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**SOLVENT EXTRACTION OF SODIUM HYDROXIDE USING
ALKYLPHENOLS AND FLUORINATED ALCOHOLS:
UNDERSTANDING THE EXTRACTION MECHANISM BY EQUILIBRIUM MODELING**

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INTRODUCTION

So-called pseudo-hydroxide extraction has been proposed as a method for separating alkali metal hydroxide from alkaline salt solutions by use of weakly acidic hydroxy compounds (HAs) such as lipophilic phenols or fluorinated alcohols¹. Under extraction conditions, these weak acids are converted to their sodium salts by a simple acid-base reaction. Because hydroxide equivalents, rather than actual hydroxide ions, are transferred to the solvent, the term "pseudo-hydroxide extraction" (PHE) has been used for this process. Recent efforts have been devoted to elucidating the equilibrium mechanism of PSE in detail for the simple four-component, two-phase system initially consisting of an HA dissolved in 1-octanol in contact with aqueous NaOH. Sodium distribution data for two HAs were successfully modeled using the mass-action program SXLSQI, confirming that the extraction behavior is quantitatively consistent with a cation-exchange process in the presence of a weak background extraction of sodium hydroxide by 1-octanol². In the present work, seven additional HA compounds have been investigated toward a comparative understanding of the obtained equilibrium constants in terms of HA structure.

MATERIALS AND METHODS

Materials

Figure 1 shows the HAs investigated in this work. As described elsewhere¹⁻⁴, these compounds were either synthesized or obtained from commercial sources and purified. Distilled, deionized water was purchased from Ricca Chemical Company and then sparged with argon before use to remove dissolved carbon dioxide. The diluent 1-octanol (Aldrich Chemical, 99+%) was further purified by vacuum distillation. To minimize volume changes in 1-octanol during the extraction experiments, 1-octanol was presaturated with water.

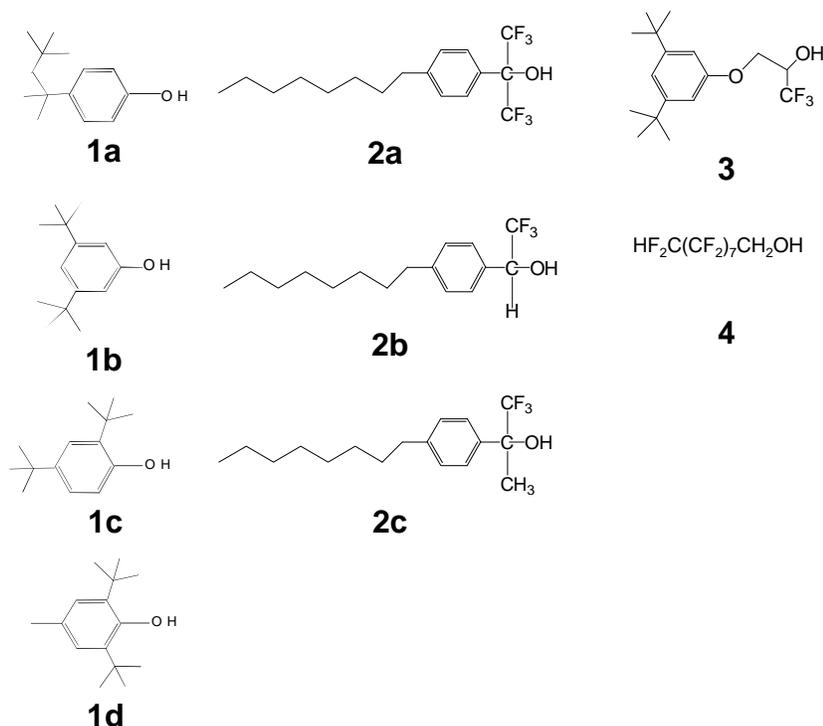


Figure 1. Compounds investigated for pseudo-hydroxide extraction

Extraction Procedures

Following detailed procedures described elsewhere², all liquid-liquid contacts were performed at 25 ± 0.5 °C in polypropylene vials using an organic-to-aqueous phase volume ratio $V_{\text{org}}/V_{\text{aq}}$ of 3.0. Tracer techniques with the *gamma*-emitting isotope ²²Na were employed for the determination of sodium by counting aliquots of each equilibrated phase. All extractions were performed in duplicate.

Data Treatment

The two-phase extraction data were treated by the solvent-extraction modeling program SXLSQI in the manner described elsewhere². Available physical parameters such as the solvent dielectric constant, solute solubility parameters, Masson coefficients, Pitzer

parameters and molar volumes required by the program were used². The solubility parameters and molar volumes of the HAs were estimated from group contributions⁵.

RESULTS AND DISCUSSION

The equilibria pertaining to the extraction of NaOH by 1-octanol alone and with each of eight HAs (**1d** did not exhibit detectable cation-exchange ability) are listed in Table 1, and the corresponding equilibrium constants are given in Table 2. Data for 1-octanol alone and **1b** and **3** have been reported elsewhere²; all other data are new results. The constants refer to the state of infinite dilution, as SXLSQI estimates activity coefficients for all organic- and aqueous-phase species.

Table 1. Equilibria Associated with Sodium Extraction

Eq. No.	Equation
1	$\text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq}) \xrightleftharpoons{K_1} \text{Na}^+\text{OH}^-(\text{org})$
2	$\text{Na}^+(\text{aq}) + \text{OH}^-(\text{aq}) \xrightleftharpoons{K_2} \text{Na}^+(\text{org}) + \text{OH}^-(\text{org})$
3	$\text{Na}^+(\text{aq}) + \text{HA}(\text{org}) \xrightleftharpoons{K_3} \text{Na}^+\text{A}^-(\text{org}) + \text{H}^+(\text{aq})$
4	$\text{Na}^+(\text{aq}) + \text{HA}(\text{org}) \xrightleftharpoons{K_4} \text{Na}^+(\text{org}) + \text{A}^-(\text{org}) + \text{H}^+(\text{aq})$

Table 2. Equilibrium Constants Obtained from SXLSQI

	Log K_1	Log K_2	Log K_3	Log K_4
1-Octanol	-2.74 ± 0.03	-7.86 ± 0.07		
1a			-13.14 ± 0.01	-18.47 ± 0.11
1b			-13.5 ± 0.01	-18.89 ± 0.11
1c			-15.60 ± 0.06	-20.23 ± 0.12
2a			-12.25 ± 0.02	-19.83 ± 0.07
2b			-15.01 ± 0.02	-19.83 ± 0.01
2c			-15.62 ± 0.04	-20.00 ± 0.10
3			-14.62 ± 0.01	-19.58 ± 0.10
4			-14.74 ± 0.02	-19.03 ± 0.09

Four independent equilibria were found to be sufficient to describe the observed extraction behavior, two corresponding to sodium extraction by 1-octanol alone and two corresponding to sodium extraction by HA. 1-Octanol possesses sufficient polarity and donor-acceptor ability to extract NaOH salt to some extent by itself. At an aqueous NaOH concentration of 1 M, the organic-phase concentration of sodium is $7.6 (\pm 0.2) \times 10^{-4} \text{ M}$. By analogy with earlier findings on salt extraction by 1-octanol⁶, a simple model for NaOH extraction by 1-octanol alone entails an ion-pair extraction to give Na^+OH^- ion pairs (eq. 1) and their free ions (eq. 2) in the organic phase. Ion pairing predominates at practical concentrations, whereas the dissociation into free ions becomes important only at organic-phase concentrations of sodium below 10^{-4} M . To account for extraction of sodium by the HAs, the model postulates formation of monomeric organic-phase ion pairs Na^+A^- and their corresponding free organic-phase ions Na^+ and A^- . Vibrational spectroscopic results have confirmed the formation of the deprotonated HA molecules in 1-octanol in contact with aqueous NaOH solutions for the cases of **1b** and **47**, leaving little doubt concerning the validity of the postulated cation exchange. As shown earlier^{1c}, the achievable concentration of sodium in the organic phase corresponds approximately to the concentration of HA employed, provided that the HA used has sufficient acidity and solubility as the sodium salt. Organic-phase concentrations of up to 1 M have been demonstrated^{1c}. In the present work, the maximum concentration of HA used was limited to 0.1 M to avoid complications due to large activity and volume-change effects.

In general, the addition of one of the HAs to 1-octanol enhances NaOH extraction over that of 1-octanol alone. Extraction efficiency follows the qualitative order of acidity of the HAs, **1a** > **1b** > **1c** > **1d** and **2a** > **2b** > **2c**, reflecting a combination of inductive effects as well as steric constraints to solvation of the deprotonated anionic product species. In summary, the results advance an equilibrium model for NaOH extraction into 1-octanol by weakly acidic hydroxy compounds based on cation exchange by the weak acids to form monomeric organic-phase Na^+A^- and corresponding free organic-phase ions.

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