Study of Extraction Characteristics of HPMBP. 1. Tautomer and Extraction Characteristics

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In this study, the extraction characteristics of 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 (abbreviation: HPMBP) are studied. HPMBP can exist in four tautomeric forms. Gaussian computations demonstrate that the order of thermodynamic stability of the isomers for HPMBP in xylene is keto(II) > keto(I), enol(III) > enol(IV), and enol(III) > keto(II). HPMBP in xylene mainly exists as the keto(II) and enol(III) isomers. When the concentration of HPMBP is beyond 0.1 M, HPMBP in xylene mainly exists as the enol(III) isomer. In xylene, the tautomeric equilibrium constant between the keto(II) and enol(III) isomers is 9.42. Our experiments show that copper ions could be extracted not only by the enol(III) isomer but also by the keto(II) isomer of HPMBP. When the concentration of HPMBP is relatively high, the enol(III) isomer extracts a high percentage of Cu^{2+}, whereas when the concentration of HPMBP is very low, the keto(II) isomer extracts a high percentage of Cu^{2+}. When the keto(II) isomer is used as extractant, the extraction of copper ions complies with an ion-pair mechanism. When the enol(III) isomer is used as extractant, the extraction of copper ions complies with an ion exchange mechanism.

1. Introduction

In recent years, liquid membranes have received increasing attention as alternatives to liquid−liquid extraction for the selective removal of ions or molecules from dilute solution.[1−4] One outstanding character of liquid membranes is the high selectivity of the membrane. To obtain high selectivity, two aspects are considered. First, an extractant having a high selectivity for the target is synthesized and selected as a carrier of liquid membrane. Then, the extraction characteristics of extractant and effect of the experimental variables on the selectivity of the membrane should be carefully studied.

1-Phenyl-3-methyl-4-benzoyl-pyrazolone-5 (abbreviation: HPMBP) is a chelating extractant for metal ions. In solvent extraction, HPMBP has widespread use in the extraction of double charged transition ions, as well as the lanthanide and actinide ions. Recently, it is also selected as a carrier of the liquid membrane. Its important extraction characteristic is that it can form a synergistic extraction system of high selectivity with other extractants. Its extraction behavior in different extraction systems is summarized in the literature.[5−9] In our liquid membrane system using HPMBP as a carrier, the differences and characteristics of extraction behavior of HPMBP between our experiments and those in the literature are found. The differences are as follows:[5,10−13] (1) HPMBP can exist in four tautomeric forms. Which form has higher stability in solution? (2) Which form has higher ability for the extraction of metal ions? (3) Are the extraction equations of stable tautomeric forms for metal ions the same? (4) Which form uses ion-pair extraction for metal ions? Which form uses ion-exchange extraction? Up to now, there is no satisfactory conclusion in the litereture. Since relatively few studies concerning the characteristics of the extraction behavior of HPMBP are encountered in the literature, more studies are required in this field to approach more practical separation problems and devise separation systems of high efficiency (for example, liquid membrane and solvent extraction systems). Consequently, in this study we first chose the transport and extraction of Cu^{2+} as a model system using 1-phenyl-3-methyl-4-benzoyl-pyrazolone-5 as a carrier in xylene for a complete understanding of the extraction characteristics of HPMBP. HPMBP is not a commonly used extractant for copper extraction, but it could form a synergistic extraction system with high selectivity for metal ions with other extractants.

Numerous studies throughout the past decade have examined the ability of Gaussian computation. The computation results are capable of predicting many properties of molecules and reactions. Consequently, Gaussian computation can serve as a powerful tool for exploring areas of chemical interest. In this study, the experiments and Gaussian computation are combined for a deep understanding of the extraction behavior of HPMBP. We hope that this study will help to devise a separation system of high efficiency.

2. Experimental Procedure

2.1. Materials. All reagents ($CuSO_4\cdot5H_2O$, $Na_2SO_4\cdot10H_2O$, HCl, H_2SO_4, $BaCl_2\cdot2H_2O$, NaOH, $Na_2S_2O_3\cdot5H_2O$, xylene, and starch) used in the present work were of analytical grade. 1-Phenyl-3-methyl-4-benzoyl-pyrazolone-5 was a commercial extractant (a product of the Shanghai Chemical Reagent Corporation) and was chemical pure grade and used without further purification.

A stock solution of Cu(II) was prepared by dissolving $CuSO_4\cdot5H_2O$ in deionized water and analyzed by $Na_2S_2O_3$ titration using starch as an indicator. To prepare the Cu(II) feed solution, a known amount of the Cu(II) stock solution was diluted with water to a given extent after adding a calculated amount of $Na_2SO_4\cdot10H_2O$.

A HPMBP solution was prepared taking a calculated amount of extractant and diluting it with xylene.

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Table 1. Thermodynamic Parameters of HPMBP Isomers by Quantum Chemistry Computation[a]

Isomer	E(RB + HF-LYP) a.u.	$H = E + RT$ a.u.	$G = H - TS$ a.u.
I	−911.97200560	−911.687943	−911.754730
II	−911.97390210	−911.690101	−911.756367
III	−911.97827917	−911.693867	−911.758487
IV	−911.96931412	−911.684806	−911.750539

[a] 1 a.u. = 2622.99 kJ·mol^{-1}. Basis set: 3-21G for C, N, H; 6-31+G** for O atom. In frequency calculation, scaling factor = 0.96 for B3LYP.[16]

Table 2. Change of Thermodynamic Parameters of HPMBP Isomers

difference for isomer	ΔH (kJ·mol^{-1})	ΔG (kJ·mol^{-1})	K
Δ(II − I) for eq 1	−5.66	−4.29	5.64
Δ(III − IV) for eq 2	−23.77	−20.85	$4.50 \cdot 10^4$
Δ(III − II) for eq 4	−9.88	−5.56	9.42

2.2. Extraction Equilibrium. An aqueous solution (10 mL) containing $1.57 \cdot 10^{-3}$ M Cu(II) and 0.167 M Na_2SO_4 was shaken with an equal volume of xylene solution of HPMBP for 15 min at 25 °C (experiments indicated that the extraction equilibrium was reached after 15 min). If necessary, H_2SO_4 was used to adjust the pH in the feed solution before extraction. The metal concentration in the organic phase was calculated from the concentration differences of metal ions in the aqueous phase before and after extraction. The back-extraction was the same as extraction (phase ratio = 1:1, back-extraction time is 15 min; when the back-extraction reagent was 3 M HCl, the back-extraction percentage was 98.7 %).

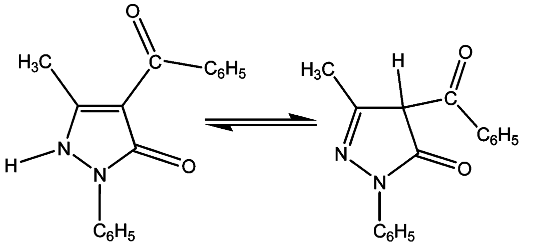
2.3. $BaSO_4$ Precipitation Analysis Method. To determine the content of SO_4^{2-} in the feed solution, a $BaSO_4$ precipitation analysis method was used. First, sufficient solution of $BaCl_2$ was added to the feed solution. Then, the $BaSO_4$ precipitate is collected, dried, and weighed (constant weight is necessary before weighing). The detailed process of analysis is given in ref 14. The content of SO_4^{2-} in the organic phase can be computed from the concentration difference of SO_4^{2-} in the feed solution before and after the extraction.

2.4. Determination of Concentration of Acid in Feed Solution. The content of H_2SO_4 in the feed solution was determined by NaOH titration. The value of pH in the feed solution was determined by a Mettler Toledo Delta 320-S pH meter.

2.5. Computational Methods. All quantum chemical calculations were performed using Gaussian03 Revision-B.04 and Gaussview 3.09.[15] For optimization, four distinct convergence criteria are used in the calculations.[16] According to modeling systems in solution, SCRF (self-consistent reaction field, scrf = dipole) calculations require an additional input line of solute molecular volume (a_0) and the dielectric constant of the solvent. Gaussian computations include a facility for estimating a_0. The dielectric constant for xylene is 2.40.[17] The combination of method and basis set specifies a chemistry model for the Gaussian computation. We elected a density functional theory method (abbreviation: DFT) for the calculation. First, the HPMBP organic molecule is preoptimized using a semi-empirical method (PM3), and then, the preoptimized molecule configuration is again optimized using DFT(B3LYP). After the optimization, frequency calculations are accomplished. The results of the frequency calculation confirm that no imaginary frequency can be listed in the output, and the optimized structure is reasonable. Because oxygen atoms in the HPMBP molecule are coordinated to metal ions and the hydrogen, carbon, and nitrogen atoms are noncoordinated in the HPMBP molecule, the mixed basis set (economic basis set) has been used in this calculation. Consequently, the 3-21G basis set was used in the calculation for the hydrogen, carbon, and nitrogen atoms and the 6-31+G** basis set for the oxygen atom in HPMBP molecule. In this way, the mixed basis set meets the needs of precise calculations for thermodynamic data. All frequency calculations include a thermochemical analysis of the system. The scaling factor of the frequency calculations is 0.96 for B3LYP.[16]

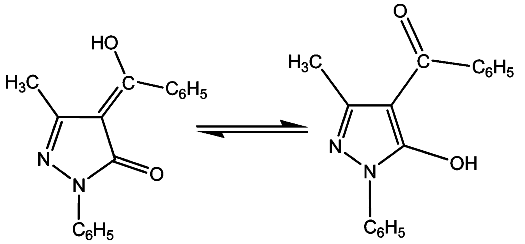
3. Results and Discussion

3.1. Analysis of Equilibrium of HPMBP in Xylene. HPMBP can exist in four tautomeric forms (in isomer of either keto- or enol-form). Their structures are different, but in xylene there is an equilibrium[5,13]



(1)

keto-(I) keto-(II)



(2)

enol-(III) enol-(IV)

Gaussian computations can be carried out in the gas phase or in solution. In this study, we conducted geometry optimization and computation of energy and frequency for the isomers of HPMBP in xylene. All frequency calculations include thermochemical analysis of the system. By default, this analysis is carried out at 298.15 K and 1 atm of pressure. Table 1 shows the results of computation. Table 2 shows that the changes of enthalpy and free energy have negative values for the forward reaction of eq 1 and back reaction of eq 2. On the basis of thermodynamics, we have

$$\Delta G^{\theta} = -RT \ln K \tag{3}$$

where R is the gas constant (= 8.314 J·K^{-1}·mol^{-1}) and T the absolute temperature (in K). K is tautomeric equilibrium constant, and ΔG^{θ} is the standard Gibbs free energy change for eqs 1 and 2. On the basis of ΔH^{θ} and ΔG^{θ} from Table 2, we have come to the conclusion that the order of thermodynamic stability of the isomers of HPMBP in xylene is keto(II) > keto(I) and enol(III) > enol(IV). Since the forward reaction of eq 1 and back reaction of eq 2 are exothermic reactions ($\Delta H < 0$), we only consider the keto(II) and enol(III) form for HPMBP in solution.

Table 3. Variation of pH in Feed Solution[a]

pH in feed solution before extraction	1.31	1.90	2.51	3.03	3.42
pH in feed solution after extraction	1.11	1.40	1.47	1.55	1.59

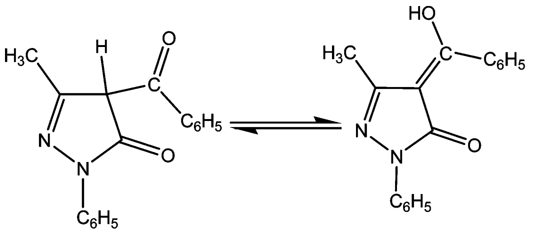
[a] Feed solution: $[Cu^{2+}] = 0.2167$ M; $C_{HPMBP} = 0.0574$ M; H_2SO_4 was used to adjust the pH in the feed solution before extraction.

Table 4. Variation of Concentration of H_2SO_4 in Feed Solution[a]

C_{HPMBP} (M)	0.0144	0.0287	0.0430	0.0574	0.1006
$[H_2SO_4]$ (M) before extraction	0.3083	0.3083	0.3083	0.3083	0.3083
$[H_2SO_4]$ (M) after extraction	0.3084	0.3082	0.3079	0.3082	0.3082

[a] Feed solution: 0.3083 M H_2SO_4, no Cu^{2+} ions.

Table 2 also indicates that the enol(III) isomer for HPMBP in xylene is thermodynamically more stable than the ketone(II) isomer. But $\Delta G^{\theta} = -5.56\ \text{kJ}\cdot\text{mol}^{-1}$, and the value of K is small. In other words, HPMBP in xylene mainly exists as the keto(II) and enol(III) isomers. The following equilibrium occurs in xylene.



(4)

keto-(II) enol-(III)

3.2. Determination of Mechanism of Extraction.

In a large amount of references,[5,10–13] the extraction of metal ions from the feed phase with HPMBP in the organic phase can be generally expressed as follows

$$M^{n+}_{aq} + nHA_{org} = (MA_n)_{org} + nH^{+}_{aq} \qquad (5)$$

where HA stands for HPMBP and aq or org indicates aqueous solution or organic solution, respectively. M^{n+} stands for metal ions. According to the structure of extractant in eq 4, the hydroxy (−OH) only exists in enol(III). Table 3 shows that the concentration of H^+ ions in the feed solution increases after extraction. The experimental result indicates that the H^+ ion is dissociated from the hydroxy and A^- anion coordinates with metal ions. Consequently, HA in eq 5 ought to be the enol(III) isomer of HPMBP. Then, eq 5 indicates the extraction mechanism of ion exchange. Table 3 verifies that eq 5 is correct when HA stands for the enol(III) isomer of HPMBP. Generally, more researchers have ignored the extraction of metal ions from the feed phase by the ketone isomer of HPMBP.

If HA is the keto(II) isomer of HPMBP, is eq 5 correct? On the basis of the stoichiometric relation and ordinary coordination number of copper = 4, when HPMBP is in the form of the keto(II) isomer, the Cu complex is formed according to eq 6

$$Cu^{2+}_{aq} + 2R_{org} + SO^{2-}_{4,aq} = [CuR_2]SO_{4,org} \qquad (6)$$

where R stands for the keto(II) isomer of HPMBP. Equation 6 indicates that copper ions are extracted according to the extraction mechanism of an ion-pair. We ought to verify the extraction of SO_4^{2-} into the organic phase. In eq 6, SO_4^{2-} in feed solution is extracted into the organic phase based on forming an electrostatic neutral compound.

According to the ion pair mechanism, we have

$$Cu^{2+}:SO_4^{2-} = 1:1 \qquad (7)$$

Table 4 shows that H_2SO_4 in the feed solution (no Cu^{2+}) is not extracted by HPMBP in xylene. To verify the reliance of this conclusion, the t-test method was used. On the basis of Table 4, we have

$$\mu = 0.3083\ \text{mol}\cdot\text{L}^{-1}$$

$$\bar{\chi} = 0.3082\ \text{mol}\cdot\text{L}^{-1} \qquad n = 5$$

$$s = \sqrt{\frac{\sum(\chi_i - \bar{\chi})^2}{n-1}} = 0.0002 \qquad (i = 1, 2, 3, 4, 5)$$

$$t = \frac{|\bar{\chi} - \mu|}{\frac{s}{\sqrt{n}}} = 1.118$$

On the basis of the statistical test of analytical data in chemical experiments, the references were looked up on the methods of mathematical statistics in analytical chemistry. According to the t-test method,[18] we have: confidence probability $P = 0.95$, degrees of freedom $f = 5 - 1 = 4$, significance level = 0.05. Looking at the distribution table of the t parameter,[18] $t = t_{0.05,4} = 2.78$.

$$t = 1.118 < t_{0.05,4} = 2.78$$

We draw a conclusion that there is not a significant difference in the H_2SO_4 concentration before and after the extraction. In other words, the statistical test demonstrates that H_2SO_4 is not extracted by HPMBP in xylene. In this way, SO_4^{2-} in the feed solution is extracted into the organic phase according to the extraction mechanism of an ion-pair.

In Table 5:

$C_{Cu^{2+}}$ (the copper concentration in the organic phase) = total concentration of copper ions extracted into the organic phase by HPMBP,

$C_{SO_4^{2-}}$ (the SO_4^{2-} concentration in organic phase) = concentration of SO_4^{2-} extracted into the organic phase by the keto(II) isomer of HPMBP,

= concentration of copper ions extracted into the organic phase by the keto(II) isomer of HPMBP (according to eq 7),

ΔC (the concentration of copper extracted by the enol(III))

Table 5. Effect of Concentration of HPMBP on the Extraction of Copper Ions[a]

C_{HPMBP} (M)	0.0072	0.0144	0.0215	0.0287	0.0359	0.0430	0.0574	0.0754	0.1006
$C_{Cu^{2+}}$ (M)	0.0071	0.0090	0.0113	0.0183	0.0235	0.0247	0.0276	0.0416	0.0500
$C_{SO_4{}^{2-}}$ (M)	0.0041	0.0040	0.0036	0.0034	0.0032	0.0031	0.0029	0.0029	0.0024
ΔC (M)	0.0030	0.0050	0.0077	0.0149	0.0203	0.0216	0.0247	0.0387	0.0476
E_1 (%) (ketone)	57.7	44.2	31.9	18.6	13.6	12.6	10.5	6.9	4.8
E_2 (%) (enol)	42.3	55.8	68.1	81.4	86.4	87.4	89.5	93.1	95.2

[a] Feed soluton: $[Cu^{2+}] = 0.2263$ M. pH = 1.75. E_1: extraction percentage of Cu^{2+} by the keto(II) isomer of HPMBP. E_2: extraction percentage of Cu^{2+} by the enol(III) isomer of HPMBP.

$= C_{Cu^{2+}} - C_{SO_4^{2-}} =$ concentration of copper ions extracted into the organic phase by the enol(III) isomer of HPMBP.

Table 5 indicates that copper ions could be extracted into the organic phase not only by the enol(III) isomer but also by the keto(II) isomer of HPMBP. When the concentration of HPMBP is relatively high, the enol(III) isomer extracts a high percentage of Cu^{2+}. Table 5 also shows that we could not ignore the extraction of Cu^{2+} ions in the feed phase by the keto(II) isomer when the concentration of HPMBP is very low.

4. Conclusion

The following conclusions have been drawn by the experiments and the Gaussian computation.

1. HPMBP can exist in four tautomeric forms. Gaussian computation demonstrates that the order of thermodynamic stability of the isomers of HPMBP in xylene is keto(II) > keto(I), enol(III) > enol(IV), and enol(III) > keto(II). HPMBP in xylene mainly exists in the keto(II) and enol(III) isomers.

2. Copper ions could be extracted by the keto(II) and enol(III) isomers of HPMBP simultaneously.

3. When the concentration of HPMBP is relatively high, the enol(III) isomer exhibits a high extraction efficiency for Cu^{2+}, whereas when the concentration of HPMBP is very low, the keto(II) isomer exhibits a high extraction efficiency for Cu^{2+}.

4. When the keto(II) isomer is used as the extractant, the extraction of copper ions complies with the mechanism of an ion-pair. When the enol(III) isomer is used as the extractant, the extraction of copper ions complies with the mechanism of ion exchange.

5. When the concentration of HPMBP is beyond 0.1 M, HPMBP in xylene mainly exists as the enol(III) isomer.

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