

Dialkyl Diethers in Solvent Extraction

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The physical properties, including solvent extraction characteristics of a number of dialkyldiethers are compared. The structure variables are the terminal alkyl groups, the oxygen-oxygen spacing and the carbon to oxygen ratio. The latter two variables are important in fixing the solvent strength. The types of complexes formed with the actinide element nitrates are discussed. Water is important in the complex and a strong acid-dependence of the extraction is indicated.

BECAUSE THE ethers are chemically inert compared to most other carbon-oxygen-hydrogen compounds, they were among the first organic compounds to be studied as solvents for inorganic salts. In an early general study of solvents, Yaffe, Herbert, and MacKintosh (4) examined about 20 ethers, several of which showed appreciable extraction for uranyl nitrate or thorium nitrate from aqueous nitrate solutions. Pentaether (dibutyl tetraethylene glycol) and dibutyl carbitol (dibutyl diethylene glycol) were later examined in more detail (5). Dibutyl carbitol was extensively studied as a process solvent for uranium and plutonium separation and purification (6). Ferraro, Katzin, and Gibson included ethers in their heat of solution study (1). The ethers have not, however, received as detailed study as have many other classes of solvents. Glueckauf and McKay (5) noted that the oxygen-to-carbon ratio was important in determining the solvent strength of ethers. This was confirmed by Googin who examined some diethers of 1,5-pentanediol (4).

The early work in this and other laboratories suggested that the solution complexes formed with ethers are often less well defined than those formed with many other oxygenated compounds, and in some cases are more complicated structurally. Considering the possible structure variations, the ethers comprise a class of compounds which should permit examination of some of the interesting questions which arise concerning the solvation mechanism.

If one imposes practical limitations on vapor pressure, water solubility, and basicity, the polyethers are an excellent choice for a study of this kind. The present work is concerned with the linear diethers which were considered to be the simplest compounds which would retain a strong solvation tendency and provide an interesting range of structure variation.

EXPERIMENTAL

Most of the compounds included in this study were prepared by Gardner at the University of Texas (3). Dibutyl carbitol, dibutyl cellosolve, and dimethoxy ethane were commercial products. They were dried and redistilled at reduced pressure. Peroxides which form after extended storage in the laboratory were removed by passing the ether through an alumina column. The purity of each compound including the water content was established by vapor phase chromatography. All except dipropoxy propane appeared to be more than 99% pure. The latter had about 4 to 5% of an isopropoxy isomer present. Viscosities were measured with Ubbelohde-type viscometers. Calibration was made against Bureau of Standards calibrated instruments and checked with water. The kinetic energy-corrected expression, $\eta/\rho = at + b/t$, was used. Densities were determined with 5-ml. pycnometers.

Solubility was investigated in several ways. The basic method for solubility in water used the cloud point technique.

Concentrations giving cloud point temperatures in the vicinity of 20° to 30° C. were found. From two or three such determinations, linear interpolation was used to give the solubility at 25° C. Water in ether was determined by Karl Fischer titration. Good estimates of both solubilities could be made by comparing the refractive indices of the saturated solutions with that of the pure compound and of water. A gas chromatographic method proved useful on about half of the compounds. A column of polyethylene glycol coated Teflon operated at about 75° C. gave good results on both phases. The various methods gave solubilities which generally agreed within 10-20%. The distribution experiments involving nitric acid and uranyl nitrate involved concentrations at the macroscopic level. Experiments involving the transuranium actinides were carried out at tracer concentrations with Pu²³⁹ and Np²³⁷, respectively, using conventional equilibration and alpha-counting techniques.

PHYSICAL PROPERTIES

The compounds studied, and their more common physical properties, are listed in Table I. The carbon chains are all linear. In the code used here, the three digits refer respectively to the number of carbon atoms in one terminal alkyl group, in the center or alkylene group, and the other terminal group.

The densities and refractive indices increase normally with molecular weight. Viscosity is also primarily a function of molecular weight. For a given molecular weight, there is a slight regular increase in density, refractive index, and viscosity with oxygen-oxygen separation.

Table I. Physical Properties of Diethers

Ether	Density 25° C.	Refractive Index n_D^{25}	Solubility, G./L. at 25° C.		Viscosity, Milli- poises 25° C.
			Ether in H ₂ O	H ₂ O in ether	
121	0.8621	1.3771	∞	∞	4.3
424	0.8337	1.4120	2	6	13.1
133	0.8403	1.3978	26	7	8.2
232	0.8312	1.3955	20	6	7.4
134	0.8378	1.4043	3	7	9.3
141	0.8529	1.3966	140	40	6.8
143	0.8407	1.4041	15	9	9.7
242	0.8335	1.4031	14	11	9.2
144	0.8406	1.4106	3	8	11.9
151	0.8516	1.4048	68	15	8.4
152	0.8433	1.4073	(13)	13	10.0
252	0.8386	1.4095	(8)	9	11.8
154	0.8409	1.4153	2	10	14.6
161	0.8518	1.4110	20	(6)	10.7
162	0.8440	1.4129	5	10	12.6

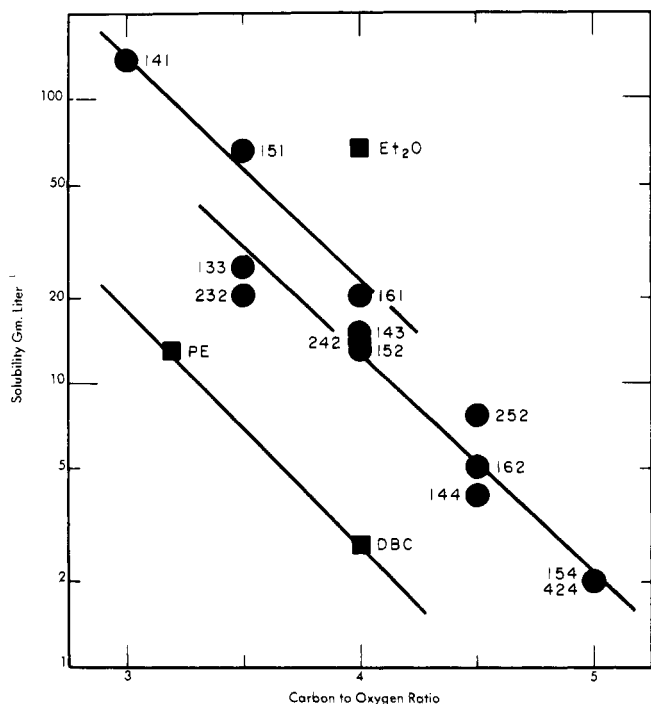


Figure 1. Ether solubility in water, 25° C.

An indication of the interaction with other molecules is seen in the solubility. Figure 1 shows the solubility, in water. Two points are of interest, the decrease in solubility with increase in carbon-to-oxygen ratio or molecular weight and the decrease in solubility of the polyether compared to the monoether having the same carbon-to-oxygen ratio. Two polyethers, dibutyl carbitol and pentaether, are included for comparison. The solubility of water in the organic phase is small, about 0.1 mole of H₂O per mole of ether.

SOLVENT EXTRACTION PROPERTIES

Distribution data were obtained for 2M HNO₃, and for 1M, 0.5M, and 0.3M UO₂(NO₃)₂ and for tracer Pu(IV) from nitrate salted systems. Representative data are shown in Figures 2 and 3, where the distribution ratio, E_x^0 (the ratio of the concentration of solute in the organic phase to that in the aqueous phase) is compared for compounds with identical terminal groups, with the same center chain, and finally with the same carbon-to-oxygen ratio. The carbon-to-oxygen ratio is an important parameter, and must be low for a high distribution ratio. A second parameter is the spacing of the two oxygen atoms. Figure 3 shows that the extraction ability increases rather uniformly with spacing, indicating the absence of intramolecular cooperation. The increase in E_x^0 with oxygen-oxygen separation is in part a result of the disappearance of the inductive effect of one oxygen on the other. This effect, however, should disappear at distances greater than about three carbon atoms.

For the extraction of uranyl nitrate, the nitrate concentration dependence indicates the species UO₂(NO₃)₂·(H₂O)_n

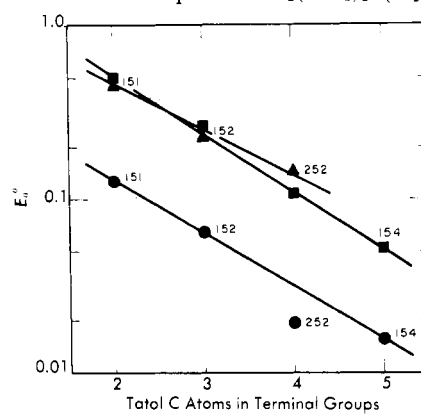
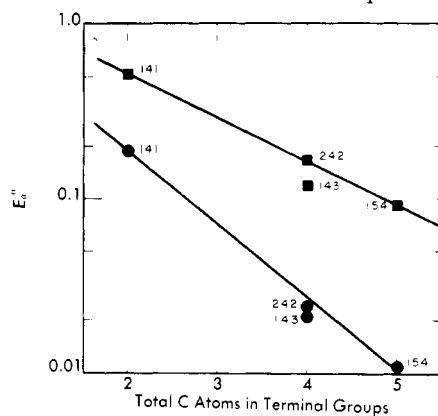
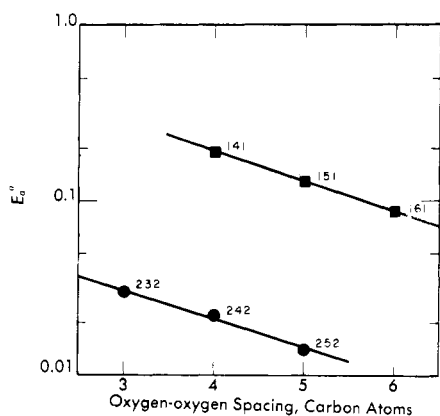


Figure 2. Distribution of nitric acid and uranyl nitrate between ethers and water, 25° C.

In aqueous phase

- ▲ 2MHNO₃
- 0.5MUO₂(NO₃)₂
- 1.0M

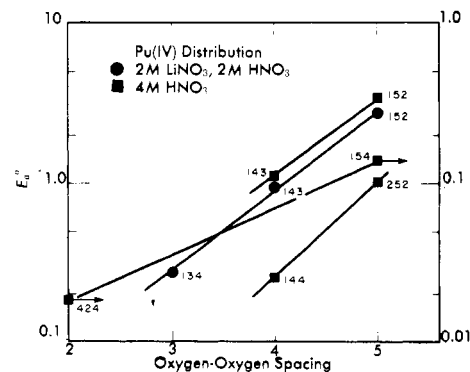
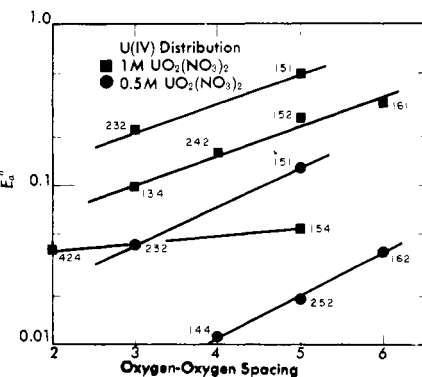
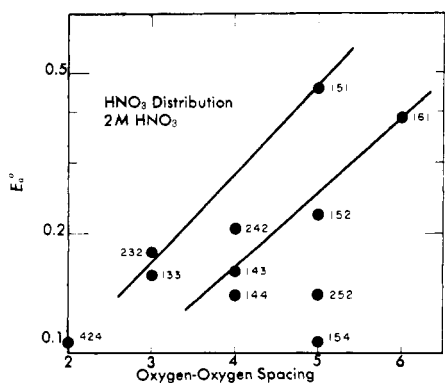


Figure 3. Effect of O-O spacing on distribution, 25° C.
(Lines drawn through points of equal carbon to oxygen ratio)

as expected. Dilution of the ether with a nonpolar solvent does not lead to an unequivocal assignment of the number of ether molecules involved. With solutions of up to 70% diethoxybutane in benzene, however, the dissolvate was indicated.

The solubility limit of uranyl nitrate in the diethers corresponds to about one uranyl nitrate to two ether molecules forming a very viscous solution. Water is part of the complex, and from two to four molecules accompany each uranyl to the organic phase. From the shift of the infrared OH-stretching band, from 3520 cm.^{-1} to 3170 cm.^{-1} , as uranyl nitrate is added to the water-saturated ether, and from the downfield nuclear magnetic resonance shift of the water proton as a function of uranyl nitrate concentration, it is considered likely that the water is bound to the uranyl group. To examine this complex further, anhydrous uranyl nitrate was prepared from UO_3 and liquid NO_2 . The excess NO_2 was removed under vacuum at 160°C . When dry 144 ether was distilled onto the salt at -78°C . and allowed to warm slowly, a vigorous reaction occurred producing the solid etherate. This was not soluble in the ether phase until a few drops of water were added.

The important role of water in solvent extraction with ethers has been discussed by Ryskin, Shvedov, and Solovéva (7). Much earlier, Gardner, McKay, and Warner (2) had investigated the water content of dibutyl carbitol, diethylether, and several ketones and found that the water accompanying uranyl nitrate was a function of both the specific solvent and the thermodynamic water activity of the system.

The effect of acid on the extraction of actinide nitrates is very marked, especially for the IV oxidation state. This is illustrated by data for Pu(IV) in Figure 4. In this case, extraction appears to be by ion pair formation involving $\text{Pu}(\text{NO}_3)_6^{-2}$. With the VI state—e.g., uranyl—more than one species may extract. A discussion of the distribution studies and the spectrophotometric investigation of the actinide species in the ether solutions has been undertaken.

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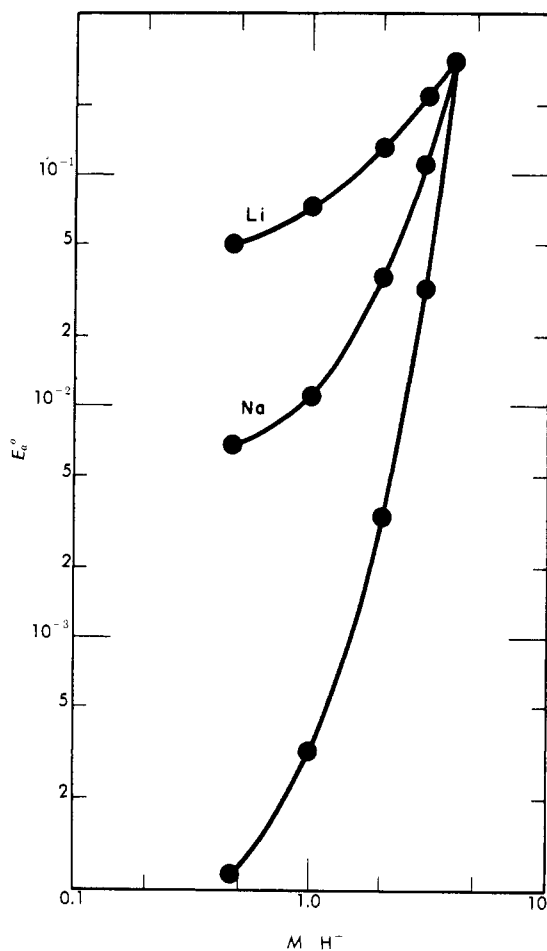


Figure 4. Effect of acid on Pu(IV) distribution, 25°C .

(Lithium and sodium data at constant NO_3^- concentration)