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Extraction of Alkali Metals by 4-*sec*-Butyl-2-(α-methylbenzyl)phenol (BAMBP)[1]

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Cesium is efficiently separated from the lighter alkali metals by extraction with 4-*sec*-butyl-2-(α-methylbenzyl)pheno (BAMBP) in various organic diluents. Equilibrium measurements on the extraction process showed an inverse first-power dependence of the extraction coefficient on acid concentration in the pH range 7.6–10.6 and a third-power reagent dependence in the concentration range of 0.1 to 1 *M*. Loading data indicated a mole ratio of Cs:BAMBP of 1:4 in the organic phase. Higher metal to reagent concentration ratios could be obtained only at high pH values with concurrent extraction of water of hydration and an abrupt change in the extraction isotherm. Separation from lighter alkali metals was efficient only under those conditions which did not permit extraction of the hydrated ion. The infrared spectrum of BAMBP, both in the fundamental and in the overtone region, was examined in various solvents. The dimer is the most abundant species except in the case of very dilute solutions. With cesium loading up to 1 Cs:4 BAMBP, the spectra are characterized by a marked decrease in both the monomer and dimer absorption bands and a concurrent increase in the region of polymeric O–H absorption. N.m.r. spectra showed a rapid downfield shift of the hydroxyl proton line with increasing cesium content to a maximum near 1 Cs:4 BAMBP; then, with the extraction of more cesium, plus water, a reversal occurred with the shift returning upfield. The extent of the shift with other alkalies varies in the same order as their extractabilities, Cs > Rb > K.

Introduction

The alkali metal ions form ionic, water-soluble compounds and have little tendency to form either insoluble precipitates or complex ions. These factors, together with a great similarity in their aqueous chemistry, have complicated their recovery, separation, and purification. Recently, the Phenex[2] solvent extraction process, which uses substituted phenols, was developed at this laboratory for the recovery of cesium from ore leach liquors and for the separation of radioactive cesium from other reactor fuel fission products.

This paper describes the extraction of alkali metal ions, especially cesium, by 4-*sec*-butyl-2-(α-methylbenzyl)phenol, BAMBP. Cesium extraction involves cation exchange with a phenolic proton to form cesium phenolate, which is solvated with additional phenol molecules. At high aqueous cesium hydroxide concentrations, the phenol is converted completely to the salt; extracted water replaces phenol as solvating molecules. Extraction of the other alkali ions is similar in nature, but the degree of extraction decreases rapidly with decreasing size.

Experimental

Reagent Purity.—Commercial 4-*sec*-butyl-2-(α-methylbenzyl)phenol,[3] nominally 98+%, was pale to deep amber in color. The concentration of BAMBP in various diluents was determined by potentiometric titration based on the method of Fritz and Marple.[4,5] The best results were obtained using tetrabutylammonium hydroxide titrant in pyridine as the titrating medium. Titration of weighed samples of BAMBP gave values for the equivalent weight within ±3% of the theoretical.

Gas chromatograms of the commercial material indicated the presence of up to 3% more-volatile and 5% less-volatile components. The assay obtained by titration indicates that these impurities are acidic and chemically similar to BAMBP.

Fractionation through a Podbielniak column yielded a colorless main fraction at 186 ± 1° (6 mm.); $n^{26.2}{}_{D}$ 1.5570, $d^{26.2}$ 1.004 g./ml. About 0.5% *p*-*sec*-butylphenol was removed. Comparison of the gas chromatograms of the commercial and redistilled products indicated that a small amount of a more-volatile impurity still remained in the distilled product. This impurity has been identified as 4-*tert*-butyl-2-(α-methylbenzyl)phenol from chromatograms of mixtures of the authentic compound with BAMBP. The extraction properties of 4-*tert*-butyl-2-(α-methylbenzyl)phenol are similar to those of BAMBP. The distilled BAMBP and the commercial product also showed similar extraction behavior.

Redistilled BAMBP was used in all experiments where the diluent was carbon tetrachloride; the commercial material was used in the others.

Chemicals.—Sodium and potassium salts were reagent grade and were purchased from the usual sources. Cesium and rubidium compounds, including concentrated solutions of the hydroxides, were purchased from the American Potash and Chemical Corp. The CsOH and $CsNO_3$ contained 0.38 and 0.09 wt. % (based on cesium) of alkali impurities, respectively.

The solvents were C.P. grade or better and were used without further purification. The carbon tetrachloride was checked for infrared transmission in the O–H region before use.

Tracers were obtained from the ORNL Radioisotopes Division.

Extractions.—Unless otherwise noted, extractions were carried out at room temperature by shaking equal volumes of the organic and aqueous phases for at least 10 min. on an automatic wrist-type shaker. Tracer experiments showed that equilibrium was reached after only about 2 min.

Spectral Measurements.—The fundamental O–H vibration was observed on a Perkin-Elmer Model 221 instrument, calibrated with a polystyrene standard. The first overtone region was observed on a Cary Model XIV-B. The n.m.r. spectra were measured on a Varian A-60 n.m.r. spectrometer. The temperature in the probe of the spectrometer magnet was determined by measuring the distance between the OH and CH_3 resonance peaks of methanol. The instrument was calibrated using the known separation between the tetramethylsilane (δ 0 p.p.m.) and chloroform (δ −7.27 p.p.m.) resonances using a mixture of the two compounds.

Analyses.—All alkali metal analyses were performed by the ORNL Analytical Division using a flame spectrometric technique. Water analyses were performed by the ORNL Analytical Division using standard Karl Fischer titrations.

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(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corporation.

(2) D. E. Horner, D. J. Crouse, K. B. Brown, and B. Weaver, *Nucl. Sci. Engr.*, **17**, 234 (1963).

(3) Purchased from the Dow Chemical Co., Midland, Mich.

(4) J. S. Fritz and L. W. Marple, *Anal. Chem.*, **34**, 921 (1962).

(5) L. W. Marple and J. S. Fritz, *ibid.*, **34**, 796 (1962).

Results

Effect of pH on the Extraction of Cesium.—The extraction coefficient, E_a°, is defined as the ratio of the concentration of metal ion in the organic phase to the concentration in the aqueous phase. Log E_a° increases linearly with slope 1.0 with increasing pH in the range 8.0 to 10.5 from 0.1 *M* Cs^+ ($CsOH-CsNO_3$) solutions.

Effect of Reagent Concentration.—An aqueous 0.01 *M* CsOH solution, containing trace amounts of ^{134}Cs, was chosen for reagent dependence studies. This concentration is high enough to eliminate any significant effect due to extraction of tracer by organic impurities and low enough so that correction for loading of the extractant is unnecessary.

Since the equilibrium pH of the aqueous phases varied from 10.9 to 11.9, all extraction coefficients were normalized to pH 11.90 by utilizing the first power pH dependence. A log–log plot of "E_a° Cs *vs.* formal reagent concentration" (Figure 1, curve (1)) gave a curve with average slope 2.8 in CCl_4 diluent. Similar behavior was observed in *n*-octane and diisopropylbenzene diluents. However, the absolute values of the extraction coefficients were about four times higher in the *n*-octane.

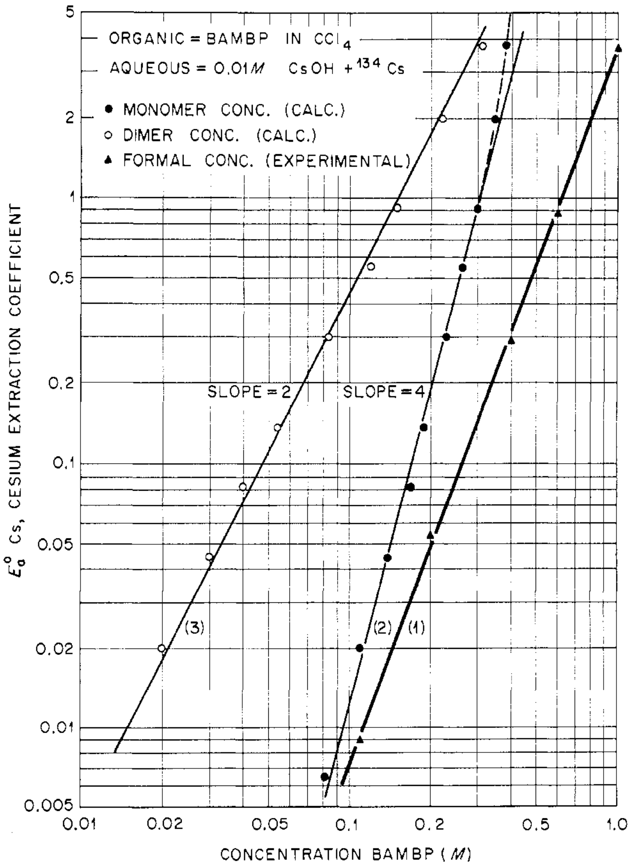

Figure 1.—Reagent dependence of cesium extraction.

Extraction Behavior.—In Figure 2, isotherms are plotted for the extraction of alkali metals from solutions of their hydroxides by 1 *M* solutions of BAMBP. Rubidium and cesium concentrations in 1 *M* BAMBP solutions approach a value of 0.25 *M*, then abruptly increase to higher values. Water concentrations in the organic phase are also plotted in Figure 2. At metal ion concentrations below 0.25 *M*, the water concentrations are similar to those obtained in 1 *M* BAMBP without metal ions, while the abrupt increase of metal ion concentrations above 0.25 *M* is accompanied by a similarly abrupt increase in water content. In solutions which were initially 1 *M* in BAMBP, the limiting concentration of cesium was 0.94 *M*. Allowing for the 7–8% increase in volume which resulted from the extraction of water, this means that all of the phenol was converted to cesium phenolate.

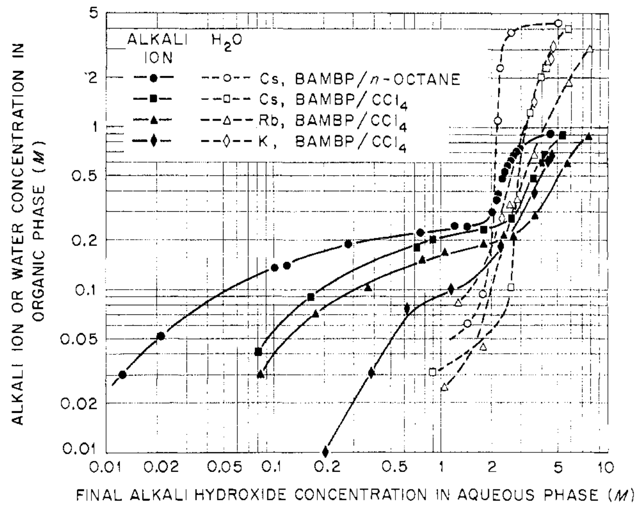

Figure 2.—Alkali metal ion extraction isotherms (BAMBP = 1 *M*).

Lithium and sodium were extracted in appreciable concentration only with their water of hydration. Consequently, sodium and lithium isotherms are not included in Figure 2. Very efficient separation of cesium and/or rubidium from other alkali metals is possible only when water is not extracted, *viz.*, at hydroxide concentrations less than 1 *M*. The importance of the hydroxide concentration is exemplified by the fact that from a saturated aqueous cesium nitrate solution adjusted to pH 11 with CsOH (1.13 *M* aqueous cesium ion) the equilibrium organic cesium ion concentration was 0.0098 *M*, but from a solution of cesium hydroxide of equal concentration the equilibrium organic cesium ion concentration was 0.22 *M*.

The amount of water extracted depended in part on which alkali metal was present (Table I). Under comparable conditions, the amount of water extracted per metal ion was generally somewhat higher for Na^+ and Li^+ than for Cs^+.

Infrared Studies.—The infrared spectrum of BAMBP is typical of those observed for phenols which undergo intermolecular hydrogen bonding.[6,7] As shown in Figure 3, at a concentration of 0.1 *M*, a sharp band characteristic of nonassociated O–H was observed at 3612 cm.$^{-1}$. A broader, well-defined absorption typically characteristic of the hydrogen-bonded O–H in the

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(6) G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," Reinhold Publishing Corp., New York, N. Y., 1960, Chapter 3.

(7) R. Mecke, *Discussions Faraday Soc.*, **9**, 161 (1950).

TABLE I

WATER EXTRACTION WITH 1 *M* BAMBP AS A FUNCTION OF THE ALKALI METAL PRESENT

Initial aqueous phase	Organic phase (equilibrium)		
	Diluent	M^+ concn., *M*	H_2O concn., *M*
3 *M* CsOH	*n*-Octane	0.602	3.78
6 *M* CsOH	*n*-Octane	0.963	3.98
3 *M* NaOH	*n*-Octane[a]	1.31[a]	16.3[a]
6 *M* NaOH	*n*-Octane[a]	1.94[a]	14.7[a]
3 *M* LiOH	*n*-Octane	0.621	6.50
6 *M* CsOH	CCl_4	0.865	3.12
4.6 *M* NaOH	CCl_4	0.64	4.51
6 *M* NaOH	CCl_4	0.752	2.96
2.6 *M* KOH	CCl_4	0.25	0.75
5.0 *M* KOH	CCl_4	0.65	2.67
3.7 *M* RbOH	CCl_4	0.28	0.66

[a] Extractions from 3 and 6 *M* NaOH solutions using *n*-octane diluent gave a distinct, dark, viscous third phase which contained nearly all of the extracted sodium and water and the phenol from the diluent. Lithium and cesium solutions did not give a third phase. Also, 6 *M* NaOH solutions did not form a third phase with CCl_4 diluent.

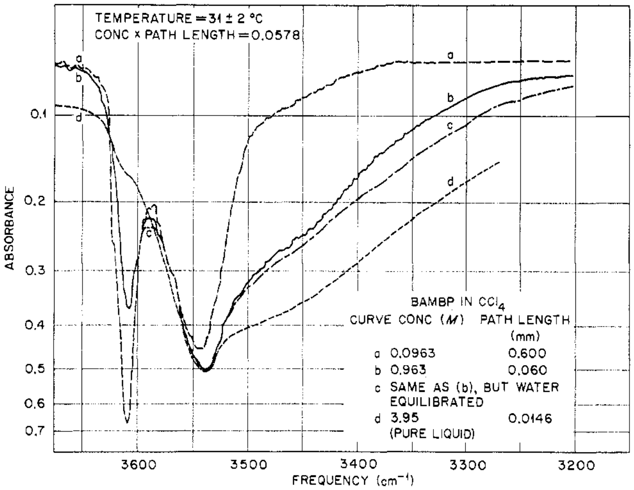

Figure 3.—Infrared absorption of BAMBP in the O–H region.

dimer was observed at 3542 cm.$^{-1}$. At this concentration there was no absorption in the 3400–3500 cm.$^{-1}$ region where the O–H stretching vibrations characteristic of more highly associated hydrogen-bonded species are expected. As the concentration of phenol was increased, the ratio of the intensities of the unbonded O–H band to the dimer band decreased rapidly and the "free" O–H absorption became barely discernible in pure liquid BAMBP. The absorption in the region of the O–H stretch in higher polymeric species remained relatively weak, even in the case of the pure phenol. The dimeric O–H absorption at 3542 cm.$^{-1}$ retained its identity at all except the very lowest concentrations.

The first overtone of the free O–H stretch was easily observed as a very sharp, intense absorption at 7061 cm.$^{-1}$.[8] Also present was a shoulder at 7006 cm.$^{-1}$, the first overtone of the dimeric O–H stretch. The use of the overtone band for the purpose of calculating

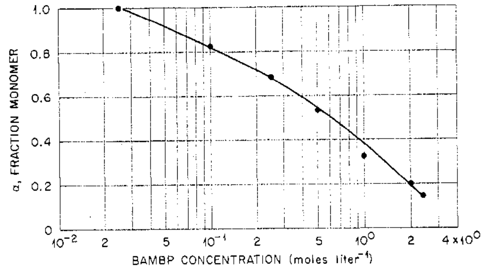

Figure 4.—Association of BAMBP in CCl_4.

the fraction of monomeric molecules has been described by Mecke[7] and by Coggeshall and Saier.[9]

The weight fraction of monomer, α, was calculated from the relationship $\alpha = \epsilon_c/\epsilon_\infty$, where ϵ_c is the extinction coefficient at concentration c and ϵ_∞ is the extinction coefficient at infinite dilution, both at 7061 cm.$^{-1}$. A constant value of ϵ_∞ of 2.02 was obtained in the concentration range from 0.025 to 0.01 *M*. The values of α plotted in Figure 4 were calculated after correction for overlap due to adjacent bands.

Independent values of α were also calculated for 0.50 and 1.0 *M* solutions from the fundamental band in the manner described by Fox and Martin.[10] This method also requires a correction for overlap of the adjacent absorption bands. The values for α calculated by the two methods are 0.33 and 0.28 for 1.0 *M* solutions and 0.54 and 0.52 for 0.50 *M* solutions. With 1 *M* BAMBP in CCl_4, using $\bar{n} = 1.62$ for the average number of molecules in all species,[11] together with $\alpha = 0.38$ (Figure 4) for the fraction of unassociated molecules, gives a value of 2.00 for the average number of molecules in the associated species.

Effect of Cesium on Infrared Spectrum.—When cesium ions are extracted without co-extraction of water, *i.e.*, the water concentration is the same as that which exists when the organic phase is in equilibrium with salt-free water,[12] the intensity of the fundamental O–H vibrations attributable to both the monomers and hydrogen-bonded dimers diminishes, but the absorption due to the bonded O–H in the higher polymers increases.

At an experimental point in the region where the water content of the organic phase increased abruptly (a solution of 0.243 *M* Cs^+, 0.0928 *M* H_2O, 0.243 *M* $BAMBP^-$, and 0.757 *M* BAMBP), changes were noted in the infrared spectrum. The 3612 cm.$^{-1}$ absorption was barely discernible and an increase in absorption was noted throughout the 3100–3650 cm.$^{-1}$ region which characterizes the polymeric O–H absorption. This effect became more pronounced as the water and alkali metal ion concentrations increased.

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(8) The fundamental and the harmonics are related by the expression $\tilde{\nu}_n = n\omega[1 - (n + 1)x]$, where ω is the natural frequency for very small displacements and x is the anharmonicity constant. Hence the frequency of the first overtone, $\tilde{\nu}_2$, will not be simply twice the frequency of the fundamental, $\tilde{\nu}_1$.

(9) N. D. Coggeshall and E. L. Saier, *J. Am. Chem. Soc.*, **73**, 5414 (1951).

(10) J. J. Fox and A. E. Martin, *Proc. Roy. Soc.* (London), **162**, 419 (1937).

(11) This value is based upon vapor pressure measurements obtained by Dr. J. W. Roddy of this laboratory.

(12) When 1 *M* BAMBP was equilibrated with water, a moderate increase was observed in the polymeric O–H stretching region, 3150–3500 cm.$^{-1}$ (Figure 3c). This was probably due to the formation of hydrogen-bonded species involving both water and BAMBP molecules. Further reference to Figure 3 shows no significant changes in either the monomer or dimer O–H absorption bands. Hence, the use of the data of Figure 4, obtained in non-water-equilibrated BAMBP solutions, was justified for use in water-equilibrated systems. The only limitation was that no additional water be carried into the organic solution by the metal ion, *e.g.*, that $(Cs)_o \leq 0.25$ *M*.

Nuclear Magnetic Resonance Studies.—As shown by the infrared spectra, the dimer is the only associated species in solutions of BAMBP in CCl_4 up to 0.10 *M*. The method of Somers and Gutowsky[13] was therefore used to calculate a dimerization constant of BAMBP in dilute solutions. A plot of the proton shift *vs.* the mole fraction of BAMBP gave a curve from which data were obtained for use in the relationship

$$(\mathrm{d}\tilde{\nu}/\mathrm{d}x_\mathrm{p})_{x=0} = 2K\Delta\tilde{\nu} \qquad (1)$$

The left side of the equation is the limiting rate of change of the O–H proton shift with mole fraction of phenol at high dilution. $\Delta\tilde{\nu}$ is the difference in the line position of the O–H proton of the pure and the infinitely dilute phenol. The calculated dimerization constant, *K*, for very dilute solutions of BAMBP in carbon tetrachloride at 34° is 2.0 ± 0.3.

That the downfield shift is due to intermolecular hydrogen bonding was further checked by observing the shift as a function of temperature. With increasing temperature, dissociation should take place, and the phenolic proton resonance should move back upfield toward the value observed in dilute solutions. That this did occur is shown by the data in Table II.

Table II

Chemical Shift in the BAMBP Phenolic Proton Magnetic Resonance Peak as a Function of Temperature

Temp., °C.	Concn. in CCl_4, *M*	Chemical shift, p.p.m.
34	2.396	−5.255
47.5	2.396	−4.722
62	2.396	−4.605
76	2.396	−4.498
86	2.396	−4.450
34	0.1	−4.133

Effect of Alkali Metal Ions on N.m.r. Spectra.—The introduction of alkali metal ions into the organic phase brought about striking changes, not only in the location and shape of the O–H resonance, but also in the intensity and fine structure of other proton resonances, especially those of the hydrogens of the methyl group attached to the 2-α carbon atom and the hydrogen *ortho* to the phenolic O–H.

As the concentration of alkali metal ion increased there was observed a rapid downfield shift and broadening of the hydroxyl proton line. The downfield shift continued and reached a limit at a point corresponding to the abrupt change in the extraction isotherm (Figure 2). As the water concentration increased, the line then shifted back upfield; the upfield shift continued and the sharpness of the O–H resonance was gradually restored. The limiting value of the chemical shift in the hydroxyl proton line and the band width were very similar to those of the water proton resonance spectrum.

When the concentration of alkali metal reached approximately 0.1 *M* the first distinct changes in the regions of both the α-methyl and ring proton resonances were observed, specifically, broadening and the loss of fine structure. This effect became even more intense as the alkali metal ion concentration increased.

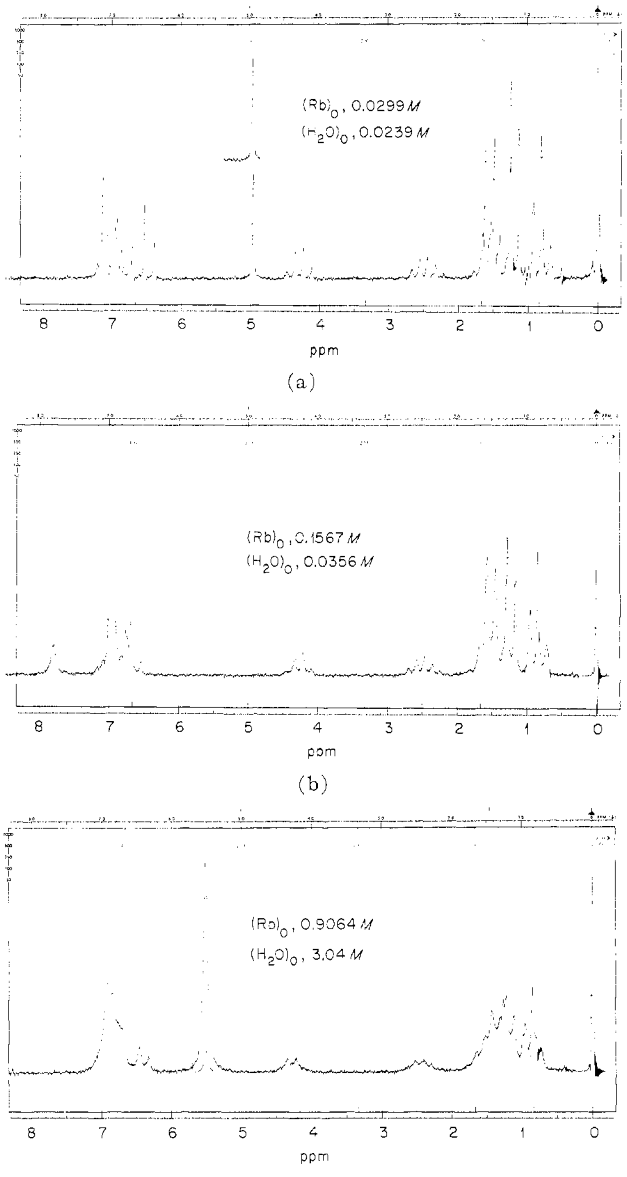

Figure 5.—Effect of introduction of alkali metal and water on the n.m.r. spectrum of BAMBP.

The general features of the n.m.r. spectra were similar for organic solutions containing Cs, Rb, and K. Sodium and lithium gave less-pronounced effects on the BAMBP spectrum. Figure 5 shows typical spectra for different rubidium and water concentrations in the organic phase. In Figure 5a, with 0.03 *M* Rb, the O–H resonance has moved from −4.537 p.p.m., the resonance for metal-free, water-equilibrated 1 *M* BAMBP in CCl_4, to −4.948 p.p.m.; the line width is about the same as that of pure BAMBP, $\Delta\tilde{\nu}_{1/2} \simeq 0.025$ p.p.m., and no perturbation in the other regions of the spectrum is apparent. In Figure 5b the rubidium ion concentration has increased fivefold and the large downfield shift to −7.797 p.p.m. along with considerable broadening, $\Delta\tilde{\nu}_{1/2} = 0.087$ p.p.m., is obvious. In addition,

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(13) B. G Somers and H. S. Gutowsky ,*J. Am. Chem. Soc.*, **85**, 3065 (1963).

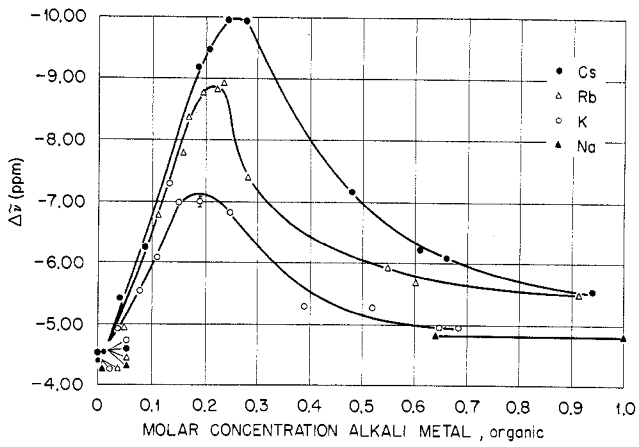

Figure 6.—Effect of alkali metal concentration on the shift of the O–H proton resonance of BAMBP (BAMBP = 1 *M* in CCl_4).

broadening and loss of fine structure in the other proton resonances become quite apparent. The effect of introducing water into the organic phase along with the metal ion is shown in Figure 5c. The O–H resonance has now moved back upfield to its final position at −5.520 p.p.m. and the line width has been largely restored, $\Delta\bar{\nu}_{1/2}$ = 0.065 p.p.m. The other resonances, however, have become even broader and display almost no fine structure.

In Figure 6 the downfield shift of the O–H proton resonance has been plotted against the metal ion concentration in the organic phase. It is to be emphasized that all the points on the positive slope correspond to water-free solutions. In each case there is a change in sign of the slope, which occurs at approximately 0.26 *M* cesium, 0.24 *M* rubidium, and 0.19 *M* potassium. All points on the negative slope correspond to solutions containing water carried into the organic phase together with the metal ion.

It is further evident from Figure 6 that, for a given concentration of metal ion, the downfield shift is in the order $Cs^+ > Rb^+ > K^+$. The change in the direction of the O–H resonance occurs at a significantly lower concentration of potassium ion.

Discussion

The extractant, 4-*sec*-butyl-2-(α-methylbenzyl)-phenol, is a classical example of a hindered phenol. Implicit in such a classification are the following properties[9,14,15]: very slight solubility in aqueous alkali, limited association through hydrogen bonding, and the predominance of the dimer as the principal hydrogen-bonded species.

Infrared Spectra.—In a classic paper[16] the infrared absorptions arising from the fundamental O–H vibrations in solutions of ethanol in carbon tetrachloride at 3628, 3523, and *ca.* 3300 cm.$^{-1}$ were attributed to the monomer, the dimer, and higher hydrogen-bonded polymers, respectively. This classification was corroborated by Smith and Creitz,[17] who demonstrated that in alcohols having sterically hindered O–H groups, *e.g.*, 2,4-dimethyl-3-ethyl-3-pentanol, there is no evidence of polymer formation. That the association of hindered phenols is dimeric in nature has also been demonstrated.[9] Finally, it has been shown[18] that the extinction coefficient for each O–H frequency characteristic of the various possible hydrogen-bonded species increases with increasing size of the aggregate. Thus, the fact that the absorbance due to the dimeric O–H is stronger than that due to polymeric O–H, even in pure liquid BAMBP, means that the dimer must be the most abundant species.

The changes which occur in the infrared spectrum when cesium ions are present in BAMBP solutions are those which are generally attributed to the formation of hydrogen-bonded aggregates larger than dimers. However, two alternate possibilities are also quite reasonable. Since the introduction of cesium ions necessarily requires that phenol molecules are converted to phenolate ions, a number of hydrogen bonds which previously existed between molecules now involve anions as well. We thus have a more strongly chelated O–H and a concurrent shift to lower frequencies.[19] The other possibility is that coordination between the phenolic oxygen and the metal ion could affect $\bar{\nu}_{OH}$ similarly, but we are unaware of any systematic study of such effects.

N.m.r. Spectra.—The effect of hydrogen bonding on n.m.r. shifts has been discussed in some detail by Somers.[20] Other factors which contribute to the downfield shift are discussed by Pople, *et al.*[21] The general conclusions[22] are that H-bond shifts are all negative (toward lower fields) and that molecular association arising from hydrogen bonding increases both the magnitude of the shift and the line width. There also exists a qualitative correlation of the n.m.r. hydrogen bond shifts with hydrogen bond strength.[21]

Coordination through the oxygen atom of the phenol to a metal ion should also result in a downfield shift of the acidic proton due to the decrease in electron density, the increase in ionic character, and a net decrease in shielding of the proton. Hence, the n.m.r. data do not necessarily distinguish a shift due to H-bonding from a shift due to metal ion–oxygen interaction. Unfortunately, no published data have yet come to our attention which actually deal with the effect of coordination on the O–H resonance. However, the shifts observed here are larger than any previously observed for hydrogen-bonded systems involving molecules of this type,[21] and both factors are probably operative.

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(14) N. D. Coggeshall, *J. Am. Chem. Soc.*, **69**, 1620 (1947).

(15) N. D. Coggeshall and E. M. Lang, *ibid.*, **70**, 3283 (1948).

(16) J. Errera, R. Gasport, and H. Sack, *J. Chem. Phys.*, **8**, 63 (1940).

(17) F. A. Smith and E. C. Creitz, *J. Res. Natl. Bur. Std.*, **46**, 145 (1951).

(18) Reference 6, p. 76.

(19) K. Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, Inc., San Francisco, Calif., 1962, p. 167.

(20) B. G. Somers, Ph.D. Dissertation, University of Illinois, 1961.

(21) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 409.

(22) Reference 6, pp. 147, 155.

Broadening of the hydroxylic proton signal could be attributed to a change in the exchange rate of that group, but the same explanation cannot account for broadening of the other signals when the metal ion concentration is increased (see Figures 5a, b, c). A better explanation is based on the size of the complex formed. As a consequence of association of organic molecules, the aggregate is large and its freedom of motion in the solution may be inhibited. The result is similar to that observed for a slow exchange, or an increase in viscosity which results in a pseudo-crystalline condition and an increase in lattice interactions. Hence, broadening of all signals in the spectrum will be observed. Electric field gradients at the alkali metal ion cannot account for the effect, and quadrupole interactions would only account for broadening of the signals of protons close to the bonding site of the alkali metal.

Extraction Chemistry.—The first power pH dependence of the cesium extraction coefficient shows that the extraction reaction involves the exchange of Cs^+ with the H^+ of the phenol. This is corroborated by the decrease in intensity of the O–H stretching band of the phenol in the presence of cesium in the organic phase.

For the average third-power reagent dependence to be consistent with an observed loading ratio of four moles of BAMBP per mole of cesium, it is necessary that the reagent be polymerized to $\bar{n} = {}^4/_3$, suggesting multiple equilibria. In Figure 1, curves (2) and (3), the extraction coefficients are plotted as a function of the monomer and dimer concentrations which were calculated from Figure 4, assuming dimers to be the only associated species. The linearity and observed slopes of these plots suggest that the following reactions are involved.

$$2\mathrm{ROH(org)} = \mathrm{(ROH)_2(org)} \qquad (2)$$

$$\mathrm{Cs^+(aq)} + 4\mathrm{ROH(org)} + \mathrm{OH^-(aq)} = \mathrm{CsOR\cdot 3ROH(org)} + \mathrm{H_2O} \qquad (3)$$

$$\mathrm{Cs^+(aq)} + 2\mathrm{(ROH)_2(org)} + \mathrm{OH^-(aq)} = \mathrm{CsOR\cdot 3ROH(org)} + \mathrm{H_2O} \qquad (4)$$

As the reagent concentration decreases, the monomer becomes the predominant species, and the equilibrium described by eq. 3 predominates. At formal reagent concentrations greater than 0.6 M (dotted portion of the monomer curve), the curves converge rapidly and the dimer equilibrium (eq. 4) predominates.

Accordingly, a fourth-power reagent dependence of the extraction coefficient would be expected in dilute solutions, and a second-power reagent dependence would be expected in concentrated solutions. Curve (1) in Figure 1 is therefore expected to change slope from a limiting value of 4 at the lower concentrations to a limiting value of 2 at the higher concentrations. An average slope of 2.8 was actually obtained.

The abrupt change in the extraction isotherm indicates a marked change in the extraction mechanism when the cesium concentration reaches and passes 0.25 M in the 1 M BAMBP. The ease of extraction of all of the alkali metal ions by BAMBP at very high aqueous hydroxide ion concentrations, where water becomes involved, results from a large shift to the right in the equilibrium given by the equation

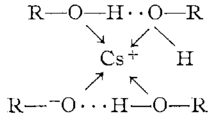
$$\mathrm{M^+(H_2O)_\mathit{x}(aq)} + \mathrm{OH^-(aq)} + \mathrm{ROH(org)} = \mathrm{M^+OR^-(H_2O)_\mathit{y}(org)} + (x - y + 1)\mathrm{H_2O} \qquad (5)$$

In the case of cesium BAMBPate solutions in carbon tetrachloride, y approaches a limiting value of 4 (Figure 2).

Basis of Extraction.—The ability of BAMBP to extract cesium to the exclusion of the smaller ions in the water-free equilibrium systems is due in part to the extremely small hydration energy which needs to be overcome. Also, the transfer of the largest ions would be favored by the decrease in free energy, resulting from rejection of the large univalent ion by the disrupted aqueous phase and re-formation of the normal water structure.[23] In addition, the larger ions can associate with more extractant molecules, giving a species which is more compatible with the organic phase.

Nature of the Extracted Species.—Because cesium is a very large ion of low charge and possesses very little tendency to coordinate, one possible species in the organic phase is an ion pair. Such an ion pair might be simply cesium phenolate itself, or a cesium–anion polymer, *i.e.*, $Cs^+[RO(ROH)_n]^-$, where n is a small integer. However, the experimental evidence emphasizes the 4:1 stoichiometry, at least at high loading, and suggests a cesium ion solvated by four phenol molecules. In this view, the extraction of water at cesium concentrations greater than 0.25 M involves replacement of BAMBP molecules by water, ultimately resulting in a hydrated cesium ion associated with a phenolate anion. This picture is also supported by the experimental fact that the amount of water extracted per metal ion decreases in the order $Na^+ > K^+ > Rb^+ > Cs^+$.

It is appropriate at this point to take note of the observations of Van der Heijde[24] and Harlow and Bruss.[25] These investigators were able to correlate the anomalies in the shapes of titration curves of phenol and 2,4-dialkyl-substituted phenols in nonaqueous solvents with the formation of a stable phenol–phenolate hydrogen-bonded dimer. In view of these observations and the established stability of the dimer in hindered phenols, a structure which involves solvation by hydrogen-bonded dimers is highly plausible. This suggested structure maintains the hydrogen bonds between pairs of the solvating phenols. Since a single acid proton resonance is observed, all acidic protons are equivalent, and hence are in rapid exchange. This structure fits the extraction data and the n.m.r. and



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infrared data, and suggests an energetic contribution to extraction by preserving the phenol dimer bonds.

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The Kinetics of Exchange of Ammonia with the Hexaamminecobalt(II) Complex in Anhydrous Ammonia[1]

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Kinetic data obtained by n.m.r. line broadening techniques are reported for the $Co^{II}(NH_3)_6$–NH_3 exchange reaction in liquid ammonia. The rate is essentially unaffected by addition of 1.7 *m* $NaClO_4$, 1.4 *m* $NaClO_4$ plus 0.25 *m* NH_4ClO_4, or 1.5 *m* H_2O. Perchlorate and nitrate salts give similar results. The rate law $R = 6k_1[Co^{II}(NH_3)_6]$ has been used. At $-40.7°$ k_1 is $2.7 \pm 0.3 \times 10^4$ sec.$^{-1}$. The extrapolated value for k_1 at 25° is $7.2 \pm 1.4 \times 10^6$ sec.$^{-1}$. Values for ΔH^* and ΔS^* (calculated from k_1) are 11.2 ± 0.4 kcal./mole and 10.2 ± 2 e.u., respectively. Some comparisons with Ni(II) systems and other Co(II) systems are made. The scalar coupling constant A/h was evaluated from the chemical shift and line broadening data and was found to be $7.5 \pm 0.1 \times 10^6$ c.p.s. for $Co^{II}(NH_3)_6$.

Introduction

The research reported here is in continuation of a general program of study on ammonia exchange rates in transition metal complexes. Previous studies have been published concerning Cr(III),[3] Ni(II),[4] and, less completely, Cu(II)[4] systems.

Experimental

The n.m.r. techniques and equipment previously described in some detail[4,5] have been employed. The ammonia was purified and solutions in ammonia were prepared and handled as described earlier.[4]

Cobalt reagents used were A.R. grade $Co(NO_3)_2 \cdot 6H_2O$, $Co(ClO_4)_2 \cdot 6H_2O$ prepared from cobaltous carbonate and perchloric acid, and CoI_2 prepared from cobaltous carbonate and hydriodic acid. The above salts were treated with anhydrous ammonia in the absence of air using a vacuum system. Upon repeated condensation of ammonia on the above salts followed by distillation of excess ammonia, violet anhydrous compounds were obtained which on the basis of Kjeldahl analysis corresponded to the tetraammine salts. The iodide salt was found not soluble enough in ammonia for these studies ($<$*ca.* 0.01 *M*). The perchlorate salt was quite soluble ($>$0.1 *M*) over the range -70 to $+30°$, giving pink solutions. The nitrate salt was soluble to the extent of $>$*ca.* 0.01 *M* at temperatures below $-20°$, also giving pink solutions. Anhydrous sodium perchlorate and ammonium perchlorate were prepared as described before.[4]

Treatment of Data and Results

Our NH_3 line broadening results are reported in terms of the quantity T_{2p}'' as in the Ni(II) studies.[4] This quantity is defined as $T_{2p}'' \equiv 2m_{Co}/\gamma\Delta'$ where m_{Co} refers to the total molality of cobalt present in solution, γ is the magnetogyric ratio for N^{14} (1934 gauss^{-1} sec.$^{-1}$), and Δ' is the line broadening (in gauss) due to Co(II), obtained from the full n.m.r. line widths at half-maximum absorption using recorded absorption curves. The results are given in Table I.

TABLE I

LINE BROADENING DATA FOR $Co^{II}(NH_3)_6$–NH_3 EXCHANGE

t, °C.	Δ′, gauss	$T_{2p}'' \times 10^5$, *m* sec.
(A) Co = 0.050 m^a		
−21.5	0.65	7.8
−30.5	0.36	14.2
(B) Co = 0.083 *m*		
−20.0	1.21	7.1
−36.3	0.44	19.4
−36.8	0.33	25.7^b
−40.0	0.26	32.4^b
−45.5	0.13	64^b
(C) Co = 0.166 *m*		
25.8	0.10	172
− 3.1	1.27	13.5
− 6.8	1.45	11.9
−11.8	2.16	7.9
−23.8	2.21	7.8
−27.8	1.87	9.2
−35.0	1.30	13.2
−41.1	0.27	64
(D) Co = 0.25 *m*		
−36.3	1.29	20.1^c
−36.3	1.24	20.9^d
−36.3	1.15	22.7^e
−48.0	0.31	84^c
−49.8	0.28	93^d
−50.2	0.21	124^e
(E) Co = 0.333 *m*		
14.2	0.66	52
11.8	0.90	38
5.6	1.46	24.2
−35.0	1.92	17.9
−41.2	0.77	45
−43.2	0.56	61
−45.2	0.57	60
−51.2	0.27	127

[a] $Co(NO_3)_2 \cdot 4NH_3$ used instead of $Co(ClO_4)_2 \cdot 4NH_3$. [b] 0.01 *m* $Co(NH_3)_6(NO_3)_3$ present. [c] 1.67 *m* $NaClO_4$ present. [d] 1.42 *m* $NaClO_4$ plus 0.25 *m* NH_4ClO_4 present. [e] 1.52 *m* H_2O present.

A chemical shift (*S*) in the N^{14} absorption frequency in NH_3 due to Co(II) was observed. The shift data relative to pure NH_3 are given in Table II.

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