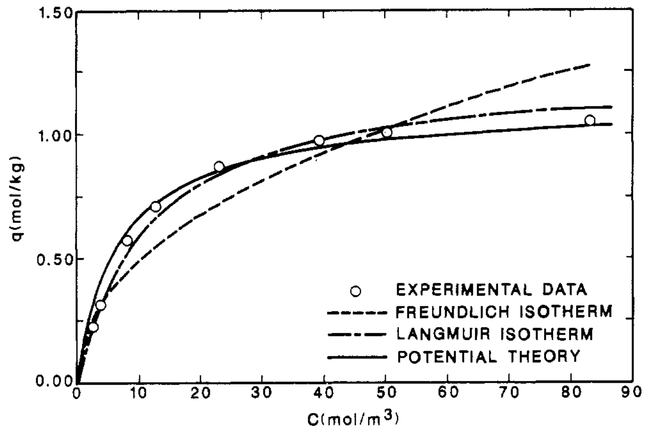

**Figure 5.** A comparison of experimental and predicted isotherms for oxalic acid at 5 °C.

## Glossary

| | |
|---|---|
| $C$ | equilibrium solution concentration |
| $C_s$ | solubility in water |
| $E$ | characteristic energy |
| $E_0$ | characteristic energy of a standard component |
| $K$ | a parameter of the Freundlich isotherm |
| $K_1$, $K_2$ | parameters of the Langmuir isotherm |
| $n$ | parameter of the Dubinin-Astakhov or Freundlich equation |
| $P$ | equilibrium pressure |
| $P_s$ | vapor pressure of the adsorbate liquid at the equilibrium temperature |
| $q$ | equilibrium uptake |
| $R$ | gas constant |
| $T$ | temperature |
| $W_0$ | parameter of the Dubinin-Astakhov equation (total pore volume) |
| $X$ | weight of substance adsorbed |
| $\beta$ | affinity coefficient |
| $\epsilon$ | adsorption potential |
| $\rho$ | liquid density |

**Registry No.** $(COOH)_2$, 144-62-7; $(CH_2)(COOH)_2$, 141-82-2; $(CH_2)_2(COOH)_2$, 110-15-6; C, 7440-44-0.

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# Extraction of Several Metals from Chloride Salt Solutions with Heptafluorodimethyloctanedione

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**Distribution coefficients for 17 metals between aqueous chloride salt solutions and 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione–trioctylphosphine oxide solutions in dodecane were determined in the pH range 2–12. Loading isotherms, distribution coefficient dependence on extractant concentration, and synergistic effects of extractant mixtures vs. the individual components are shown for several metals, representative of their periodic class.**

## Introduction

The solvent extraction of metals from near-neutral to basic salt solutions with β-diketones has been reported by many investigators (*1–7*). In general, the extraction mechanism involves the formation of an organic-phase-soluble chelate of the metal with the β-diketone. Studies of the extraction of lithium from aqueous solutions of alkali metal salts (*8*, *9*) with β-diketones have shown lithium distribution coefficients adequately high for efficient extraction and significant separation from the other alkali metals; however, pH values of 10–12 are necessary for enolization of the diketone, exchange of the proton, and formation of the lithium chelate. It is known that substitution of fluorine for hydrogen in the alkyl radicals adjacent to the keto group lowers the pH at which β-diketones enolize and ionize the hydrogen (*10*), thus making such extractants more useful in the pH range 5–9 (*11*, *12*). The addition of a neutral coordinator such as trioctylphosphine oxide (TOPO) appears to further decrease the pH at which compound formation occurs, as evidenced by increased metal extraction (*8*, *9*, *11*, *12*). Additionally, the β-diketone–TOPO mixture is found to be synergistic in the extraction of most metals; that is, the distribution coefficient shown by the mixture is greater than the sum of the coefficients obtained when the two extractants are used separately. Considerable interest has been shown in these compounds because of their ability to form volatile metal complexes (*13–18*). This would add the interesting potential for separation of the metal diketonates by gas chromatography. This paper describes the extraction of the alkali metals, alkaline earths,

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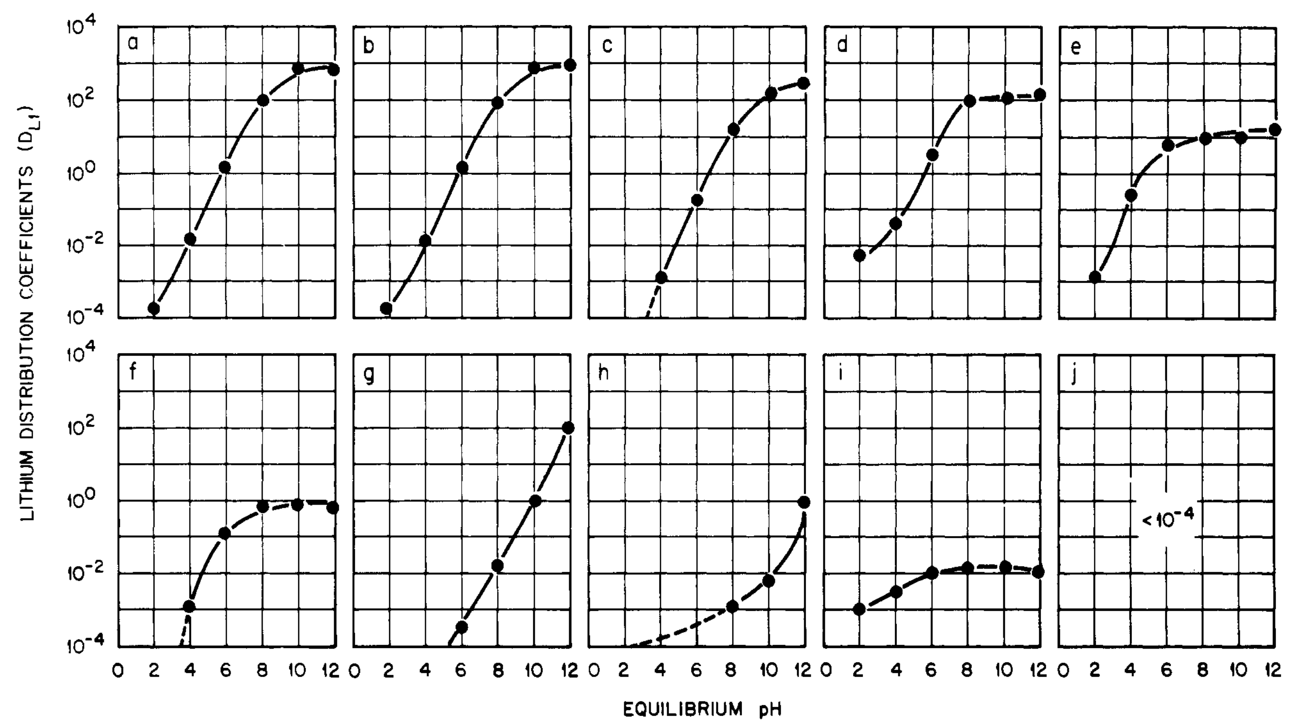

**Figure 1.** Effects of β-diketone structure and pH on lithium extraction. Aqueous phase: 0.01 M LiCl in 1 M CsCl. Organic phase: 0.1 M β-diketone–0.05 M TOPO in dodecane; (a) HFDMOD, (b) PFDMHD, (c) TFDMHD, (d) TTA, (e) HFAA, (f) TFAA, (g) DPPD, (h) DMHD, (i) TOPO only, and (j) dodecane.

representative rare earths, and transition metals as a function of pH, reagent and metal concentration, reagent type, and synergistic combination with TOPO.

## Experimental Section

***Materials*.** The β-diketones used in this study, along with their sources and acronyms, are listed in Table I. These compounds were used as an as-received basis. No further purification was attempted. Dodecane of 99.56% purity (Union Carbide product) was used as the diluent exclusively. All other chemicals were of reagent grade. When possible, appropriate radioactive tracers were employed for analytical purposes. These were obtained from the New England Nuclear Co.

***Procedure*.** Since all of the extraction data reported here required close monitoring of the equilibrium pH, our experimental procedure included an initial equilibration of equal volumes of the organic and aqueous phases in an open-top separatory funnel equipped with a perforated stainless steel cylindrical stirrer, while adjustment to a constant pH was made by the addition of an appropriate alkali metal hydroxide (usually CsOH). After a constant pH had been achieved, the contact was continued for a period of 15 min; then the metal ion concentrations in the two phases were determined by atomic absorption, spectrophotometric, or radioactive-tracer-counting techniques.

Distribution of each of the metal ions investigated (except Cs) was measured in the presence of 1.0 M CsCl in order to maintain a more nearly constant ionic strength with varying extraction and also to minimize the distribution of the β-diketone reagent to the aqueous phase.

Many of the metal extraction tests were made using a mixture of one of the fluorinated β-diketones, HFDMOD (see Table I), and TOPO. The mixture was always 0.1 M in HFDMOD and 0.05 M TOPO in dodecane unless noted otherwise. Although a plot of the data obtained in the initial continuous-variation lithium extraction tests gave no maximum, a definite decrease in slope of the $D$ vs. [HFDMOD]/[TOPO] plot was seen at 2; thus, this molar ratio was chosen as optimum. This specific mixture will be referred to as HFDMOD/TOPO in the following text unless other reagent compositions are indicated.

**Table I. β-Diketones Used in Extraction Tests**

| acronym | compound | source[a] | mol wt |
|---|---|---|---|
| HFDMOD | 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione | A | 296 |
| PFDMHD | 1,1,1,2,2-pentafluoro-6,6-dimethyl-3,5-heptanedione | A | 246 |
| TFDMHD | 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione | A | 196 |
| TTA | 2-thenoyltrifluoroacetone | B | 222 |
| HFAA | hexafluoroacetylacetone | A | 208 |
| TFAA | trifluoroacetylacetone | A | 154 |
| DPPD | 1,3-diphenyl-1,3-propanedione | C | 224 |
| DMHD | 2,6-dimethyl-3,5-heptanedione | D | 184 |

[a] A, PCR Research Chemicals, Inc. B, Columbia Organic Chemicals Co., Inc. C, Eastman Organic Chemicals. D, Chemical Procurement Laboratories, Inc.

## Results and Discussion

***Extraction of Alkali Metals. Effects of β-Diketone Structure and pH Lithium Extraction*.** Figure 1 shows lithium extraction as a function of pH for the β-diketones listed in Table I. Here, an aqueous solution of 0.01 M LiCl in 1 M CsCl was equilibrated with 0.1 M solutions of six fluorinated (a–f) and two nonfluorinated β-diketones (g and h), all in the combination with 0.05 M TOPO in dodecane. Data for 0.05 M TOPO (i) and the dodecane blank (j) are also included. These data show that replacement of the $CH_2$ group (near the keto group) with a $CF_2$ group increases lithium distribution to the organic phase in the pH range of 4.0–9.0. Increasing the number of fluorinated alkyl groups and/or increasing the molecular weight of the β-diketone also contributes to an increase in lithium extraction. This latter effect may be due, in part, to a decrease in aqueous solubility as the molecular weight is increased. Most of the tests reported in this paper were made with 0.1 M 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione (HFDMOD) (formula weight of 296.2) because of its superior extraction properties and expected lower aqueous-phase distribution.

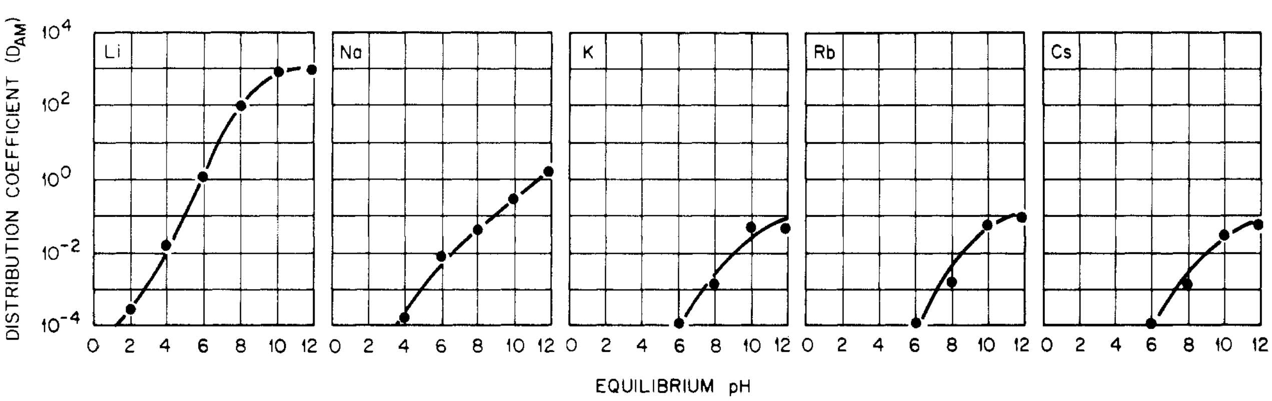

**Figure 2.** Relative extractability of the alkali metals as a function of pH. Aqueous phase: 0.01 M solutions of the alkali metal chloride in 1 M CsCl ($NH_4Cl$ for Cs extraction tests). Organic phase: 0.1 M HFDMOD-0.05 M TOPO in dodecane.

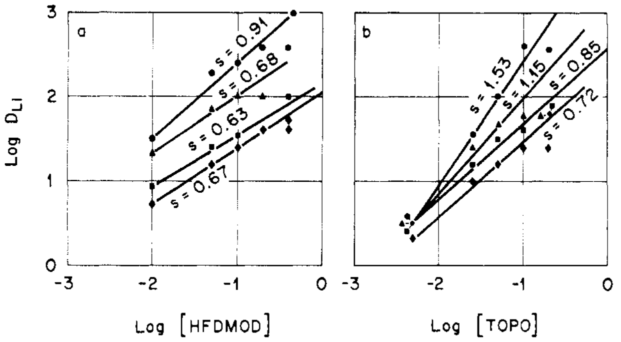

**Figure 3.** Effect of supporting salt matrix on the reagent concentration dependence for both HFDMOD and TOPO. Organic phase: (HFDMOD) constant ratio of 2 mol of HFDMOD to 1 mol of TOPO in docecane,; (TOPO) constant 0.1 M HFDMOD, varying TOPO concentration. Aqueous phase: 0.01 M LiCl in 1 M solutions of (◆) CsCl, (■) KCl, (▲) $NH_4Cl$, and (●) NaCl.

## Relative Extractability of the Alkali Metals as a Function of pH.

Distribution of the five alkali metals to HFDMOD/TOPO in dodecane is shown in Figure 2. Distribution coefficients for lithium are more than 3 orders of magnitude greater than those of sodium at an equilibrium pH of 8 and greater than 5 orders of magnitude higher than those of potassium, rubidium, and cesium in the same pH range. The supporting salt solution for cesium extraction tests were 1 M $NH_4Cl$. These large separation factors (Li/Na, etc.) suggest that systems of this type have great potential for use in processes to recover lithium from natural brines.

## Effect of Supporting Salt Matrix on the Reagent Concentration Dependence.

The dependence of lithium distribution coefficients (at pH 8) on the concentration of HFDMOD/TOPO varies, depending on which supporting salt is used. The slope of log $D_{Li}$ vs. log (reagent concentration) is nearly the same (0.66 ± 0.03) for the electrolytes KCl, $NH_4Cl$, or CsCl but changes significantly to 0.91 when NaCl is the supporting salt (Figure 3a). Assuming the $\beta$-diketone that is not complexed with lithium to be monomeric in the organic phase, the nearly first-power dependence of the lithium distribution coefficient on the (mixed) reagent concentration when the supporting electrolyte is CsCl, but only the 0.7 power dependence when the other three salts are present, indicates that the organic-phase lithium complex stoichiometry may depend on the aqueous supporting electrolyte. Alternatively, the results also suggest a higher degree of competition of $K^+$, $Na^+$, and $NH_4^+$ than that of $Cs^+$ for association with the $\beta$-diketone. However, when the concentration of TOPO is changed but that of (HFDMOD) is held constant, the dependence of the lithium distribution coefficient (also at pH 8) appears to be different with each electrolyte investigated, ranging from a slope of 0.72 with NaCl to 1.53 with CsCl (Figure 3b).

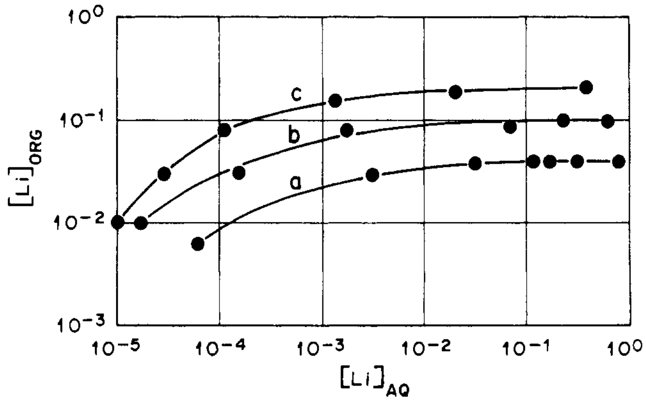

**Figure 4.** Lithium extraction isotherms. Aqueous phase: varying concentratrions of LiCl (0.001–0.2 M) in 1 M CsCl, pH 8.0. Organic phase: HFDMOD-TOPO (2:1) mixtures in dodecane: (a) 0.05 M HFDMOD-0.025 M TOPO, (b) 0.10 M HFDMOD-0.05 M TOPO, and (c) 0.20 M HFDMOD-0.1 M TOPO.

Although the lines have been drawn assuming a linear function, the data actually deviate from linearity at the higher TOPO concentrations with the suggestion of a maximum at 0.1 M TOPO, or 1 mol of TOPO per mol of HFDMOD, rather than at the ratio (i.e., 0.5 to 1) at which most of these tests were made. This, in turn, suggests an optimum complex stoichiometry at this ratio. It is not clear why the apparent reagent dependence of lithium extraction is different for each of the four supporting salts.

## Lithium Extraction Isotherms.

Saturation loading isotherms were determined for lithium with three concentrations of HFDMOD/TOPO. In each case, the loading level indicated 1 mol of $\beta$-diketone per mol of lithium (Figure 4).

## Alkaline Earths. Relative Extractability of the Alkaline Earths as a Function of pH.

Distribution of the six alkaline earth metals to HFDMOD/TOPO in dodecane from 1 M CsCl is shown in Figure 5. The effect of increasing atomic weight on the extraction of the alkaline earth metals appears to be much less than that observed for the alkali metals. Distribution coefficients for beryllium and magnesium are relatively high over the pH range of 4–10; those for calcium and barium are moderate, while strontium and radium are lower by 1–3 orders of magnitude in the same range.

## Synergistic Extraction of Be, Ca, Sr, and Ba by HFDMOD/TOPO.

Distribution coefficients for Be, Ca, Sr, and Ba as a function of equilibrium pH are shown in Figures 6, 7, 8 and 9, respectively, for 0.1 M HFDMOD, for 0.05 M TOPO, and for HFDMOD/TOPO, all in dodecane. The aqueous phase contained 0.01 M alkaline earth metal ions in 1 M CsCl. The distribution coefficients with the mixed extractants over the sum of the individual distribution coefficients are more than 2 orders

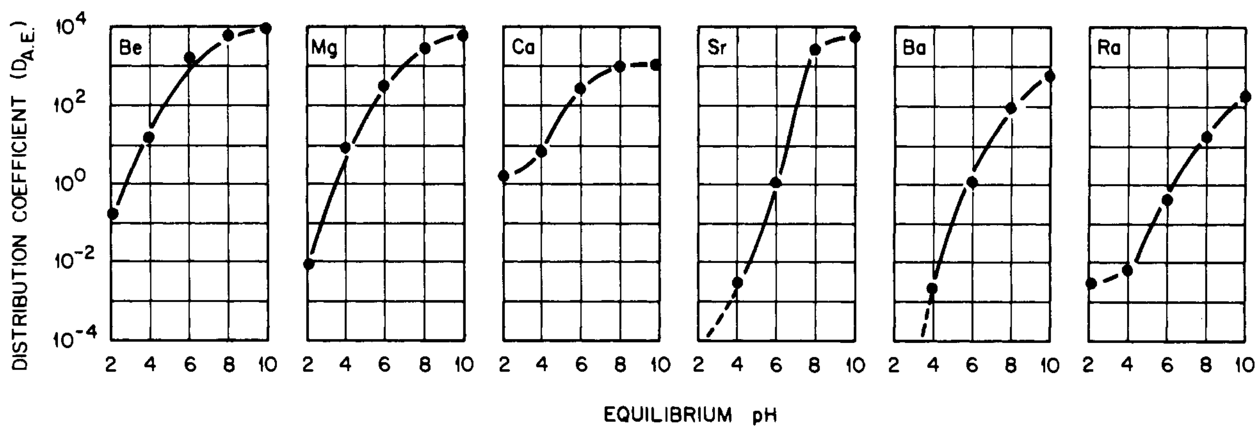

**Figure 5.** Relative extractability of the alkaline earth metals as a function of pH. Aqueous phase: 0.01 M solutions of the alkaline earth metal chlorides in 1 M CsCl. Organic phase: 0.1 M HFDMOD-0.05 M TOPO in dodecane.

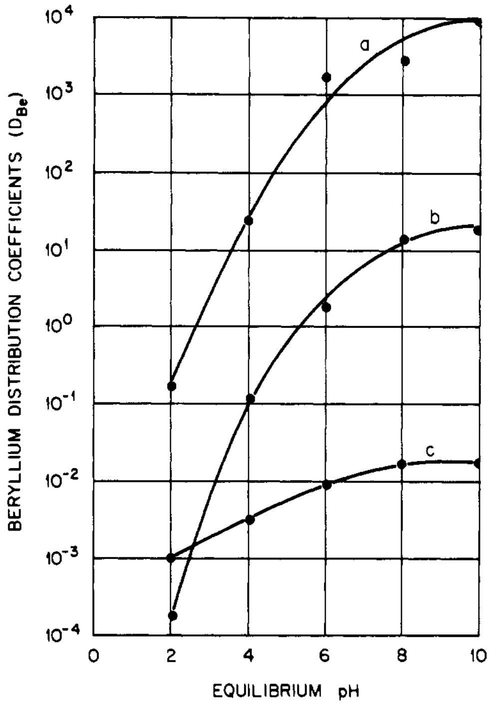

**Figure 6.** Effect of TOPO on the synergistic extraction of beryllium. Aqueous phase: 0.01 M solutions of $BeCl_2$ in 1 M CsCl. Organic phase: dodecane solutions of (a) 0.1 M HFDMOD-0.05 M TOPO, (b) 0.1 M HFDMOD, and (c) 0.05 M TOPO.

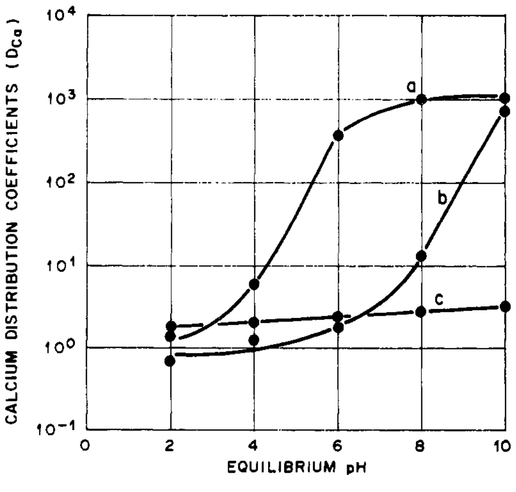

**Figure 7.** Effect of TOPO on the synergistic extraction of calcium. Aqueous phase: 0.01 M solutions of CaCl in 1 M CsCl. Organic phase: dodecane solutions of (a) 0.01 M HFDMOD-0.05 M TOPO, (b) 0.1 M HFDMOD, and (c) 0.05 M TOPO.

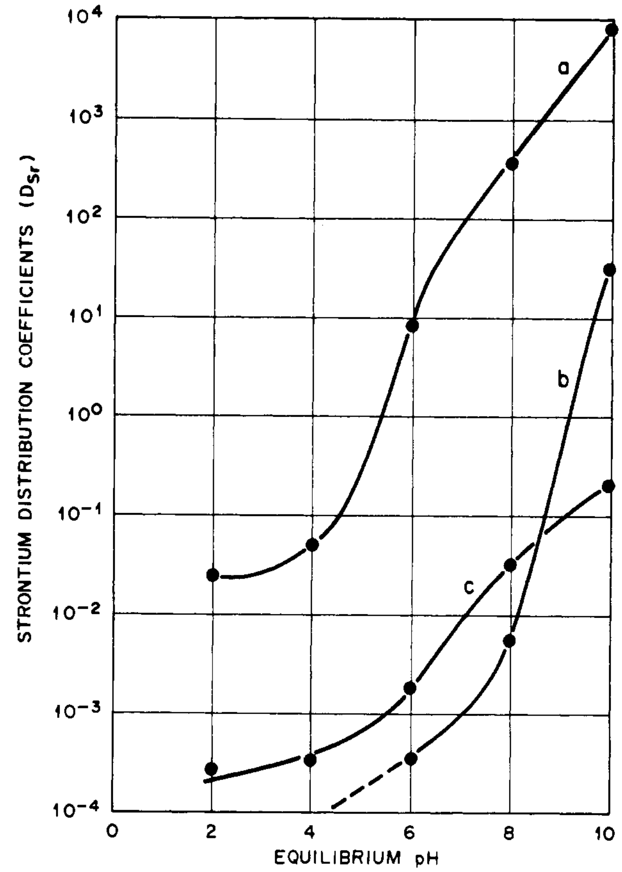

**Figure 8.** Effect of TOPO on the synergistic extraction of strontium. Aqueous phase: 0.01 M solutions of $SrCl_2$ in 1 M CsCl. Organic phase: dodecane solutions of (a) 0.1 M HFDMOD-0.05 M TOPO, (b) 0.1 M HFDMOD, and (c) 0.05 M TOPO.

of magnitude greater for beryllium over the entire pH range of 2-10, by 2 orders of magnitude for calcium in the pH range of 6-8, by 2-4 orders of magnitude for strontium over the pH range of 2-10, and by 2-3 orders of magnitude for barium in the pH range of 6-10. Useful separation process application of these types of reagents is again suggested by such data.

***Effect of Reagent Concentration on Beryllium Extraction.*** Distribution coefficients as a function of reagent concentration were determined for beryllium at an equilibrium pH of 8.0 (1 M CsCl solution) for HFDMOD/TOPO in the concentration range 0.01-0.4 M (Figure 10). The slope of the line obtained with these data (i.e., 2.14) suggests that 1 mol of beryllium is associated with 2 mol of $\beta$-diketone.

***Beryllium and Strontium Extraction Isotherms.*** Loading isotherms were determined for beryllium at pH 2 with four

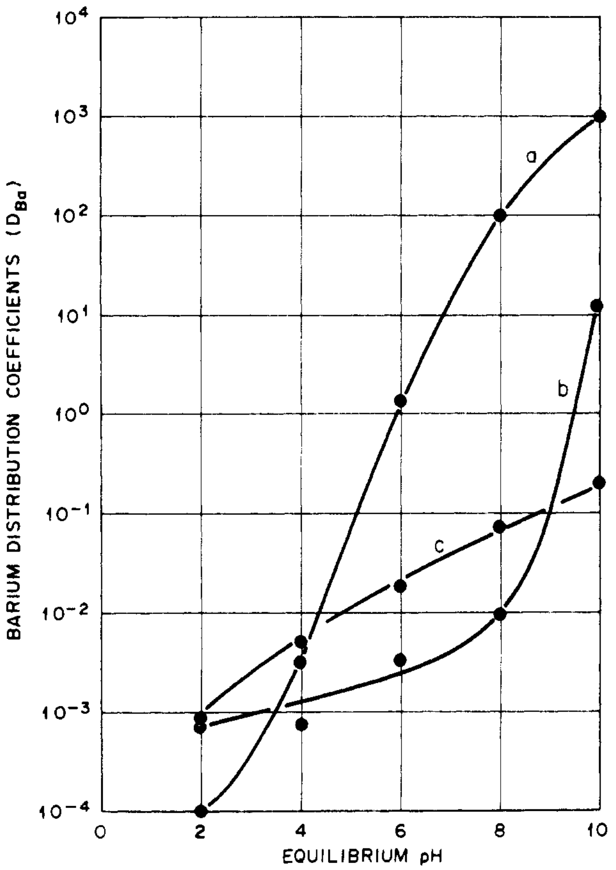

**Figure 9.** Effect of TOPO on the synergistic extraction of barium. Aqueous phase: 0.01 M solutions of $SrCl_2$ in 1 M CsCl. Organic phase: dodecane solutions of (a) 0.1 M HFDMOD–0.05 M TOPO, (b) 0.1 M HFDMOD, and (c) 0.05 M CsCl.

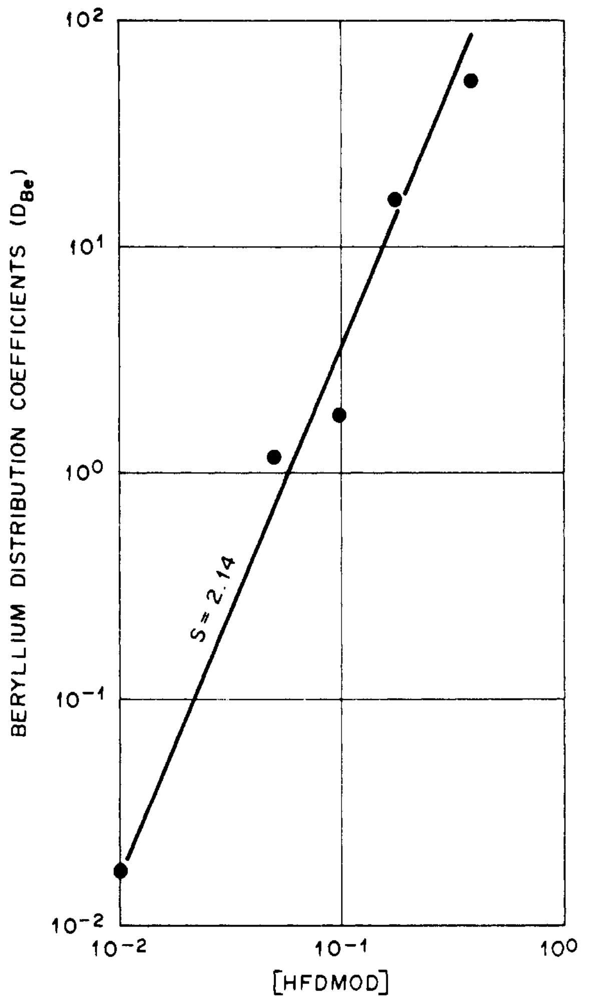

**Figure 10.** Effect of reagent concentration on beryllium extraction. Aqueous phase: 0.01 M $BeCl_2$ in 1 M CsCl solution at pH 8. Organic phase: HFDMOD–TOPO (2:1) mixtures in dodecane; concentration of HFDMOD was varied from 0.01 to 0.4 M.

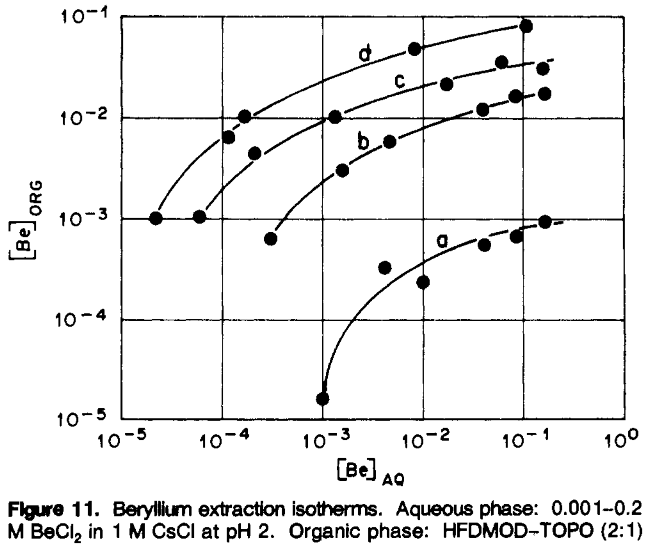

**Figure 11.** Beryllium extraction isotherms. Aqueous phase: 0.001–0.2 M $BeCl_2$ in 1 M CsCl at pH 2. Organic phase: HFDMOD–TOPO (2:1) mixtures in dodecane; HFDMOD concentrations: (a) 0.01 M, (b) 0.1 M, (c) 0.2 M, and (d) 0.4 M.

concentrations of HFDMOD/TOPO in dodecane. Although saturation loading was not attained in any of the isotherms (Figure 11), projection of the curves suggests a probable loading of approximately 4 mol of $\beta$-diketone to 1 mol of beryllium at saturation levels. Extraction isotherms were determined at pH 2 under low loading conditions for strontium with two concentrations of HFDMOD/TOPO. Data for these tests, shown in Figure 12, give a slope of approximately 1, indicating that strontium is self-associated to the same degree in both phases (probably monomeric); however, the increasing slope at higher loading for the lower reagent concentration may indicate some organic-phase association of the complex.

***Rare Earths. Relative Extractability of the Rare Earths as a Function of pH.*** Distribution of three rare earths, cerium, europium, and thulium, between HFDMOD/TOPO in dodecane and 1.0 M CsCl solutions is shown in Figure 13. There appears to be a small but significant decrease in the maximum distribution coefficients as the atomic weight of the rare earths increases. Maximum extraction was attained in the pH range 6–8.

***Effect of Reagent Concentration on Europium Distribution.*** Distribution coefficients for europium were determined at an equilibrium pH of 8.0 with HFDMOD/TOPO in dodecane in the concentration range 0.01–0.4 M. The slope of the line, shown in Figure 14, suggests that 4 mol of HFDMOD are associated with 1 mol of europium.

***Synergistic Extraction of Europium by HFDMOD/TOPO.*** Distribution coefficients for europium are shown in Figure 15 as a function of equilibrium pH for 0.1 M HFDMOD, for 0.05 M TOPO, and for the two reagents mixed at these concentrations. The diluent in each case was dodecane. The enhancement of the distribution coefficients with the combination of the extractants over the sum of these coefficients obtained with the individual reagents is 3–5 orders of magnitude in the pH range 2–4 and approximately 1 order of magnitude in the pH range 6–8.

***Effect of pH on the Extraction Loading Isotherms for Europium.*** Extraction loading isotherms for europium were de-

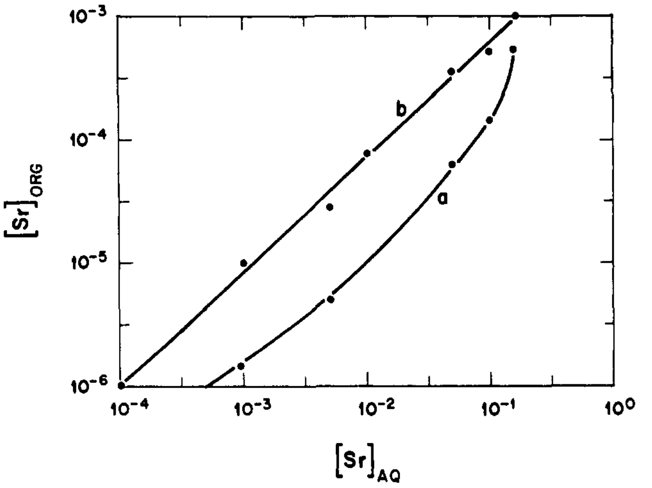

**Figure 12.** Strontium extraction isotherms. Aqueous phase: 0.001–0.2 M $SrCl_2$ in 1 M CsCl at pH 2. Organic phase: HFDMOD–TOPO (2:1) mixtures in dodecane; HFDMOD concentrations: (a) 0.01 M and (b) 0.4 M.

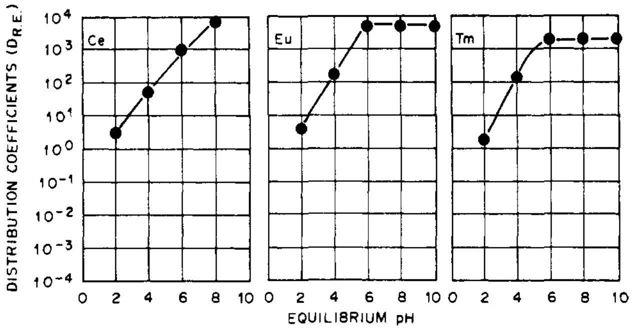

**Figure 13.** Relative extractability of the rare earths as a function of pH. Aqueous phase: 0.01 M rare earth in 1 M CsCl. Organic phase: 0.1 M HFDMOD–0.5 M TOPO in dodecane.

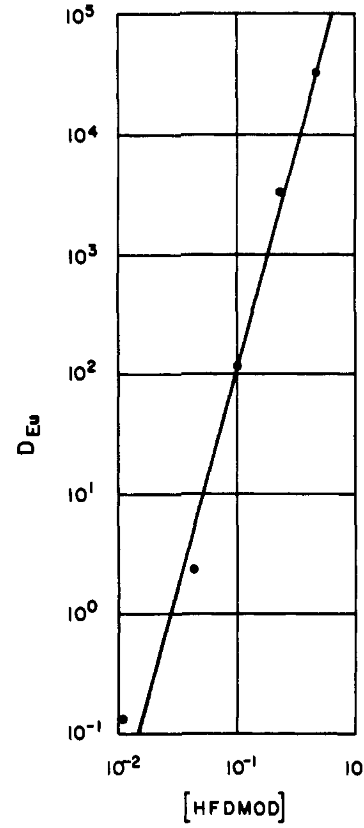

**Figure 14.** Effect of reagent concentration on europium distribution. Aqueous phase: 0.01 M $EuCl_3$ in 1 M CsCl. Organic phase: HFDMOD–TOPO (2:1) mixtures in dodecane; concentration of HFDMOD varied from 0.01 to 0.4 M.

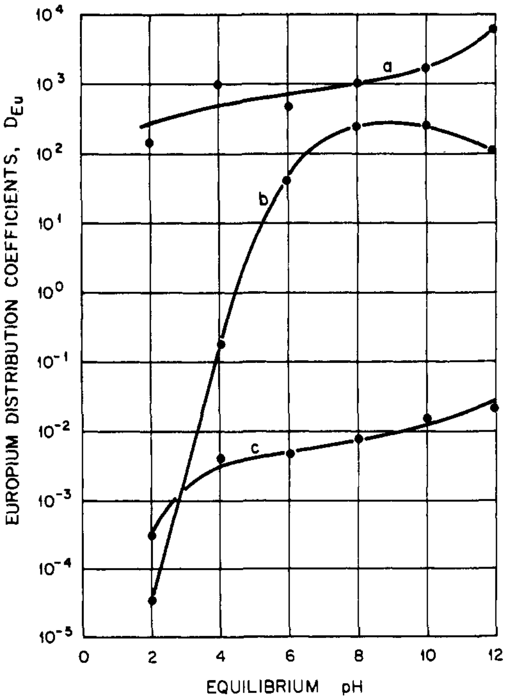

**Figure 15.** Effect of TOPO on the synergistic extraction of europium. Aqueous phase: 0.01 M $EuCl_3$ in 1 M CsCl. Organic phase: dodecane solutions of (a) 0.1 M HFDMOD–0.05 M TOPO, (b) 0.1 M HFDMOD, and (c) 0.05 M TOPO.

termined at pH 2 and 3 for five concentrations of HFDMOD/TOPO. These low pH levels were chosen for two reasons, namely, to take advantage of the extremely high $D_{Eu}$ values in this pH range and to avoid the possibility of hydrolytic precipitation of the europium at the higher concentrations. The data, shown in Figure 16, show significantly increased loadings at the higher pH level. This may be an indication of a higher order complex at pH 3. This speculation is supported by the tendency of curve a at pH 2 to swing upward above $10^{-4}$ M europium in the aqueous phase, which suggests the beginning of the formation of a higher order complex. The loading appears to be approaching 4 mol of HFDMOD per mole of europium in the extraction isotherms determined at pH 3.

***Cerium Extraction Isotherms.*** Extraction loading isotherms for cerium, shown in Figure 17, were determined at pH 2 for three concentrations of HFDMOD/TOPO mixtures. At near-saturation loading, the organic solution concentration of cerium approached 1 mol per 4 mol of HFDMOD.

***Transition Metals. Effect of pH on the Extraction of Copper, Cobalt, and Nickel.*** Extraction coefficients as a function of equilibrium pH were determined for copper, cobalt, and nickel with HFDMOD/TOPO in dodecane. The data, shown in Figure 18, exhibit maximum $D$ values of approximately 104 in the pH range 6–8. At pH 2, the distribution coefficient for copper is higher by a factor of 104 than that for nickel and higher by a factor of 103 than that for cobalt.

## Summary of Metal Extraction vs. pH Data

For easy comparison purposes, some of the data obtained in this study are summarized in Figure 19, which shows the extraction of 13 metals as a function of pH. The extractant in all cases was 0.1 M HFDMOD–0.05 M TOPO in dodecane, and the aqueous phase contained 0.01 M metal chloride in 1 M CsCl solution.

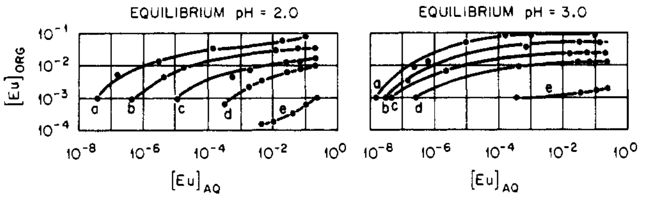

**Figure 16.** Effect of pH on the extraction loading isotherms for europium. Aqueous phase: 0.001–0.2 M $EuCl_3$ in 1 M CsCl. Organic phase: dodecane solutions of HFDMOD–TOPO (2:1) mixtures; HFMOD concentration: (a) 0.4 M, (b) 0.2 M, (c) 0.1 M, (d) 0.05 M, and (e) 0.01 M. Equilibrations made at pH 2 and 3.

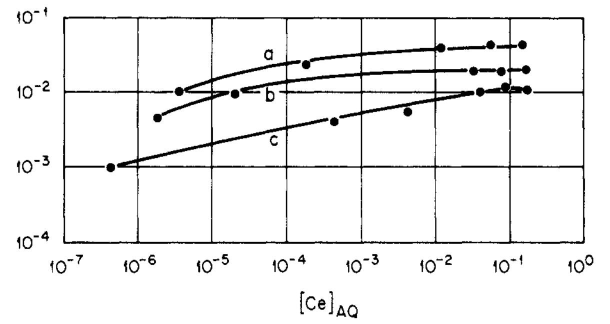

**Figure 17.** Cerium extraction isotherms. Aqueous phase: 0.001–0.2 M $CeCl_3$ in 1 M CsCl at pH 2. Organic phase: dodecane solutions of HFDMOD–TOPO (2:1) mixtures; HFDMOD concentration: (a) 0.4 M, (b) 0.2 M, and (c) 0.1 M.

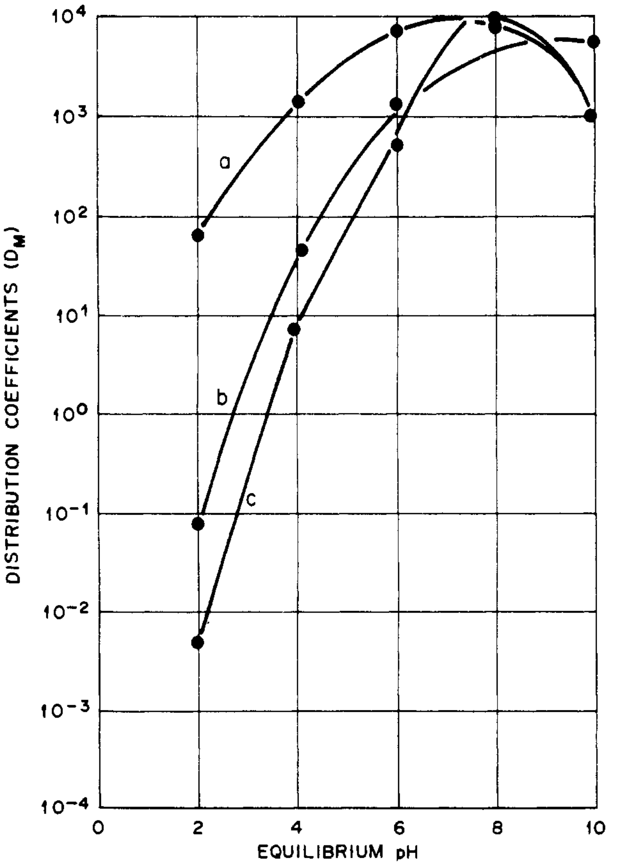

**Figure 18.** Effect of pH on the extraction of copper, cobalt, and nickel. Aqueous phase: 0.01 M solutions of (a) $CuCl_2$, (b) $CoCl_2$, and (c) $NiCl_2$, all in 1 M CsCl. Organic phase: 0.1 M HFDMOD–0.05 M TOPO in dodecane.

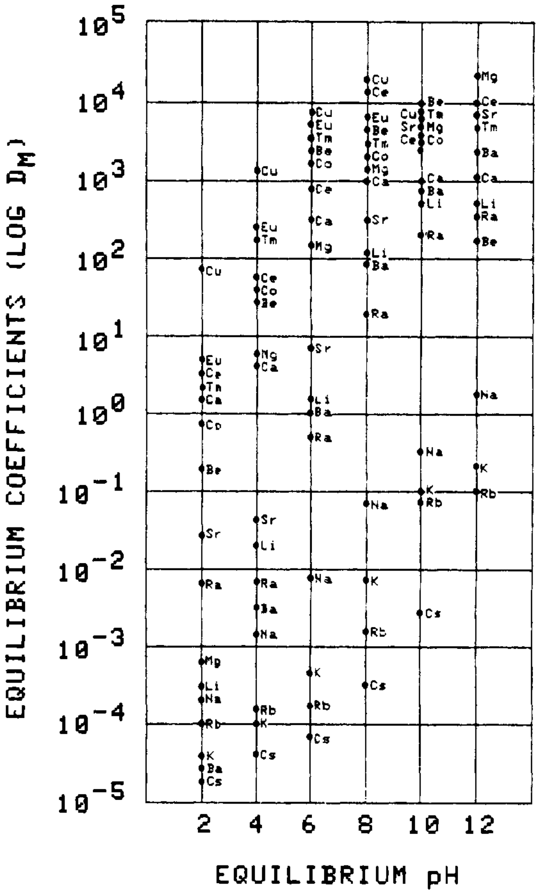

**Figure 19.** Summary of the effect of pH on the extraction of 13 metals. Aqueous phase: 0.01 M metal chloride in 1 M CsCl. Organic phase: 0.1 M HFDMOD–0.05 M TOPO in dodecane.

Although many potential metal separations are suggested by these data and only a few of the commonly used liquid/liquid extraction systems are effective in the near-neutral range, the current price of fluorinated β-diketones would preclude their widespread use in commercial-scale hydrometallurgical separation schemes. The price of these compounds would, however, be expected to decrease if a sizable demand for them developed.

**Registry No.** HFDMOD, 17587-22-3; TOPO, 78-50-2; Li, 7439-93-2; Na, 7440-23-5; K, 7440-09-7; Rb, 7440-17-7; Cs, 7440-46-2; Be, 7440-41-7; Mg, 7439-95-4; Ca, 7440-70-2; Sr, 7440-24-6; Ba, 7440-39-3; Ra, 7440-14-4; Ce, 7440-45-1; Eu, 7440-53-1; Tm, 7440-30-4; Cu, 7440-50-8; Co, 7440-48-4; Ni, 7440-02-0.

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**Supplementary Material Available:** The distribution data shown in Figures 1–19 in tabular form (20 pages). Ordering information is given on any current masthead page.

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# Viscosity of Some *n*-Alkane/1-Chloroalkane Binary Liquid Mixtures

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**In the present work, we have measured the viscosities, densities, and refractive indexes of nine *n*-alkane/1-chloroalkane binary liquid mixtures, at 25 °C. At the same time, the experimental data of all the studied systems have been correlated by using three models given in the literature. These are the equations proposed by Grunberg, McAllister, and Heric to correlate viscosities of binary liquid mixtures.**

## Introduction

The viscosities of liquid mixtures are required for many practical problems concerning heat and mass transport and fluid flow. A summary of the equations proposed for the calculation of liquid mixture viscosities can be seen in the work of Irving (*1*). But as this author points out, the number of systems for which we dispose of some experimental data is relatively small.

In the present work, viscosities of nine binary liquid mixtures, *n*-alkane/1-chloroalkane, at 25.0 °C, have been measured by means of a capillary viscometer. Densities and refractive indexes have also been measured.

## Experimental Section

All the chemicals used were supplied by Merck. They were distilled in a distillation column equivalent to 100 theoretical plates.

Refractive indexes were measured with a RL-PZO (Warszawa) refractometer, and densities were measured with a previously calibrated Anton Paar, Model DMA 35, digital densimeter. All solutions were prepared by weighing the individual compounds. A Mettler balance with an accuracy of ±0.0001 g was used.

The viscosities of the pure compounds and mixtures were measured with eight Ubbelohde modified viscometers, previously calibrated with pure substances for which viscosities and densities were known from the literature. These values are given in Table I.

The viscosity measurements were made in a thermostat controlled to ±0.1 °C.

The following equation was used to calculate the viscosities (*7*, *8*)

$$\eta/\rho = At - B/t \qquad (1)$$

where $\eta$ is the viscosity, $\rho$ is the liquid density, $t$ is its flow time in the viscometer, and $A$ and $B$ are viscometer constants, determined by the calibration fluids.

Table I. Viscosities and Densities of Pure Compounds Used in the Calibrations at 25.0 °C

| compd | $\eta$, cP | ref | $\rho$, g cm$^{-3}$ | ref |
|---|---|---|---|---|
| *n*-pentane | 0.2250 | (*2*) | 0.6214 | (*2*) |
| acetone | 0.3029 | (*3*) | 0.7844 | (*3*) |
| ethyl acetate | 0.4244 | (*4*) | 0.8945 | (*4*) |
| toluene | 0.5526 | (*5*) | 0.8621 | (*5*) |
| chlorobenzene | 0.7580 | (*4*) | 1.1010 | (*4*) |
| *n*-dodecane | 1.363 | (*1*) | 0.7451 | (*1*) |
| butyl alcohol | 2.524 | (*6*) | 0.8056 | (*6*) |
| aniline | 3.770 | (*2*) | 1.0175 | (*2*) |
| hexyl alcohol | 4.592 | (*2*) | 0.8159 | (*2*) |
| octyl alcohol | 7.363 | (*6*) | 0.8211 | (*6*) |

Flow time was taken as an average of 10 measurements.

## Results and Discussion

The measured properties of pure compounds used in this work as well as the experimental values found in the literature appear in Table II.

Experimental results for the nine systems studied are shown in Tables III–XI. All measurements were made at 25.0 ± 0.1 °C.

A very large number of equations has been proposed in the literature for predicting mixture viscosities from pure compounds. The majority of these are purely empirical.

In this paper, a few of the predictive equations of mixture viscosities have been tested.

The Grunberg and Nissan (*9*) equation has been recommended by Irving (*1*) to represent viscosity data for binary mixtures; this empirical expression may be written as

$$\ln \nu_m = x_1 \ln \nu_1 + x_2 \ln \nu_2 + x_1 x_2 G \qquad (2)$$

where $G$ is a characteristic constant of the system.

McAllister (*10*) derived a semitheoretical equation based upon Eyring's absolute reaction rate theory, assuming 3-body or 4-body interactions, depending upon the relative size of the components molecules.

For 3-body interaction the equation derived by him is

$$\ln \nu_m = x_1^3 \ln \nu_1 + 3x_1^2x_2 \ln \nu_{12} + 3x_1x_2^2 \ln \nu_{21} + x_2^3 \times \ln \nu_2 - \ln (x_1 + x_2M_2/M_1) + 3x_1^2x_2 \ln [(2 + M_2/M_1)/3] + 3x_1x_2^2 \ln [(1 + 2M_2/M_1)/3] + x_2^3 \ln (M_2/M_1) \qquad (3)$$

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