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Extraction Equilibrium of Aqueous Phenol–Long-Chain Alkylamine Solution System

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Abstract

Distribution equilibrium of the aqueous phenol–Amberlite LA-2, a long-chain secondary alkylamine solution system was studied with diluents such as *n*-hexane, cyclohexane, benzene, and carbon tetrachloride at 30 °C. The physical partition coefficient of phenol between two phases and the equilibrium constant for dimerization of phenol in the organic phase were obtained for each diluent under the amine-free condition. The experimental results obtained with amine present were explained by a model in which an amine molecule is added by a few molecules of phenol in the organic phase. The equilibrium constants for these reactions were evaluated.

INTRODUCTION

Although much work has been carried out on the solvent extraction of acids with long-chain alkylamines (*2*, *4*), most of it is related to the extraction of mineral acids rather than the extraction of organic acids. The authors have previously studied the extraction of acetic acid by Amberlite LA-2, a long-chain secondary alkylamine (shortened hereafter to amine), and reported that the experimental results were quantitatively explained by a model in which an amine molecule is added by several molecules of acetic acid (*1*, *3*).

In the present paper the distribution equilibrium in the extraction of aqueous phenol by amine solution diluted with several kinds of diluents (e.g., *n*-hexane, benzene, cyclohexane, and carbon tetrachloride) is studied. The information obtained in the present work will become useful

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as fundamental data in the removal operation of phenol from the effluent dumped out in the commercial coal liquefaction process.

EXPERIMENTAL

Reagents

Amberlite LA-2, supplied from Rohm and Haas Co., was first purified by washing alternatively with 10 wt-% hydrochloric acid and aqueous sodium hydroxide solution several times followed by washing with ion-exchanged water. It was then diluted with the previously mentioned diluents to the required concentration. Phenol, NaOH, HCl, and all of the diluents were Wako GR grade reagents and used without further purification.

Procedure

Equal volumes of the aqueous and organic phase of known concentration were shaken in a flask and allowed to attain equilibrium in a water bath maintained at 30 ± 0.1°C. After about 12 hr the phases were separated and analyzed for their phenol content.

The concentration of amine in the organic phase was determined by titration with hydrochloric acid diluted with a methanol–butanol mixture with bromocresol green as indicator. The phenol content in the aqueous phase was determined by spectrophotomeric analysis using the Shimazu model UV-140 spectrophotometer according to the 4-aminoantipyrine method. The concentration in the organic phase was calculated from the mass balance of its content in the aqueous phase before and after equilibration.

EXPERIMENTAL RESULTS

In Figs. 1A–D the experimental results are shown as plots of m (equilibrium concentration of phenol extracted into the organic phase) vs C_{AW} (equilibrium concentration of phenol in the aqueous phase) for various values of C_{BO} (concentration of amine in the organic phase) and for each diluent. From the results it is evident that m increases with an increase of either C_{AW} or C_{BO} and that the distribution curves are remarkably influenced by the diluents used.

DISCUSSION

First of all, it was presumed that the total concentration of phenol in

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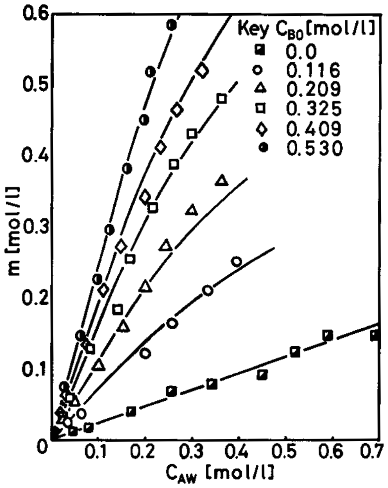

FIG. 1A. Relation between total concentration of phenol in the organic phase (m) and that in the aqueous phase (C_{AW}). Diluent = n-hexane.

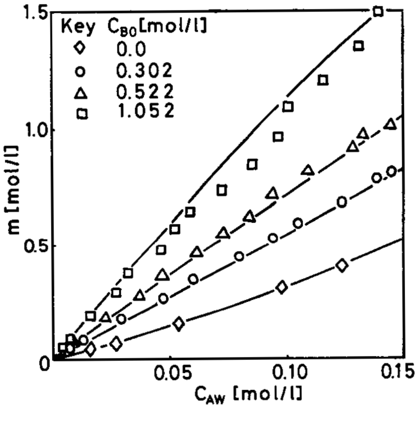

FIG. 1B. Relation between total concentration of phenol in the organic phase (m) and that in the aqueous phase (C_{AW}). Diluent = benzene.

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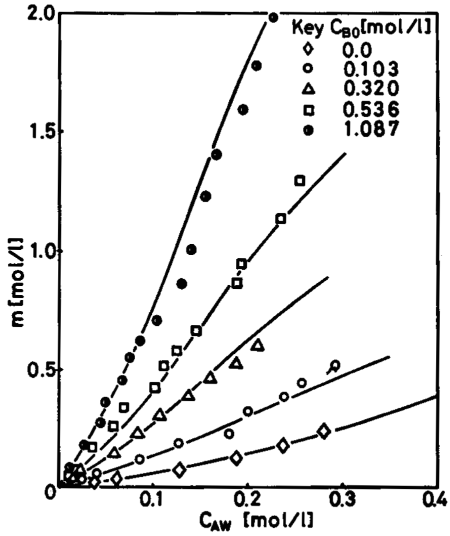

FIG. 1C. Relation between total concentration of phenol in the organic phase (m) and that in the aqueous phase (C_{AW}). Diluent = carbon tetrachloride.

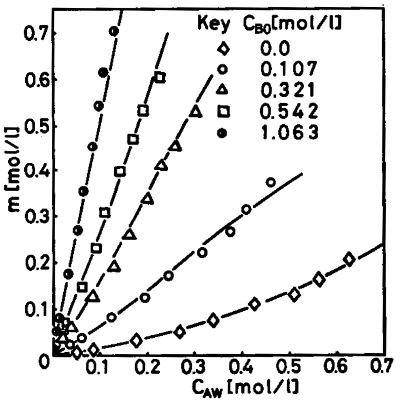

FIG. 1D. Relation between total concentration of phenol in the organic phase (m) and that in the aqueous phase (C_{AW}). Diluent = cyclohexane.

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the organic phase (m) can be represented as the simple summation of the concentration of phenol extracted by the physical distribution with diluent itself (m_2) and that extracted by chemical interaction with amine (m_1) as described by Eq. (1); that is, the activity coefficient of all species in the organic phase was assumed to be unaffected by the increase of C_{BO}.

$$m = m_1 + m_2 \tag{1}$$

Extraction with Diluent Itself

In case $C_{BO} = 0$, all of the plotted points in Figs. 1B–D lie on concave curves. These results suggest the formation of the dimer of phenol in the organic phase. On the other hand, the plotted points in Fig. 1A lie on a straight line which intersects the origin when $C_{BO} = 0$. These results suggest the absence of the dimer of phenol in n-hexane solution. As mentioned in the previous paper, the relation between m_2 and C_{AW} is described by Eq. (4) which takes into account the physical partition of phenol (A) between the aqueous and the organic phase (Eq. 2) and the dimerization in the organic phase (Eq. 3):

$$A_{aq} \rightleftharpoons A_{org} \quad D \tag{2}$$

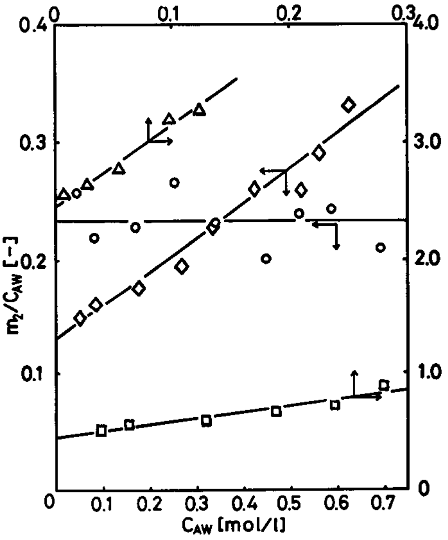

FIG. 2. Relation between the concentration of phenol extracted by diluent only (m_2) and the aqueous phenol concentration (C_{AW}): ○, n-hexane; △, benzene; □, carbon tetrachloride; ◇, cyclohexane.

$$2A_{org} \rightleftharpoons A_{2org} \qquad K_d \tag{3}$$

$$m_2/C_{AW} = D(1 + 2K_dDC_{AW}) \tag{4}$$

where D and K_d denote the partition coefficient and the equilibrium constant for the dimerization of phenol, respectively. Figure 2 shows plots of m_2/C_{AW} vs C_{AW} for each diluent.

The values of D and K_d were evaluated from these results based on Eq. (4), and they are listed in Table 1.

Comparison of the magnitude of these values for each diluent shown in Table 1 indicates the largeness of D for benzene compared to those for other diluents although the magnitude of K_d for benzene is significantly smaller than those for the other diluents except *n*-hexane. A similar tendency was also observed in the extraction of acetic acid (*1*, *3*). These facts indicate the large affinity between solutes and aromatic diluents, which is probably due to the π-electrons of the benzene ring.

Extraction by the Interaction with Amine

The values of m_1 were calculated from the values of m, which are obtained as experimental results, and m_2, which is estimated from Eq. (4) with the values of D and K_d for each diluent.

Figures 3A–D illustrate plots of m_1/C_{BO} (moles of phenol extracted by the chemical interaction with amine per unit mole of amine) against C_{AW} for each diluent. From these figures it seems that most of the plotted points nearly lie on a single curve irrelevant to C_{BO} although there are considerable scatterings in the cases of benzene and carbon tetrachloride. The values of m_1/C_{BO} become greater than unity as C_{AW} increases for all diluents, indicating that more than a unit equivalent of phenol is extracted by amine in the higher concentration range of C_{AW}. These results resemble those observed in the extraction of acetic acid as previously reported (*1*, *3*). Therefore, similarly to the previous work, the authors propose the following reaction scheme in which several kinds of reaction products composed of a molecule of amine and several molecules of phenol are formed in the organic phase, analogous to the formation of complexes with a metal cation and many kinds of anions in the aqueous phase, in order to interprete the interaction of phenol with amine in the organic phase.

$$B_{org} + A_{org} \rightleftharpoons BA_{org} \qquad K_1 \tag{5}$$

$$B_{org} + 2A_{org} \rightleftharpoons BA_{2org} \qquad K_2 \tag{6}$$

$$B_{org} + 3A_{org} \rightleftharpoons BA_{3org} \qquad K_3 \tag{7}$$

where K_1, K_2, K_3, . . . are the equilibrium constants for each reaction.

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TABLE 1

Distribution Equilibrium Constants

Diluents	D	K_d (L/mole)	K_1 (L/mole)	K_2 [(L/mole)^2]	K_3 [(L/mole)^3]
n-Hexane	2.34×10^{-1}	—	1.40×10^{1}	2.56×10^{2}	—
Benzene	2.46×10^{0}	5.70×10^{-1}	3.51×10^{0}	7.86×10^{0}	—
Carbon tetrachloride	4.58×10^{-1}	3.09×10^{0}	1.38×10^{1}	—	1.91×10^{3}
Cyclohexane	1.30×10^{-1}	8.58×10^{0}	4.47×10^{1}	—	2.57×10^{4}

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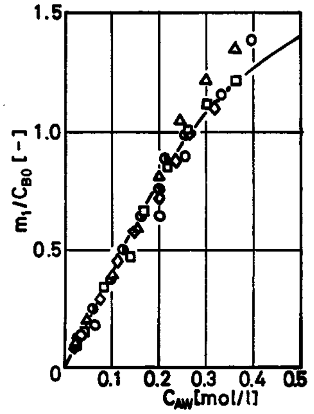

FIG. 3A. Relation between the concentration of phenol extracted by the interaction with amine per unit mole of amine (m_1/C_{BO}) and the aqueous phenol concentration (C_{AW}). Diluent = *n*-hexane. The symbols are defined in Fig. 1A.

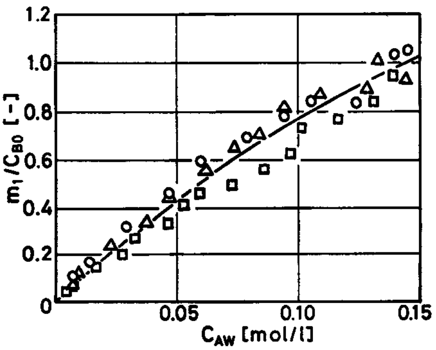

FIG. 3B. Relation between the concentration of phenol extracted by the interaction with amine per unit mole of amine (m_1/C_{BO}) and the aqueous phenol concentration (C_{AW}). Diluent = benzene. The symbols are defined in Fig. 1B.

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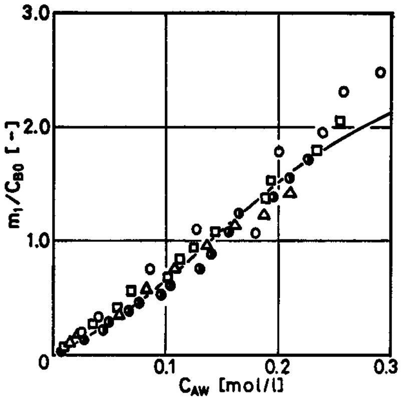

FIG. 3C. Relation between the concentration of phenol extracted by the interaction with amine per unit mole of amine (m_1/C_{BO}) and the aqueous phenol concentration (C_{AW}). Diluent = carbon tetrachloride. The symbols are defined in Fig. 1C.

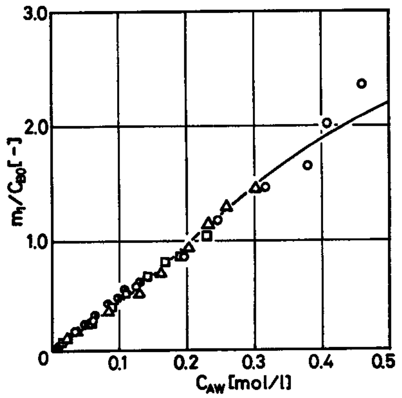

FIG. 3D. Relation between the concentration of phenol extracted by the interaction with amine per unit mole of amine (m_1/C_{BO}) and the aqueous phenol concentration (C_{AW}). Diluent = cyclohexane. The symbols are defined in Fig. 1D.

According to Eqs. (5) to (7), the total concentration of amine in the organic phase (C_{BO}) and the total concentration of phenol existing as the reaction products with amine in the organic phase (m_1) are described by Eqs. (8) and (9), respectively:

$$\begin{aligned} C_{BO} &= C_B + \sum_{i=1}^{n} C_{BA_i} \\ &= C_B + \sum_{i=1}^{n} K_i C_{AO}^{i} C_B \\ &= \left(1 + \sum_{i=1}^{n} K_i C_{AO}^{i}\right) C_B \end{aligned} \tag{8}$$

$$\begin{aligned} m_1 &= \sum_{i=1}^{n} i C_{BA_i} \\ &= \sum_{i=1}^{n} i K_i C_{AO}^{i} C_B \end{aligned} \tag{9}$$

where C_B and C_{AO} are the concentration of free amine and free phenol in the organic phase, respectively, and the latter is described as

$$C_{AO} = D C_{AW} \tag{10}$$

Therefore, m_1/C_{BO} is defined from Eqs. (8) to (10) as

$$\frac{m_1}{C_{BO}} = \frac{\sum_{i=1}^{n} i K_i (D C_{AW})^i}{1 + \sum_{i=1}^{n} K_i (D C_{AW})^i} \tag{11}$$

It is obvious that the relationship between m_1/C_{BO} and C_{AW} expected from Eq. (11) depends only on C_{AW} and is irrelevant to C_{BO}, which is in agreement with the experimental results. Furthermore, it is also expected from Eq. (11) that the value of m_1/C_{BO} tends toward n with an increase of C_{AW}.

For the analysis of the experimental data according to Eq. (11), it is necessary to determine the value of n, the maximum number of phenol molecules added to a molecule of amine. As mentioned above, it can be determined as the asymptotic constant value which the value of m_1/C_{BO} approaches with an increase of C_{AW}. However, as shown in Figs. 3A–D, such an asymptotic constant value cannot be found in the concentration range of this experiment. In the present work n is defined for convenience as the apparent maximum number of phenol molecules added to an amine molecule in the concentration range of this experiment, i.e., that which is necessary for the quantitative interpretation of the experimental results on the basis of the model described above. For example, in Figs. 3C and D there are some plotted points which are greater than 2, but no plotted

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points rise above 3 in the concentration range of aqueous phenol in the present experiment. Hence, as a reaction product in the organic phase, the existence of the species BA_3, which is composed of one molecule of amine and three molecules of phenol, should be taken into account for the quantitative interpretation of the relationship between m_1/C_{BO} and C_{AW} shown in these figures.

The existence of other reaction products composed of less than three molecules of phenol, such as BA and BA_2, may also be considered. Although other reaction products such as BA_4, BA_5, etc., which are composed of more than three molecules of phenol, might be also formed in the organic phase, they are ignored in this work since the experimental results should be explained with the least number of parameters. Consequently, $n = 3$ in these cases. Similarly, $n = 2$ for *n*-hexane and benzene because some plotted points in Figs. 3A and B exceed 1 but do not exceed 2.

The values of K_i ($i = 1$ and 2 for *n*-hexane and benzene but $i = 1, 2$, and 3 for cyclohexane and carbon tetrachloride) which minimize the standard deviation between the experimental results and the results calculated by Eq. (11) were evaluated for each diluent. These are listed in Table 1. In the evaluation of K_i for cyclohexane and carbon tetrachloride, the sensitivity of K_2 to the standard deviation was small, i.e., the standard deviation scarcely varied with the variation of K_2, hence the value of K_2 was ignored for these diluents.

The solid lines in Figs. 3A–D are the calculated results obtained from Eq. (11) by using these values, and the solid lines in Figs. 1A–D are the calculated results obtained from

$$\begin{aligned} m &= m_1 + m_2 \\ &= \frac{\sum_{i=1}^{n} iK_i(DC_{AW})^i}{1 + \sum_{i=1}^{n} K_i(DC_{AW})^i} C_{BO} + D(1 + 2K_d DC_{AW})C_{AW} \qquad (12) \end{aligned}$$

The agreement of the calculated results obtained from Eq. (11) by using these values with the experimental results for the relationship between m_1/C_{BO} and C_{AW} is good in the lower concentration range of C_{AW}, especially for *n*-hexane and cyclohexane diluents. Though the experimental values of m_1/C_{BO} are somewhat greater than the results calculated at the higher concentration range of C_{AW}, which is probably due to the restriction of the number of parameters for the description of the extraction curve, these discrepancies do not seem to be too serious because the corresponding discrepancies in the relationship between m and C_{AW} (Figs. 1A–D) are small.

Accordingly, it is considered that Eq. (12) and the equilibrium constants listed in Table 1 are satisfactory enough to estimate the distribution

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equilibrium of aqueous phenol–Amberlite LA-2 solution system for practical purposes.

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