.

ACKNOWLEDGEMENTS

This work was financially supported by a grant from the Industrial Source Technology Development Programs (10032124) of the Ministry of Knowledge Economy (MKE) of Korea. And the authors thank Dr. R. N. Rao for helpful discussions.

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