Measurement of Distribution Coefficients for Phenols in Ionic Liquid/Water Two-Phase System

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ABSTRACT

The distribution coefficients for phenols (phenol, *o*-cresol, *m*-cresol, *p*-cresol, 3,5-xylenol and *α*-naphthol) in ionic liquid (1-butyl-3-methylimidazolium haxafluorophosphate ([bmim][PF$_6$]))/water two-phase system were measured at 298 K to examine a removal ability of phenols in wastewater by the liquid-liquid extraction. Judging from these distribution coefficients, it is feasible that phenols can be extracted from wastewater by using the present ionic liquid. The infinite dilution distribution coefficients of phenols obtained in this study were correlated by the regular solution theory. Further, ASOG, which is one of the successful group contribution activity coefficient models, was applied and the group interaction parameters were determined. The correlated results based on the above two models are in good agreement with the experimental results.

Keywords: distribution coefficient, ionic liquid, phenol, regular solution theory, ASOG

1. INTRODUCTION

Ionic liquids have received increased attention in recent years. They are particularly suitable as new solvents or electrolytes because of their low vapor pressures, high boiling points, nonflammability and existence as liquids over wide temperature range. Most works have been invested in the development of synthetic methods and applications of ionic liquids for reaction processes [1,2]. However, the thermodynamic properties of ionic liquids have not been studied systematically. Relatively few papers have been published on the liquid-liquid equilibria [3,4], the vapor-liquid equilibria [5-7] and the extraction [8] of the mixtures containing ionic liquids.

The distribution coefficients of hydrocarbons in ionic liquids are important for design of separation process using ionic liquid as separation solvents. In this work, therefore, the distribution coefficients of phenols in ionic liquid/water two-phase system were measured at 298 K to examine a removal ability of phenols in wastewater by the liquid-liquid extraction. The infinite dilution distribution coefficients of phenols obtained in this work

were correlated by using the regular solution theory and the ASOG.

2. EXPERIMENTAL

2.1 Materials

The ionic liquid; 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF$_6$], C$_8$H$_{15}$F$_6$N$_2$P, MW=284.18) which is 1.37 g cm^{-3} in density at 298 K was supplied by Kanto Kagaku Co. Ltd. The structural formula is shown in **Fig. 1**. The solutes; phenol, *o*-cresol, *m*-cresol, *p*-cresol, 3,5-xylenol and *α*-naphthol were purchased from Wako Pure Chemical Co. Ltd. They were special grade reagents and the purities were more than 99.9, 99.9, 99.8, 99.9, 99.8 and 99.9 % for phenol, *o*-, *m*- and *p*-cresols, 3,5-xylenol and *α*-naphthol, respectively. The values of pH in aqueous phase were 4.85, 5.41, 4.96, 4.87, 4.55 and 4.15 for phenol, *o*-, *m*- and *p*-cresols, 3,5-xylenol and *α*-naphthol, respectively.

[PF$_6$]
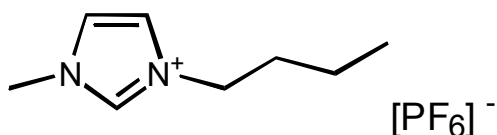
Fig. 1 Molecular structure of 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF$_6$])

2.2 Apparatus and Procedure

The measurement of distribution coefficients was carried out by using a 10 mL glass vial as an equilibrium cell. The solutes were adjusted 4×10^{-4} ~ 4×10^{-3} mol L^{-1} as aqueous solutions. The ionic liquid and the aqueous solutions were weighed and charged into the cell by 1mL each. The cell was set in a constant temperature bath keeping at 298 K and mixed by a magnetic stirrer for 10 min. After settling for 1 h, it was re-mixed for 10 min and settled for at least 2 h. After checking the both phases were clear, the samples from the both liquid phases were carefully withdrawn with micropipettes. UV spectrophotometer measurements were adopted to analyze the compositions of the

$K_3 = 15.14$
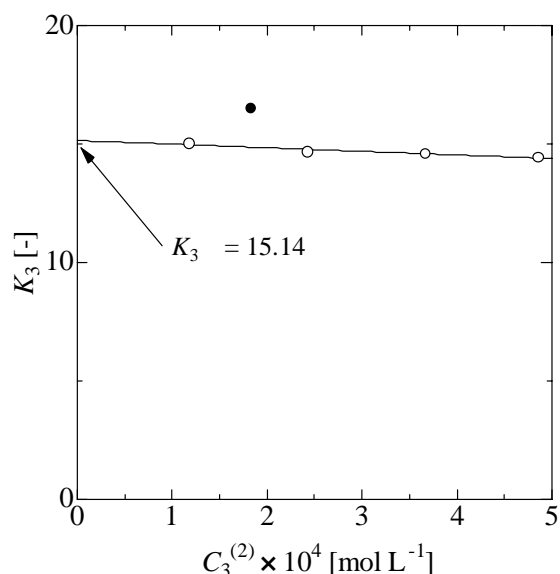
Fig. 2 Distribution coefficients of phenol between [bmim][PF$_6$]/water system, this work at 298 K:○, reference 3 at 294 K:●

phenols in ionic liquid and water phases. The distribution coefficient of phenols(3) in [bmim][PF$_6$](1) / water(2) two phase system K_3 based on molar concentration is defined by the following equation.

$$K_3 = \frac{C_3^{(1)}}{C_3^{(2)}}$$
(1)

where C_3 is the molar concentration in [mol L^{-1}] of phenols. The superscripts (1) and (2) denote [bmim][PF$_6$] and water phases, respectively.

3. RESULTS

The distribution coefficients decrease slightly with increasing $C_3^{(2)}$. The infinite dilution partition coefficients K_3^{∞} were also determined by the extrapolation of K_3 to zero concentration as shown in **Fig. 2**. The values of $K_{x,3}^{\infty}$ based on mole fraction and the infinite dilution activity coefficients of solutes $\gamma_3^{(i)\infty}$ were calculated by equation (2).

$$K_{x,3}^{\infty} = K_3^{\infty} \frac{M_1 \rho_2}{M_2 \rho_1} = \frac{x_3^{(1)\infty}}{x_3^{(2)\infty}} = \frac{\gamma_3^{(2)\infty}}{\gamma_3^{(1)\infty}}$$
(2)

where M and ρ are the molar mass and the density, and the subscripts 1, 2 and 3 are [bmim][PF$_6$], water and solutes, respectively. The values of K_3^{∞} and $K_{x,3}^{\infty}$ are listed in **Table 1**. Judging from these distribution coefficients, it is feasible that phenols can be extracted from wastewater by using the present ionic liquid.

Table 1 Infinite dilution distribution coefficients of phenols in [bmim][PF$_6$] / water two-phase system at 298 K

Solute	ln K_3^{∞} (exp.) [-]	ln $K_{x,3}^{\infty}$ (exp.) [-]	ln K_3^{∞} (calc., R.S.T.*) [-]	ln $K_{x,3}^{\infty}$ (calc., ASOG) [-]
phenol	2.72	5.16	5.25	5.04
o-cresol	3.33	5.77	5.77	5.69
m-cresol	3.63	6.08	5.77	5.69
p-cresol	3.43	5.87	5.77	5.69
3,5-xylenol	3.94	6.39	6.29	6.34
α- naphthol	5.72	8.17	8.68	-

* R.S.T. : Regular Solution Theory

4. CORRELATIONS
4.1 Regular Solution Theory

Based on the regular solution theory [9,10], the infinite dilution activity coefficients of solutes in the ionic liquid and aqueous phases can be expressed by the following

equations:

$$\ln \gamma_3^{(1)\infty} = \frac{V_{m,3}}{RT}\left[(\delta_1 - \delta_3)^2 + 2l_{13}\delta_1\delta_3\right] \tag{3}$$

$$\ln \gamma_3^{(2)\infty} = \frac{V_{m,3}}{RT}\left[(\delta_2 - \delta_3)^2 + 2l_{23}\delta_2\delta_3\right] \tag{4}$$

where δ_i is the solubility parameter of component i, $V_{m,3}$ the molar volume of solute, and l_{ij} the interaction parameter between components i and j. The values of $V_{m,3}$ and δ_3 at 298 K were estimated by the group additive method proposed by Fedors[11]. The solubility parameter of water δ_2 was calculated using the molar enthalpy of vaporization. The infinite dilution distribution coefficient $K_{x,3}^{\infty}$ can be expressed by the ratio of the infinite dilution activity coefficients in both phases as Eq. (2). Thus, Eq. (5) for $K_{x,3}^{\infty}$ based on the regular solution theory is given by Eqs. (2)-(4).

$$\frac{RT}{V_{m,3}}\ln K_{x,3}^{\infty} = (\delta_2^2 - \delta_1^2) + 2\left\{(1 - l_{13})\delta_1 - (1 - l_{23})\delta_2\right\}\delta_3$$
$$= \alpha + \beta\delta_3 \tag{5}$$

The values of α and β can be evaluated by plotting the left hand side versus δ_3 if it was assumed that $\ln K_{x,3}$ changes linearly with δ_3. The value of δ_1 was determined from α in Eq. (5). The interaction parameter l_{23} was determined by Eq. (4) using the literature data of $\gamma_3^{(2)}$ for phenols in water[12]. Moreover, l_{13} was obtained from β in Eq. (5). The value of $K_{x,3}^{\infty}$ can be predicted by the regular solution theory using the values of solubility parameters δ_i and interaction parameters l_{ij}. Table 1 shows the comparisons of $K_{x,3}^{\infty}$ between the experimental and calculated results. The correlated results are in good agreement with the experimental data.

4.2 ASOG

The experimental results were correlated by using ASOG(Analytical Solution of Groups)[13,14], which is one of the successful group contribution activity coefficient models. In this study, ASOG groups are assumed to be consisted of CH_2, ArCH, H_2O, ArOH, [imidazolium] and [PF_6]. **Table 1** shows the comparisons of $K_{x,3}^{\infty}$ between the experimental and calculated results. The correlated results are in good agreement with experimental data.

5. CONCLUSIONS

The distribution coefficients of phenols in ionic liquid ([bmim][PF_6])/water two-phase system were measured at 298 K. The infinite distribution coefficients obtained in this work were correlated by the regular solution theory and ASOG. The correlated results of both methods are in good agreement with the experimental results.

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