

EXTRACTION OF LOWER CARBOXYLIC ACIDS FROM AQUEOUS SOLUTION BY TRI-*n*-OCTYLAMINE

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Key Words: Extraction, Liquid-Liquid Equilibrium, Dominant Association, Carboxylic Acid, Tri-*n*-octylamine

To investigate the mechanism of extracting organic acids from water by amine, the extraction equilibria of the ternary systems of tri-*n*-octylamine (TOA), water, and each of four lower carboxylic acids were measured at 30°C. The experiments show that the distribution ratio of an organic acid strongly depends on the kind of acid when the concentration in the aqueous phase is very low. An extraction model where both association and physical distribution are taken into consideration has been proposed. By this model the experimental data can be explained well, while the association mechanism of the model is estimated from the excess volumes of TOA/organic acid binary mixtures. The model suggests that the 1:1 complex between amine and an organic acid strongly contributes to the distribution and selectivity of the acid in the region of very low concentration.

Introduction

Recently, many studies have been carried out on the extraction of organic acids from aqueous solutions using long-chain alkylamines.^{2,3,4,6,7)} In general, a mixture of amine and diluent is used as an extractant so as to improve the physical properties of the extractant such as viscosity and density. Hence, most previous studies have investigated mixed solvents, and concluded that the association between an amine and an organic acid plays an important role in the extraction scheme, and also that the distribution ratio, D_A , of the organic acid can be changed by adding a diluent. For optimum design of an extraction process, it is necessary to develop a method for selecting a diluent that gives high D_A and selectivity. However, none of the previous models has succeeded in explaining the effect of the diluent in the extraction process. Prior to development of such a model, it is necessary to clarify the mechanism of extraction of organic acids and water by pure amine without diluent.

The equilibrium constants of associations between tri-*n*-octylamine (TOA) and lower carboxylic acids can be estimated from the excess volumes.¹⁾ The result shows that the dominant complexes can represent the characteristics of their associations. These parameters may well be applied for evaluating the extraction equilibrium of organic acid with amine.

This paper discusses the mechanism of extraction of lower carboxylic acids such as formic, acetic, propionic and butyric acids, and water from aqueous solution with pure TOA. A model of the extraction mechanism where both chemical and physical interactions are involved simultaneously is proposed. The applicability of the equilibrium constant of the dominant association estimated from the excess volume data is investigated.

1. Experimental

1.1 Reagents

Organic acids (formic, acetic, propionic and butyric acids), TOA and ethanol of extra-pure grade and ion-exchanged water were used.

1.2 Measurement of compositions in liquid-liquid equilibrium

20 ml TOA, 20 ml water and some amount of acid were mixed in a flask and shaken in a water bath at 30°C for three hours. Then the mixture was kept at the same temperature for a further ten hours. The organic and aqueous phases were separated to measure the density of the organic phase with a pycnometer. The concentrations of acid and water in each phase were measured by gas chromatography. Ethanol was used as the reference substance. The concentration of TOA was calculated from the density of the organic phase and the concentrations of organic acid and water in the organic phase.

Received March 18, 1988. Correspondence concerning this article should be addressed to Y. Naka. F. Chen is now at Dept. of Applied Chem., Harbin Institute of Technology, Harbin, China.

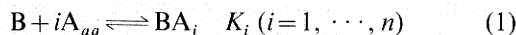
2. Extraction Equilibria of Organic Acids

2.1 Experimental results

Figure 1 shows the relationship between Z_A and $C_{A,aq}$. Each of the symbols for the experimental data denotes a different organic acid. Z_A is defined as moles of an organic acid extracted per mole of TOA, and $C_{A,aq}$ (subscript "aq" denotes aqueous phase and a symbol without subscript "aq" denotes organic phase) is the overall concentration of the same acid in the aqueous phase. In the region of low $C_{A,aq}$, Z_A increases sharply as $C_{A,aq}$ increases, while in the region of higher $C_{A,aq}$ the relation becomes nearly linear. The following general conclusion can be drawn except for formic acid. The larger the number of carbon atoms in the organic acid the larger is Z_A at the same $C_{A,aq}$. Also, the lower the critical concentration of $C_{A,aq}$ the steeper the rise of Z_A becomes. The slope of the straight line for the region of high $C_{A,aq}$ becomes larger with increasing molecular weight of the organic acid.

2.2 Extraction mechanism

1) Previous work Some models for extraction of organic acid from aqueous solution with mixed solvent of amine in the presence of a diluent have been proposed.^{2,4)} The model proposed by Kawano *et al.* distinguishes the contribution of amine from that of diluent. The contribution of amine is evaluated in terms of association alone as follows:



Neglecting the non-idealities such as association between organic acid and water in the aqueous phase, Z_A can be calculated as follows:

$$Z_A = \frac{\sum_{i=1}^n i K_i C_{A,aq}^i}{1 + \sum_{i=1}^n K_i C_{A,aq}^i} \quad (2)$$

Provided that their extraction scheme with regard to amine is applicable to the present situation, Eq. (2) should explain the experimental data shown in Fig. 1. Assuming the association order, n , the equilibrium constants K_i ($i = 1$ to n) were estimated so as for Eq. (2) to fit the experimental data. But no matter how n is chosen, Eq. (2) could not explain the data.

2) Association model with physical distribution

Characterization of association of amine with organic acid is equivalent to determination of the order and the equilibrium constant of association. Both can be estimated on the basis of excess volume data.¹⁾ According to those data, it is found that the association model can be simplified so as to be represented by the dominant complexes BA_i ($i = N, N+1$), and N depends on the kind of acid. If this assumption can be applied to the organic phase in equilibrium with an aqueous phase, the association equilibrium is described as follows:

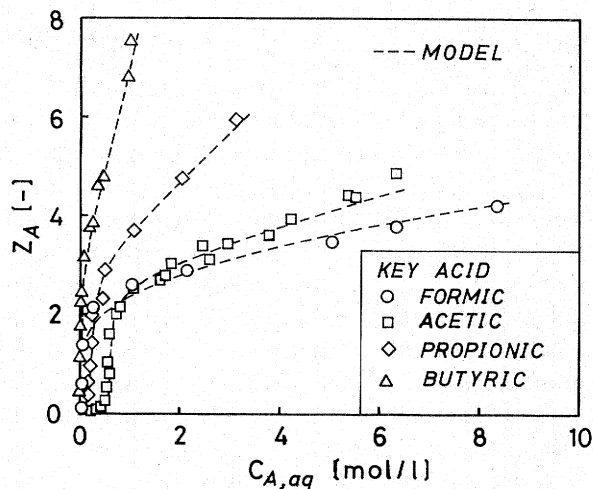
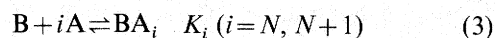


Fig. 1. Relationship between Z_A and $C_{A,aq}$



Here, it should be noted that A represents the free acid in the organic phase. Assuming that water in the organic phase has no influence on the association between amine and organic acid, the association is considered to be independent of the aqueous phase as seen from Eq. (3). The concentrations of the complexes in the organic phase can be calculated as follows:

$$[BA_i] = K_i [B][A]^i \quad (4)$$

The total concentrations of acid and amine in the organic phase, C_A and C_B , are obtained in terms of chemical species in organic phase as follows:

$$\begin{aligned} C_A &= [A] + \sum_{i=N}^{N+1} i [BA_i] \\ &= [A] + \sum_{i=N}^{N+1} i K_i [B][A]^i \end{aligned} \quad (5)$$

$$\begin{aligned} C_B &= [B] + \sum_{i=N}^{N+1} [BA_i] \\ &= [B] + \sum_{i=N}^{N+1} K_i [B][A]^i \end{aligned} \quad (6)$$

To describe the extraction equilibrium of the organic acid, the distribution of the free acid between the aqueous and organic phases is taken into account as follows:



where K_A denotes the distribution coefficient of the free acid. Neglecting the non-idealities of the aqueous phase, the concentration of the free acid in the organic phase is represented as follows:

$$[A] = K_A C_{A,aq} \quad (8)$$

By using the measured data of phase equilibrium

and the values of K_i estimated from the excess volume¹⁾, the relations among $[A]$, $[B]$, $[BA_N]$, $[BA_{N+1}]$ and $C_{A,aq}$ can be calculated. **Figure 2** shows such relation in the case of acetic acid. As $C_{A,aq}$ increases, $[A]$ always increases but is not proportional to $C_{A,aq}$. In other words, K_A is not constant but depends on $C_{A,aq}$. In the region where the free amine in the organic phase is rich, which corresponds to the region of low $C_{A,aq}$, the free acid seems to be distributed predominantly between the aqueous phase and the free amine in the organic phase. Meanwhile, in the region of more than 1 mol/l of $C_{A,aq}$, free amine is scarce and the concentrations of the complexes increase, where the free acid is presumed to be distributed between the aqueous phase and the mixed solvent of the complexes. It is conjectured that the complexes may behave like solvents, and that the change in composition of the complexes has a strong influence on K_A .

To explain the behavior of distribution of the free acid between the aqueous and organic phases, a physical distribution model is employed as shown in Fig. 3, where $K'_{A,0}$, $K'_{A,N}$, $K'_{A,N+1}$ designate the equilibrium constants of physical distribution of the free acid between the aqueous phase and the individual substances, e.g., the free amine and the dominant complexes in the organic phase.

If the organic phase were composed of a single substance "j", the concentration of the free acid in the organic phase, $[A]_j$, could be described as follows:

$$[A]_j = K'_{A,j} C_{A,aq} \quad (9)$$

In reality, the organic phase is composed of several substances. Assuming that there is no change in volume or extracting capacity with mixing, the total concentration of the free acid in the organic phase is calculated by

$$[A] = \sum [A]_j \phi_j \quad (10)$$

where ϕ_j is the volume fraction of substance "j" and is related to C_j by the following equation:

$$\phi_j = v_j C_j \quad (11)$$

Substituting Eqs. (4), (9) and (11) into (10), $[A]$ is represented as follows:

$$\begin{aligned} [A] &= (K_{A,0}[B] + \sum_{i=N}^{N+1} K_{A,i}[BA_i]) C_{A,aq} \\ &= [B](K_{A,0} + \sum_{i=N}^{N+1} K_{A,i}K_i[A]^i) C_{A,aq} \end{aligned} \quad (12)$$

where $K_{A,i} = K'_{A,i} v_i$.

Comparing with Eq. (8), K_A is

$$K_A = [B](K_{A,0} + \sum_{i=N}^{N+1} K_{A,i}K_i[A]^i) \quad (13)$$

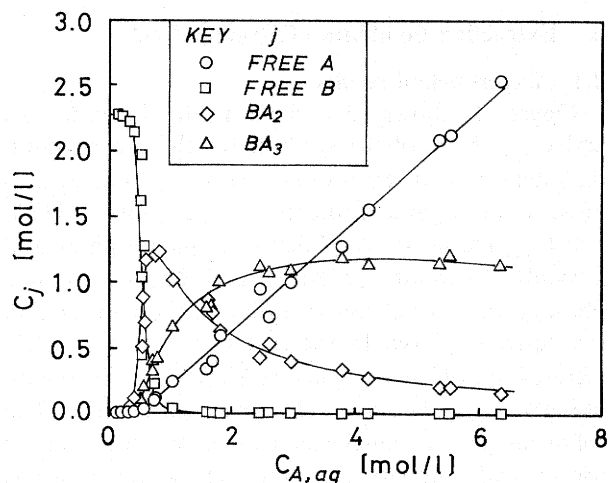


Fig. 2. Relations among $[A]$, $[B]$, $[BA_2]$, $[BA_3]$ and $C_{A,aq}$ for acetic acid

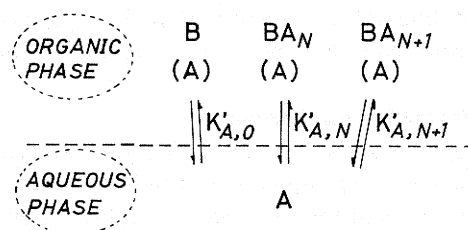


Fig. 3. Model for physical distribution of free acid

According to Eqs (5), (6) and (12), as $C_{A,aq}$ increases and $K_{N+1}[A] \gg K_N$, $Z_A (= C_A/C_B)$ approaches a straight line with slope $K_{A,N+1}$ and intercept $N+1$.

The values of $K_{A,i}$ ($i=0, N, N+1$) are estimated by using SIMPLEX so as to minimize the objective function as Eq. (14).

$$F = \sum_{j=\text{all data points}} (1 - [A]_{\text{cal}}/[A]_{\text{exp}})_j^2 \quad (14)$$

where $[A]_{\text{cal}}$ is calculated from Eq. (12) and $[A]_{\text{exp}}$ is determined from the experimental data as shown in Fig. 2. The estimated values of $K_{A,i}$ ($i=0, N, N+1$) are listed in **Table 1**.

The calculated results of the proposed model represented by the broken line in Fig. 1, explain the data of all acids as well as acetic acid. It is therefore found that the equilibrium constants of the dominant association estimated from the excess volume can be applied extensively to the extraction of organic acids with amine.

2.3 Distribution ratio

Figure 4 shows the distribution ratio, $D_A (= C_A/C_{A,aq})$, vs. $C_{A,aq}$ for formic and acetic acids. D_A takes a maximum value at a certain value of $C_{A,aq}$ for both acids. But in the case of formic acid, $C_{A,aq}$ to give maximum D_A is quite near the origin compared to the case of acetic acid.

If BA is one of the dominant complexes, as

Table 1. Equilibrium constants of physical distribution of free acid and water

unit = [l/mol]				
Acid	Formic	Acetic	Propionic	Butyric
$K_{A,0}$	1.0×10^{-2}	9.0×10^{-3}	1.8×10^{-1}	8.6
$K_{A,1}$	2.2	—	—	—
$K_{A,2}$	0.0	3.2×10^{-2}	3.2×10^{-1}	5.4
$K_{A,3}$	—	3.0×10^{-1}	1.0	4.1
$K_{W,1}$	3.2×10^{-2}	—	—	—
$K_{W,2}$	9.4×10^{-3}	2.8×10^{-2}	1.2×10^{-2}	1.2×10^{-2}
$K_{W,3}$	—	2.5×10^{-2}	1.9×10^{-2}	8.8×10^{-3}
$K_{W,A}$	1.7×10^{-2}	2.9×10^{-2}	1.5×10^{-2}	1.5×10^{-2}

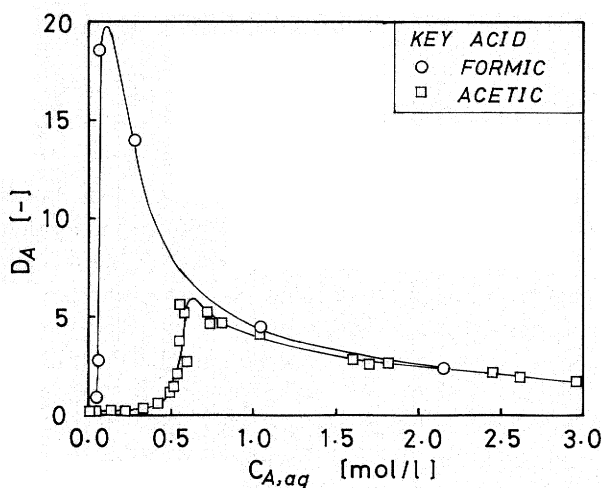


Fig. 4. Relationship between D_A and $C_{A,aq}$

$C_{A,aq} \rightarrow 0$, D_A can be calculated according to the proposed model as follows:

$$D_A = K_{A,0} C_B (1 + K_1 C_B) | C_{A,aq} \rightarrow 0 \quad (15)$$

Eq. (14) contains the parameter K_1 , suggesting that the formation of a 1:1 complex between amine and organic acid as well as $K_{A,0}$ strongly contributes to the value of D_A in the region of very low $C_{A,aq}$. For example, as shown in Fig. 4, D_A of formic acid is much larger than that of acetic acid, though $K_{A,0}$ of formic acid is very similar to that of acetic acid. This is because BA is one of the dominant complexes of formic acid. Although it is known that lower carboxylic acids other than formic acid form dominant complexes of BA_2 and BA_3 with amine, if there is any means of changing such complexes to the form of BA, such as application of a diluent,¹⁾ the distribution ratio could be modified.

3. Coextraction Equilibrium of Water

3.1 Experimental results

Figure 5 shows the relationships between Z_W , moles of water extracted per mole of TOA, and $C_{A,aq}$. The curves of Z_W vs. $C_{A,aq}$ have a trend similar to those of Z_A vs. $C_{A,aq}$ for different acids. However, the solubility of water in pure TOA measured at 30°C is

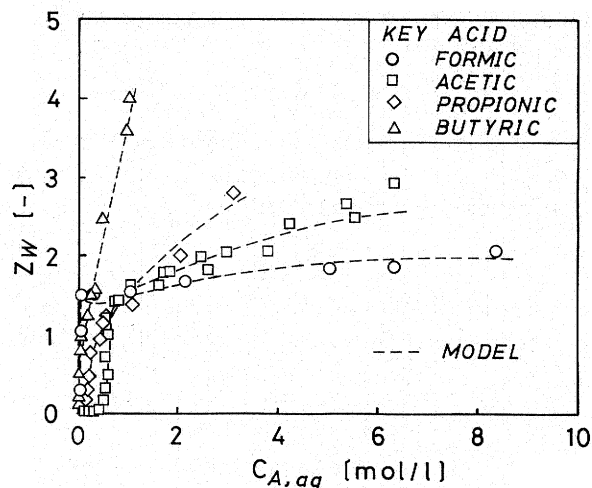


Fig. 5. Relationship between Z_W and $C_{A,aq}$

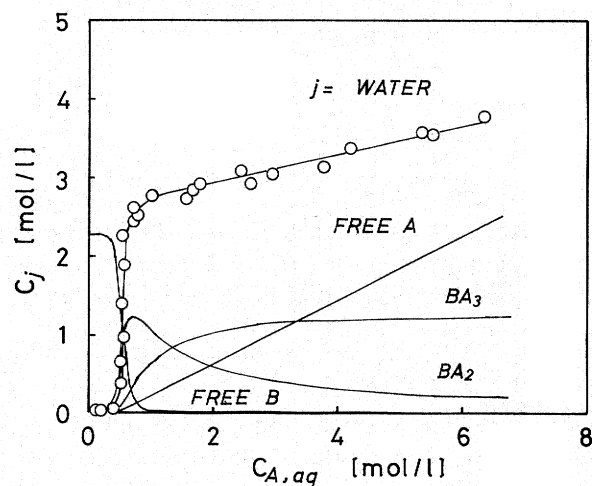


Fig. 6. Relations among $[W]$, $[A]$, $[B]$, $[BA_2]$, $[BA_3]$ and $C_{A,aq}$ for acetic acid

0.040 mol/l, which is quite small. TOA may have almost nothing to do with the coextraction of water.

3.2 Coextraction mechanism

Few studies⁵⁾ have been carried out to investigate the mechanism of coextraction of water along with organic acid by amine. No appropriate model has been proposed so far.

Figure 6 shows the relation among C_W , $[B]$, $[BA_2]$, $[BA_3]$, $[A]$ and $C_{A,aq}$ in the case of acetic acid. When the concentrations of complexes and free acid increase, C_W becomes large. Especially in the region of high $C_{A,aq}$, C_W increases in proportion to $[A]$. It suggests that substances other than the free amine may contribute to the free amine may contribute to the coextraction of water.

If it is assumed that the association of water with both TOA and organic acid can be neglected, the coextraction of water is due only to the physical distribution. Let us consider the distribution mechanism of water to be similar to that of the free acid.

The overall distribution equilibrium of water is described as follows:

$$W_{aq} \rightleftharpoons W \quad K_W \quad (16)$$

where K_W is the overall distribution coefficient of water. The overall concentration of water in the organic phase can be calculated by

$$C_W = K_W C_{W,aq} \quad (17)$$

As the distribution of water is induced by B, BA_N , BA_{N+1} , as well as A, K_W can be described as follows:

$$K_W = K_{W,A}[A] + K_{W,0}[B] + \sum_{i=N}^{N+1} K_{W,i}[BA_i] \quad (18)$$

where $K_{W,i}$ and $K_{W,A}$ denote the equilibrium constants of physical distribution of water between aqueous phase and the individual substances, e.g., BA_i ($i=0, N, N+1$) and A in the organic phase.

From Eqs. (4), (16) and (17), we have

$$C_W = \left\{ K_{W,A}[A] + [B] \sum_{i=N}^{N+1} (K_{W,0} + K_i K_{W,i}[A]^i) \right\} C_{W,aq} \quad (19)$$

$K_{W,0}$ is determined as $K_{W,0} = 3.2 \times 10^{-4}$ l/mol from the solubility data of water in pure TOA. The unknown parameters in Eq. (19) are determined by using an approach similar to that of Eq. (14) as follows:

$$F = \sum_{j=\text{all data points}} (1 - C_{W,Cal}/C_{W,Exp})_j^2 \quad (20)$$

where $C_{W,Cal}$ is calculated from Eq. (19) and $C_{W,Exp}$ is from the experimental data. The estimated values of $K_{W,i}$ ($i=0, N, N+1, A$) are listed in Table 1. The calculated values of Z_W in accordance with the proposed model are shown in Fig. 5 with broken lines. It is seen that the proposed model can explain well the mechanism of coextraction of water along with the organic acid by TOA.

3.3 Selectivity

Figure 7 shows the selectivity, S , which is defined as D_A/K_W , for formic and acetic acids. S for formic acid in the region of very low $C_{A,aq}$ is larger than that for acetic acid, which can also be explained by the proposed model. According to the model, for the case where BA is one of the dominant complexes and $C_{A,aq} \rightarrow 0$, S is represented as follows:

$$S = K_{A,0}(1 + K_1 C_B)/K_{W,0} \quad | C_{A,aq} \rightarrow 0 \quad (21)$$

Eq. (21) suggest that a 1:1 complex between amine and an organic acid as well as $K_{A,0}$ strong contributes to S at low $C_{A,aq}$. Again, it is presumed that by giving the condition under which the formation of BA is dominant, the selectivity could be modified.

Conclusion

The extraction equilibria of low carboxylic acids

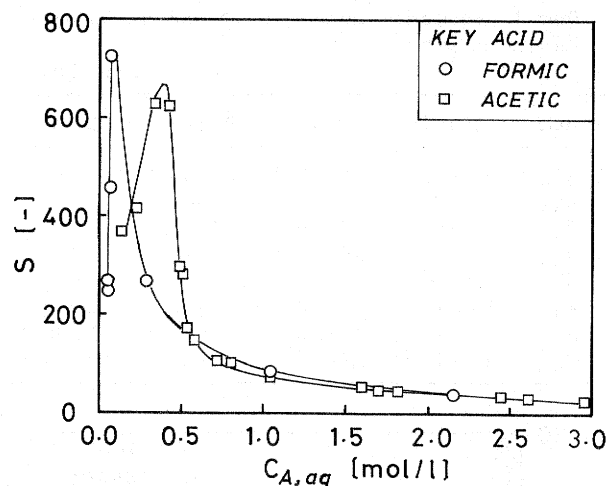


Fig. 7. Relationship between S and $C_{A,aq}$

and water by pure TOA were measured. It was found by experiment that the distribution ratio of an organic acid in the range of very low $C_{A,aq}$ depends very greatly on the kind of acid. An extraction model involving both association and physical distribution has been proposed. The experimental data can be explained well by the model. Especially, the association scheme where the equilibrium constants are estimated from the excess volume of TOA/organic acid binary mixture can be applied to the proposed model. The model suggests that the formation of a 1:1 complex between amine and an organic acid strongly contributes to the distribution ratio and selectivity of the acid in the region of very low $C_{A,aq}$. As the final target of this study is to make clear the effect of diluent on the distribution of organic acid in extraction equilibrium, a future paper will extend the present results to mixed solvent systems.

Nomenclature

C	= overall concentration of a component in a phase	[mol/l]
D	= distribution ratio	[—]
K_A	= distribution coefficient of free acid	[—]
$K_{A,i}$	= $K_{A,i} v_i$	[l/mol]
K_i	= equilibrium constant of association of BA_i	[l/mol ⁱ]
K_W	= distribution coefficient of water	[—]
$K_{W,i}$	= equilibrium constant of physical distribution of water between aqueous phase and substance "i" in organic phase	[l/mol]
$K'_{A,i}$	= equilibrium constant of physical distribution of free acid between aqueous phase and substance "i" in organic phase	[—]
N	= minimum order of dominant association	[—]
n	= order of association in Eq. (1)	[—]
S	= selectivity	[—]
v	= molar volume	[l/mol]
Z	= moles of a component extracted per mole of TOA	[—]

ϕ = volume fraction [—]
 [] = molar concentration of a substance [mol/l]

<Subscript>

A = organic acid
aq = aqueous phase
B = amine
 Cal = calculated value
 Exp = experimental value
W = water

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