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# An Equilibrium Model of Pseudo-Hydroxide Extraction in the Separation of Sodium Hydroxide from Aqueous Solutions using Lipophilic Fluorinated Alcohols and Phenols

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**Abstract:** So-called pseudo-hydroxide extraction has been proposed as a method for separating alkali metal hydroxide from alkaline salt solutions by use of weak-acid cation exchangers such as lipophilic phenols or fluorinated alcohols. Under extraction conditions, these lipophilic weak acids (HAs) are converted to their salt forms when dissolved in a suitable water-immiscible polar diluent like 1-octanol. Upon contact with water, the loaded solvents release alkali metal hydroxide to the aqueous phase by hydrolysis, thereby regenerating the extractant. This type of cycle has been demonstrated in previous work, wherein it was shown that bulk concentrations of sodium hydroxide could be selectively separated from alkaline high-level waste simulants. In the present work, it has been the aim to identify the controlling equilibria and predominant species involved in the extraction process within the framework of a thermochemical model. Using 1-octanol as the diluent, distribution ratios for sodium ($D_{Na}$)

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extraction were measured as a function of organic-phase HA and aqueous-phase NaOH molarity at 25°C. The tested weak acids, 3,5-di-*tert*-butylphenol (HA-1) and 1-trifluoromethyl-2-(3,5-di-*tert*-butylphenoxy)ethanol (HA-2), significantly enhanced the extraction of NaOH over the minor amount that is extracted by 1-octanol alone. The extraction efficiency of HA-1 was approximately 10-fold higher than that of HA-2. By use of the equilibrium modeling program SXLSQI, it was shown that a simple model is sufficient to quantitatively explain the observed extraction behavior based upon (a) ion-pair extraction to give $Na^+OH^-$ ion pairs and corresponding free ions in 1-octanol and (b) cation exchange by monomeric HA molecules to form monomeric organic-phase $Na^+A^-$ ion pairs and corresponding free organic-phase ions.

## INTRODUCTION

The recovery and recycle of caustic reagents in industrial processes offer potential means of pollution prevention. Through our current research, we have found "pseudo-hydroxide extraction" to be a promising approach to NaOH separation from alkaline salt solutions, such as those found in alkaline nuclear wastes in the U.S. Department of Energy (DOE) complex (1–3). This research has focused on the use of lipophilic weak acids such as alkylphenols or fluorinated alcohols in the well-studied water-immiscible alcohol 1-octanol. Contact with alkaline aqueous solutions converts these weak acids to their sodium salts by a simple acid-base reaction, resulting in extraction of sodium. Because hydroxide *equivalents*, rather than actual hydroxide ions, are transferred to the solvent, the term "pseudo-hydroxide extraction" has been used for this process. Contacting the loaded solvent with water regenerates the organic-phase weak acids by hydrolysis, releasing sodium hydroxide to the aqueous phase. The equivalence of sodium and hydroxide concentrations in the strip solutions was earlier demonstrated by performing parallel sodium ($^{22}Na$ tracer or inductively coupled plasma atomic emission) and hydroxide (acid-base titration) measurements (1, 3). 1-octanol represents a useful diluent for such a process in that it possesses good solvation properties for organic-phase sodium salts and very low solubility in aqueous solutions (4).

The present study was undertaken to elucidate the mechanism of sodium hydroxide extraction from aqueous media by weak acids (HAs) dissolved in 1-octanol. Previously, a cation-exchange mechanism was proposed based on reasonable acid-base arguments, selectivity behavior, loading capacity, and the results of approximate slope analysis at the low-loading end of extraction isotherms (1, 3). The deprotonation of the weak acids to form their salts was confirmed by infrared spectroscopy (5). In the present work, it is the object to demonstrate that the cation-exchange hypothesis is quantitatively consistent with experimental extraction isotherms, to identify the species formed, and to determine their equilibrium formation constants. Accordingly, we report the results of a complete equilibrium analysis of NaOH extraction data as treated using the program SXLSQI (6). Two representative weak acids, 3,5-di-*tert*-butylphenol (HA-1) and 1-trifluoromethyl-2-(3,5-di-*tert*-butylphenoxy) ethanol (HA-2), were selected for the study. In comparative work (1, 3), these compounds were found to exhibit favorable extraction and phase behavior for use in pseudo-hydroxide extraction, where the positioning of the two *tert*-butyl groups on the aromatic ring promotes extractant solubility and reduces organic-phase viscosity upon moderate loading.

Like its forerunners SXLSQ (7) and SXLSQA (8), SXLSQI uses mass-action principles to numerically model multiple extraction equilibria. In relation to the present work, SXLSQI possesses the capability to treat organic-phase ions, a required feature here, since 1-octanol has a sufficiently high dielectric constant to weakly dissociate ion pairs at very low organic-phase ionic strength (9). Activity effects in both organic and aqueous phases are included in the treatment. The physical chemistry used in the program has been thoroughly described (10), and a number of examples of its use have been published, including the extraction of LiCl by a crown ether in 1-octanol (11).

## EXPERIMENTAL SECTION

### Materials

Figure 1 shows the structures of the alkyl phenol and fluorinated alcohol used in this study. The 3,5-di-*tert*-butylphenol (HA-1) was purchased from Aldrich Chemical and recrystallized from petroleum ether. 1-Trifluoromethyl-2-(3,5-di-*tert*-butylphenoxy)ethanol (HA-2) was synthesized as described elsewhere (12). Following two recrystallizations from hexanes, it was determined to be 99.8% pure by gas chromatography. Tetraheptylammonium bromide was obtained from Eastman Organic Chemicals, and the stock solution in 1-octanol was converted to its hydroxide form by contacting repeatedly with 1 M NaOH.

All salts and solvents were obtained as reagent-grade commercial chemicals and were used as received unless otherwise noted. Distilled, deionized water was purchased from Ricca Chemical Company and then sparged with argon before

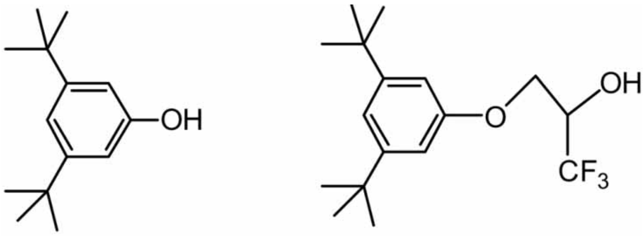

***Figure 1.*** Weakly acidic alcohol extractants used in this study.

use to remove dissolved carbon dioxide. Sodium hydroxide solutions were prepared from a 5.0 N NaOH stock solution (VWR) in Nalgene polypropylene volumetric flasks. All aqueous solutions containing variable sodium hydroxide molarity were prepared using argon-sparged deionized water. The diluent 1-octanol (Aldrich Chemical, 99 + %) was further purified by vacuum distillation through an 11.5-in. glass Vigreux column. To minimize volume changes in 1-octanol during the extraction experiments, 1-octanol presaturated with water was used in all experiments; hence, the term "1-octanol" in the extraction experiments always refers to water-saturated 1-octanol. Volume changes in 1-octanol/water systems have been considered (3, 13) and, given the limited aqueous-phase ionic strength ($\leq 1$ M) and loading ($<0.1$ M) used here, are expected to be small compared to expected experimental error (see the next section). For extraction with HA, organic phases having up to 0.1 M extractant were prepared gravimetrically using water-saturated 1-octanol. This rather low upper limit of extractant concentration was chosen to render negligible any effects due to organic-phase activity, aggregation, and water transfer. Use of this chemistry for process applications, however, would most likely require extractant concentrations up to 1 M (3).

## Extraction Procedures

All liquid–liquid contacts were performed in polypropylene vials using an organic-to-aqueous phase volume ratio $V_{org}/V_{aq}$ of 3.0. Gamma radiometric techniques using $^{22}$Na tracer possess the required sensitivity for this work and were chosen as the means to determine the sodium distribution ratios. Acid-base titrimetry is equivalent in principle and has been used (1, 3), but it lacks the needed sensitivity for the low aqueous NaOH concentraction encountered here. The radiotracer $^{22}$Na was obtained from Isotope Products (Burbank, CA). Each aqueous sample (250 μL) was initially spiked with 15 μL of 50 μCi/mL $^{22}$NaCl to obtain a $^{22}$Na activity of approximately 3 μCi/mL. Extraction temperatures were controlled using a water bath (25 ± 0.2°C) or a temperature-controlled airbox (25 ± 0.1°C). Vials were agitated by rocking (water bath) or end-over-end tumbling (airbox) for 4 h, which was shown in independent kinetic runs to be sufficient time to achieve equilibrium. After contacting, to ensure complete phase disengagement, the samples were centrifuged for 5 min at 2060 × $g$ in a temperature-controlled centrifuge maintained at 25 ± 1°C. An appropriate aliquot of each phase was then subsampled for analysis. The distribution of $^{22}$Na between the two phases was determined by counting each aliquot using the 1022 keV peak of the gamma emission (Cobra Quantum Model 5003, Packard Instruments, Downers Grove, IL). Standard radiometric assay and counting procedures were employed. Sodium distribution ratios ($D_{Na}$) were determined as the ratio of $^{22}$Na activity per milliliter of the organic phase to that in the aqueous phase. All extractions were performed in duplicate.

An accurate estimate of the standard error $\sigma_I$ of individual values of $D_{\mathrm{Na}}$ was necessary for proper weighting of data points in the least-squares analysis by SXLSQI. Points $i$ are weighted according to $w_i = 1/\sigma_i^2$ in the program (see the following) (6), and $\sigma_i$ was taken to be the maximum of the replicate error and estimated counting and volumetric errors. Generally, cumulative volumetric error is no better than ±3% with the techniques used in this work, and therefore the minimum possible error was taken to be $\sigma_i = 0.03D_{\mathrm{Na}}$. However, the statistical counting and replicate errors were greater for values of $D_{\mathrm{Na}}$ less than approximately 0.002 and increased with decreasing $D_{\mathrm{Na}}$. Further, the counting error tended to be the largest component of the replicate error for $D_{\mathrm{Na}} < 0.002$, where the percent counting error generally lay in the range ±5 to 25% with few exceptions.

Extraction experiments consistently showed evidence for a minor acidic impurity. For both extractants and for 1-octanol alone, the distribution ratio $D_{\mathrm{Na}}$ converged to a near constant value of 0.001 as [NaOH] decreased to 0.001 M. Similar behavior was noted previously (13, 14), and it has generally been possible to simulate the behavior or worsen it by adding an organic acid (e.g., 1-octanoic acid) or surfactant anion. Moreover, the effect could be approximately modeled with SXLSQI by assuming the presence of an organic acid or lipophilic anion at a concentration of 1 μM in the organic phase. In accord with previous results (13, 14), we noted that the interference is masked by adding 1 μM of a lipophilic quaternary ammonium salt in the hydroxide form to the organic phase. In this case, the quaternary ammonium cation serves as the cation for the acidic impurity, thereby preventing the extraction of sodium by the impurity. Since the low apparent concentration of impurity was resistant to purification procedures, it was deemed most expeditious to carry out subsequent experiments in the presence of 1 μM of the quaternary ammonium hydroxide.

## Data Treatment

The two-phase extraction data were treated by the solvent-extraction modeling program SXLSQI. The program uses a modification of the Hildebrand-Scott treatment (15), the Debye-Hückel expression, and the Pitzer treatment (16) to respectively calculate the neutral contribution to the organic-phase solute activity coefficients, the electrostatic contribution to the charged organic-phase solute activity coefficients, and aqueous-phase ion activity coefficients (implicitly includes effects of weak ion pairing). Various parameters such as the solvent dielectric constant (9), solute solubility parameters (17), Masson coefficients (18), Pitzer parameters (16), and molar volumes (17) required by the program were taken from available sources and summarized in Table 1. The solubility parameters and molar volumes of HA-1 and HA-2 were estimated from group contributions (17).

SXLSQI refines the values of log $K$ for the defined equilibria iteratively. Input to the program consists of two files. One contains the experimental data,

***Table 1.*** Summary of parameters used in SXLSQI modeling

Masson coefficients

| Species | $V_o$ cm$^3$ mol$^{-1}$ | $S_v$* cm$^3$ L$^{1/2}$ mol$^{-3/2}$ |
|---|---|---|
| $Na^+$ | $-1.21$ | 1.203 |
| $OH^-$ | $-4.04$ | 2.32 |
| $H^+$ | 0 | 0 |

Pitzer parameters

| Species | $\beta^{(0)}$ | $\beta^{(1)}$ | $C^{\Phi}$ | $\alpha_1$ |
|---|---|---|---|---|
| NaOH | 0.0864 | 0.253 | 0.0044 | 2.0 |

Other parameters

| Species | Molar volume cm$^3$ mol$^{-1}$ | Dielectric constant | Solubility parameters cal$^{1/2}$ cm$^{-3/2}$ |
|---|---|---|---|
| HA-1 | 206.0 | | 10.382 |
| HA-2 | 282.4 | | 9.600 |
| 1-octanol | 157.63 | 10.4 | 10.750 |
| $Na^+$ | $-1.2$ | | |
| $OH^-$ | 18.0 | | |
| $H^+$ | 0.0 | | |

consisting of $D_{Na}$ and $\sigma_i$ values for each point together with corresponding values of component concentrations. The other contains the physical parameters needed by the program as described above, including initial estimates for the log $K$ values that are to be refined. In each cycle of refinement, the program uses the current estimates of log $K$ and the input parameters to calculate the equilibrium concentrations of all organic- and aqueous-phase species for each data point. From these concentrations, the experimental observable, in this case $D_{Na}$, is calculated for each point, allowing the goodness of fit to be estimated for that cycle. As the measure of goodness of fit, the agreement factor $\sigma$ is defined as $\sigma = [\sum w_i\,(Y_i - Y_{c,i})^2/(N_o - N_p)]^{1/2}$, where $Y_i$ and $Y_{c,i}$ are, respectively, the $i$th observed experimental quantity and the corresponding quantity calculated from the model; $w_i$ is the weighting factor equal to $1/\sigma_i^2$; and $N_o$ and $N_p$ are the number of observations and the number of adjusted parameters, respectively. At the end of each cycle of refinement, except the last, the program estimates new log $K$ values, and then proceeds on to the next cycle. The refinement continues until the changes in log $K$ values become negligible according to a predefined increment limit.

## RESULTS AND DISCUSSION

1-Octanol possesses sufficient polarity and donor-acceptor ability to extract NaOH to some extent by itself (4, 9, 11). The distribution ratio of NaOH as a function of the initial concentration of NaOH in the aqueous phase is shown as the baseline extraction in Figs. 2 and 3. By analogy with earlier findings (9, 11), a simple formal model for NaOH extraction by 1-octanol alone entails an ion-pair extraction to give $Na^+OH^-$ ion pairs via Eq. (1) and their free ions via Eq. (2) in 1-octanol. It should be noted that we could equivalently treat the system as cation exchange of the 1-octanol to give the sodium alkoxide. Based on the weak acidity of primary alcohols relative to water (19) and the high mole fraction of water in the organic phase [mole fraction 0.27 (9)], such a model is not preferred, though this question remains open.

$$Na^+(aq) + OH^-(aq) \xrightleftharpoons{K_1} Na^+OH^-(org) \qquad (1)$$

$$Na^+(aq) + OH^-(aq) \xrightleftharpoons{K_2} Na^+(org) + OH^-(org) \qquad (2)$$

According to the graphical analysis presented earlier (11), Eq. (1) predicts a slope of approximately unity in plots of log $D_{Na}$ vs. log $[NaOH]_{aq}$. Likewise, Eq. (2) predicts a slope of zero. It follows from the observed behavior in Figs. 2 and 3 that Eq. (2) predominates at low aqueous NaOH concentrations. As the

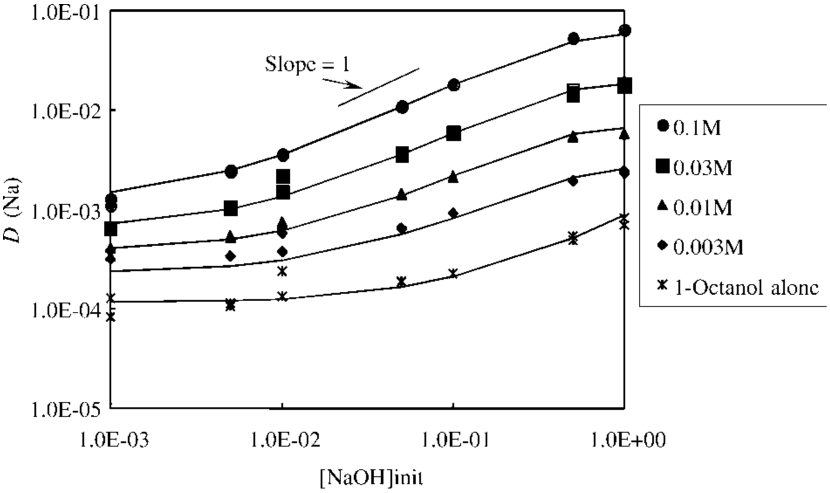

*Figure 2.* Dependence of Na distribution ratio ($D_{Na}$) for HA-1 in 1-octanol on initial aqueous-phase NaOH concentrations and effect of the concentration of HA-1 on NaOH extraction. The solid lines represent modeling results based on the parameters given in Tables 1 and 2. Volume ratio O/A = 3/1. T = 25°C.

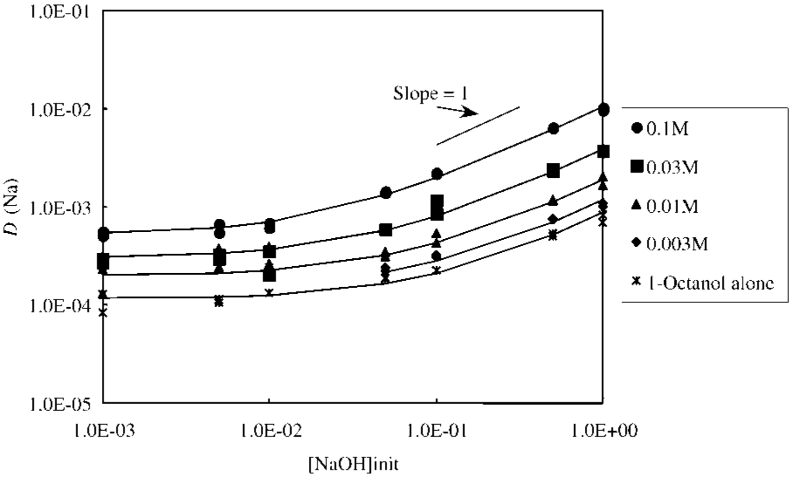

***Figure 3.*** Dependence of Na distribution ratio ($D_{Na}$) for HA-2 in 1-octanol on initial aqueous-phase NaOH concentrations and effect of the concentration of HA-2 on NaOH extraction. The solid lines represent modeling results based on the parameters given in Tables 1 and 2. Volume ratio O/A = 3/1. T = 25°C.

concentration of $Na^+$ and $OH^-$ ions in the organic phase increases, ion pairing becomes increasingly important, and eventually Eq. (1) predominates.

The effect of extractant concentration up to 0.1 M in 1-octanol at 25°C was examined with two representative ionizable hydroxy compounds (Fig. 1). The dependencies of the sodium distribution ratio on initial aqueous-phase NaOH concentration and initial organic-phase HA concentrations are plotted in Fig. 2 (for HA-1) and Fig. 3 (for HA-2). Even at the lowest extractant concentration in 1-octanol ($3 \times 10^{-3}$ M), marked enhancement of sodium hydroxide removal was demonstrated over that of 1-octanol alone. It may be seen that the extraction efficiency of phenol HA-1 is approximately 10-fold higher than that of fluorinated alcohol HA-2. This result is consistent with the order of estimated p$K_a$ values for the phenol ~10 and for the fluorinated alcohol ~12–13 (1). The resultant acidity of the extractant is reflected by the net extent of cation exchange and sodium extraction.

To account for the NaOH extraction by HA, two additional equilibria are required:

$$Na^+(aq) + HA(org) \overset{K_3}{\rightleftharpoons} Na^+A^-(org) + H^+(aq) \qquad (3)$$

$$Na^+(aq) + HA(org) \overset{K_4}{\rightleftharpoons} Na^+(org) + A^-(org) + H^+(aq) \qquad (4)$$

Equation (3) was suggested previously (1a, 3) from graphical analysis, and Eq. (4) merely assumes that the ion pair may dissociate under sufficiently dilute conditions. These equations are rewritten here in terms of $OH^-$ rather than $H^+$ ions:

$$Na^+(aq) + OH^-(aq) + HA\ (org) \xrightleftharpoons{K_5} Na^+A^-(org) + H_2O \tag{5}$$

$$Na^+(aq) + OH^-(aq) + HA\ (org) \xrightleftharpoons{K_6} Na^+(org) + A^-(org) + H_2O \tag{6}$$

Evidence for the dissociation was not observed previously (1, 3), but in that work it was only possible to carry out experiments down to 0.01 M aqueous NaOH, as no precautions were taken to protect solutions from $CO_2$ absorption from the air during transfers. With greater precautions to exclude air, the working range was extended in this work an order of magnitude lower, providing a better opportunity to see the postulated behavior. According to the previous analysis and observations, plots of log $D_{Na}$ vs. log $[NaOH]_{aq}$ should exhibit a slope of approximately 1 if Eq. (5) predominates. Because of aqueous activity effects, the expected slope is somewhat lower, and indeed, that is qualitatively what may be seen in Figs. 2 and 3 at the upper range of NaOH concentrations. With decreasing aqueous NaOH concentration, Eq. (6) predicts log $D_{Na}$ should level off with decreasing aqueous NaOH concentration, and again the data reflect the expectation. As shown in Fig. 2, HA-1 exhibits loading behavior that appears to approach a 1 : 1 loading of extractant with $Na^+$ ion. Experiments under even more forcing conditions (1a,3) were consistent with such a stoichiometry, at least approximately with allowance for phase-volume changes.

Because of conventions employed by the program SXLSQI, the model represented by Eqs. (1)–(4) is expressed on output by the program as

$$Na^+(aq) + H_2O \xrightleftharpoons{K_7} Na^+OH^-(org) + H^+(aq) \tag{7}$$

$$Na^+(aq) + H_2O \xrightleftharpoons{K_8} Na^+(org) + OH^-(org) + H^+(aq) \tag{8}$$

$$HA(org) + OH^-(org) \xrightleftharpoons{K_9} A^-(org) + H_2O \tag{9}$$

plus Eq. (3) as written, when $OH^-$(org) is defined as the reference ion (6). Equations (1) and (2) are obtained respectively from Eqs. (7) and (8) by subtracting the autohydrolysis of water:

$$H_2O \xrightleftharpoons{K_w} H^+ + OH^- \tag{10}$$

where $pK_w = 14.004$ at 25°C [20]. Accordingly, $\log K_1 = \log K_7 + 14.004$ and $\log K_2 = \log K_8 + 14.004$. Log $K_3$ is directly output from the program, and $\log K_4 = \log K_9 + \log K_8$. Also, $\log K_5 = \log K_3 + 14.004$, and $\log K_6 = \log K_4 + 14.004$.

The data shown in Figs. 2 and 3 were fit with SXLSQI, demonstrating that the model agrees with the observed extraction behavior. First, the extraction of NaOH by 1-octanol alone was fit, with resulting refinement of log $K_7$ and log $K_8$. These constants were then fixed in the fitting of NaOH extraction by HA-1 and HA-2, resulting in the refinement of log $K_3$ and log $K_9$. These refined constants together with the statistical agreement factor $\sigma$ are reported in Table 2. Derived constants, log $K_1$, log $K_2$, log $K_4$, log $K_5$, and log $K_6$, are also reported in Table 2. It may be seen from the values of $\sigma$ that the data were reasonably well fit, where a perfect fit is given by $\sigma = 1$ (6–8, 10). Hence, postulation of further species is unwarranted. In this regard, it may be appreciated that the fitting reproduces the loading behavior for HA-1 and HA-2 well. Especially in the case of the higher-loading extractant HA-1, this result implies that aggregated species are likely unimportant under the limited conditions employed.

The results generally support the inclusion of organic-phase free ions in the model. Obviously, the dissociation of the $Na^+OH^-$ (org) and $Na^+A^-$ (org) ion pairs only becomes relatively important at extremely low organic-phase sodium content. As this region pushes the limit of experimental measurement, entailing greater error due to all sources (see Experimental section), it is not surprising that the equilibrium constants corresponding to formation of organic-phase dissociated ions are less precisely determined than those corresponding to formation of the ion-pair species. However, if free organic-phase ions are not included in the model, the computer fit clearly cannot reproduce the data trends. In particular, the calculated values

***Table 2.*** Equilibrium constants obtained from SXLSQI[a]

| | 1-Octanol alone ($\sigma = 0.80$) | HA-1 ($\sigma = 2.06$) | HA-2 ($\sigma = 1.13$) | Note |
|---|---|---|---|---|
| Log $K_1$ | $-2.74 \pm 0.03$ | — | — | Derived |
| Log $K_2$ | $-7.86 \pm 0.07$ | — | — | Derived |
| Log $K_3$ | — | $-13.53 \pm 0.01$ | $-14.62 \pm 0.01$ | Refined |
| Log $K_4$ | — | $-18.89 \pm 0.11$ | $-19.58 \pm 0.10$ | Derived |
| Log $K_5$ | — | $0.47 \pm 0.01$ | $-0.62 \pm 0.01$ | Derived |
| Log $K_6$ | — | $-4.89 \pm 0.11$ | $-5.57 \pm 0.10$ | Derived |
| Log $K_7$ | $-16.74 \pm 0.03$ | — | — | Refined |
| Log $K_8$ | $21.86 \pm 0.07$ | — | — | Refined |
| Log $K_9$ | — | $2.97 \pm 0.08$ | $2.28 \pm 0.07$ | Refined |
| Log $K_{11}$ | $-5.12 \pm 0.07$ | — | — | Derived |
| Log $K_{12}$ | — | $-5.36 \pm 0.11$ | $-4.95 \pm 0.10$ | Derived |

[a] In the modeling of 1-octanol extraction, log $K_7$ and log $K_8$ were refined. In the modeling for the extraction with HA, only log $K_3$ and log $K_9$ were refined, while the values of log $K_7$ and log $K_8$ were fixed at the values shown. All other constants were derived from log $K_3$, log $K_7$, $K_8$, and log $K_9$.

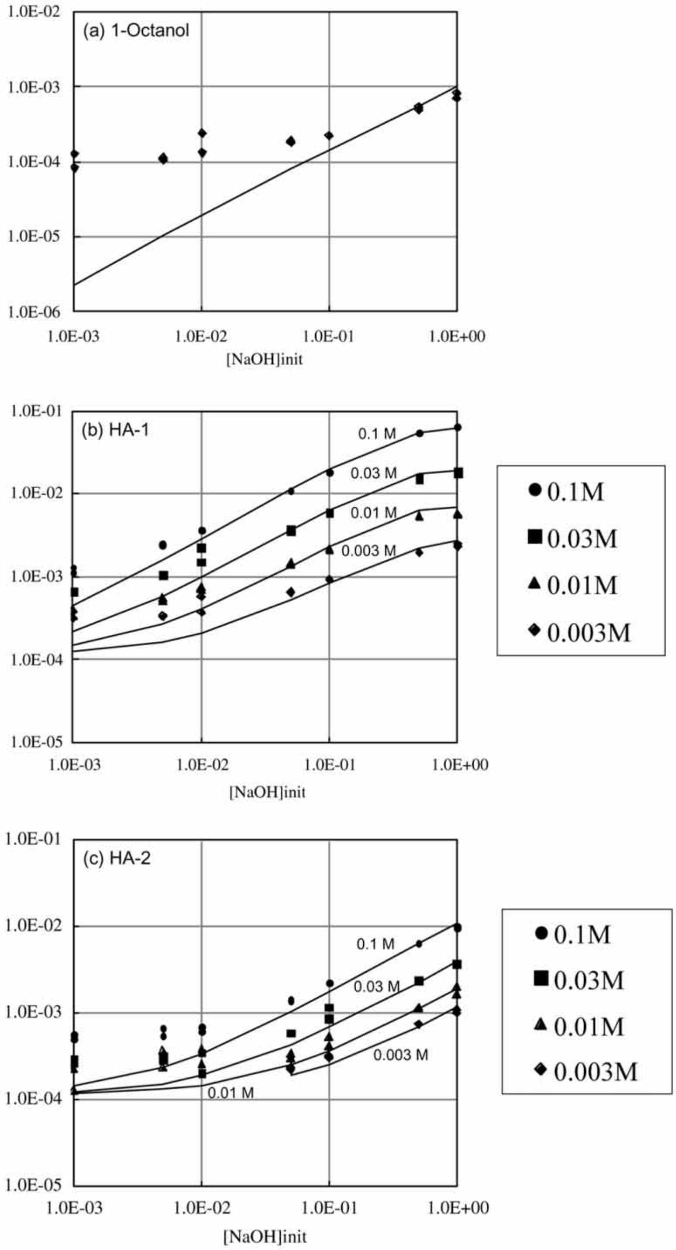

***Figure 4.*** Modeling results corresponding to the hypothetical formation of only ion pairs in the organic phase (solid lines). Dependence of Na distribution ratio ($D_{\mathrm{Na}}$) is plotted for 1-octanol alone (a), HA-1 (b), and HA-2 (c).

of log $D_{Na}$, either for 1-octanol alone or with extractant, cannot exhibit a flat (or zero) dependence on log$[NaOH]_{aq}$. This result is demonstrated in Fig. 4a, showing poor agreement for 1-octanol used alone. For the exercise with HA-1 and HA-2 (Figs. 4b and 4c), it was assumed that the $Na^+OH^-$ (org) ion pairs can dissociate, but that the $Na^+A^-$ (org) ion pairs cannot; assuming that no ion pairs dissociate produces an even worse fit. Values of $\sigma$ corresponding to neglect of ion-pair dissociation for the trials shown in Fig. 4 ($\sigma = 2.99$ for 1-octanol alone, 5.26 for HA-1, and 2.60 for HA-2) may be seen to be much worse than the case when ion-pair dissociation is included (Table 2).

From these results, it is possible to derive values of ion-pair dissociation constants corresponding to

$$Na^+OH^-(org) \underset{}{\overset{K_{11}}{\rightleftharpoons}} Na^+(org) + OH^-(org) \tag{11}$$

$$Na^+A^-(org) \underset{}{\overset{K_{12}}{\rightleftharpoons}} Na^+(org) + A^-(org) \tag{12}$$

Here, $\log K_{11} = \log K_2 - \log K_1$ and $\log K_{12} = \log K_4 - \log K_3$. Derived values are given in Table 2. The values of $\log K_{11}$ and $\log K_{12}$ have comparable magnitude, consistent with strong solvation of the ionic species and solvent-separated ion pairs.

## CONCLUSIONS

The weakly acidic alcohol extractants HA-1 (3,5-di-*tert*-butylphenol) and HA-2 [1-trifluoromethyl-2-(3,5-di-*tert*-butylphenoxy)ethanol] in 1-octanol enhanced NaOH extraction over that of 1-octanol alone. An equilibrium model for NaOH extraction into 1-octanol by two different hydroxy acids has been advanced based on an ion-pair extraction by the diluent to give organic-phase $Na^+OH^-$ and corresponding free ions and cation exchange by the HA alcohols to form monomeric organic-phase $Na^+A^-$ and corresponding free organic-phase ions. SXLSQI modeling of the Na distribution ratio results agrees well with results from the experiments for aqueous concentrations of NaOH as low as $1 \times 10^{-3}$. Having established the applicability of the present equilibrium model, we are proceeding to determine the extraction constants for a series of weakly ionizable hydroxy compounds toward a greater understanding of the effect of extractant structure.

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