Both $(C_4F_9)_3N$ and $(C_4H_9)_2O$ give low conductivities, which is evidence of the formation in the solutions of few ions. As the only expected means of the production of ions from these solutes requires that they function as bases, it must be concluded that in this solvent they are extremely weak bases. In other words, the extent of the following reactions must be small

$$(C_4F_9)_3N + CF_3CO_2H \rightleftarrows (C_4F_9)_3NH^+ + CF_3CO_2^-$$
$$(C_4H_9)_2O + CF_3CO_2H \rightleftarrows (C_4H_9)_2OH^+ + CF_3CO_2^-$$

The potassium salt of the acid gives a moderate conductivity to its solution in the acid. $(C_4H_9)_3N$ in contrast to its fluorocarbon analog gives a relatively high conductance showing evidence of considerable basicity as per the reaction

$$(C_4H_9)_3N + CF_3CO_2H \rightleftarrows (C_4H_9)_3NH^+ + CF_3CO_2^-$$

There is also some evidence of the crystallization of the indicated salt, $(C_4H_9)_3NHCF_3CO_2$, as it was noticed on dissolving the amine in the acid that a white solid was first formed. This dissolved in larger quantities of the solvent on mixing.

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The Solubility of Organic Solids in Fluorocarbon Derivatives

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The solubility of naphthalene, *p*-nitrotoluene and hexachlorethane were determined in a fluorocarbon oxide, $(C_4F_9)_2O$ and a fluorocarbon nitride, $(C_3F_7)_3N$ at 25 and at 35°. Consistent with the concept of interpenetration as postulated by Simons and Dunlap, the first two substances were far below ideally soluble whereas the last was more nearly so. The temperature coefficient of solubility gives a heat of solution greater than the ideal heat of solution by an amount which gives a measure of the heat of interpenetration. The two solvents do not differ appreciably in solubility properties.

The demonstrated failure to even approach ideal solubility of fluorocarbons and hydrocarbons as illustrated in a recent paper,[2] increases the interest in the solubility properties of fluorocarbons and their derivatives. The availability of $(C_4F_9)_2O$ and $(C_3F_7)_3N$ from the operation of the electrochemical process[3] made possible the determination of the solubility of several organic solids in these liquids.

Materials and Apparatus.—Naphthalene, hexachlorethane and *p*-nitrotoluene were obtained as chemically pure reagents and were further purified by two recrystallizations from ethanol. The fluorocarbon derivatives were purified by distillation; the $(C_4F_9)_2O$ was taken from a cut boiling between 100.7 and 101.0°, and the $(C_3F_7)_3N$ was taken from a cut boiling between 128.1–128.5°.

The solubility vessel was a tube about 20 mm. in diameter about 8 cm. long with a sintered glass disk sealed in the center. The ends were drawn down and attached to 8 mm. ground glass joints. The female portions of these joints served as caps. With the 20-mm. tube vertical, the tube to the lower joint was bent 180° to bring the two joints parallel and level.

Procedure.—A weighed amount of solute and solvent was placed in the lower portion of the solubility vessels. This was then shaken in a constant temperature bath for 48 hours. The vessel was now inverted to the bath and the saturated solutions withdrawn by suction. The vessel with the undissolved solute was then weighed. As both solute and solvent are volatile, there is an uncertainty whether the weighed undissolved solute contains unevaporated solvent or whether some of the solute has evaporated. To obtain a reliable reproducible value, the following procedure was employed.

The first weight was taken as soon as the excess liquid had been removed. Air was then drawn through the vessel for a measured period of time (30 seconds). The vessel was then again weighed. This was repeated some ten times. By plotting the weight of the vessel against the time of air passage under a fixed set of conditions and extrapolating the linear portion of the curve back to zero time, a reliable reproducible value was obtained. The loss of weight for the first few measurements represented the loss of both absorbed solvent and evaporated solute. After the solvent had been lost, the loss of weight represented the evaporation of the solute under a fixed set of conditions for a determined period of time. This gave a straight line on the graph, the extrapolation of which to zero time gave the weight of the undissolved solute uncontaminated by absorbed solvent. From this weight, solubilities were readily calculated.

Results.—In Table I are shown the results of the measurements. The ideal solubility was calculated using the equation

$$\log_{10}\frac{1}{N_2} = (\bar{H}_2 - H_2)\,\frac{T_m - T}{4.575T_mT}$$

where

N_2 = ideal solubility in mole fraction
$\bar{H}_2 - H_2$ = difference in heat content of the solute in solution and as pure solid
T_m = melting point of solute in °K.
T = temperature in °K. at which solubility is taken

For naphthalene, the melting point is taken as 80.2° and $\bar{H}_2 - H_2$ in cal. per mole as the heat of fusion[4] 4580. For *p*-nitrotoluene, the melting point is taken as 51.8 and the heat of fusion[5] 4010. For hexachloroethane, the melting point is taken as 186.8 and $\bar{H}_2 - H_2$ as the sum of the heat of fusion[6] and the heat of transition[7] 4900.

Conclusions.—As can be readily seen from the table, the solubilities of both naphthalene and *p*-nitrotoluene are far below ideal at both temperatures in both fluorocarbon solvents. For comparison, the solubility of naphthalene in dibutyl ether was obtained from extrapolation of the data of Bennet and Philip.[8] At 25° it was 0.190 mole

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TABLE I

SOLUBILITIES IN FLUOROCARBON DERIVATIVES

		Solubility, g./100, g. solvent at 25°		Solubility, mole fraction at 25°		Solubility, g./100 g. solvent at 35°		Solubility, mole fraction at 35°	
Solute	Solvent	Measured	Average	Measured	Ideal	Measured	Average	Measured	Ideal
$C_{10}H_8$	$(C_4F_9)_2O$	0.0726	0.0730	0.00257	0.299	0.116	0.114	0.00402	0.384
		.0733				.112			
$C_{10}H_8$	$(C_3F_7)_3N$	.0774	.0740	.00300	.299	.115	.114	.00461	.384
		.0723				.113			
		.0723							
$C_7H_7NO_2$	$(C_4F_9)_2O$	.0818	.0812	.00268	.571	.123	.121	.00399	.712
		.0806				.119			
$C_7H_7NO_2$	$(C_3F_7)_3N$	.0850	.0850	.00323	.571	.134	.137	.00517	.712
		.0850				.140			
C_2Cl_6	$(C_4F_9)_2O$	.474	.474	.00901	.0526	.781	.781	.0148	.0709
		.475				.780			
C_2Cl_6	$(C_3F_7)_3N$	.516	.508	.0111	.0526	.743	.742	.0160	.0709
		.509				.741			
		.525							
		.480							

fraction and at 35° 0.304. This is much closer to the ideal figure despite the fact that dibutyl ether has a dipole moment whereas neither naphthalene or $(C_4F_9)_2O$ have an appreciable moment. From this, one might expect naphthalene to be more ideally soluble in $(C_4F_9)_2O$ than in $(C_4H_9)_2O$. The reverse is found. This can be explained using the concept of interpenetration.[2]

The solubility of nitrobenzene falls far below the ideal in both fluorocarbon derivatives. This is due primarily to interpenetration but also to the fact that it is a dipolar material, differing in this respect from the fluorocarbon derivatives.

Hexachloroethane comes much more nearly being ideally soluble in the fluorocarbon derivatives, probably because of the lack of hydrogen atoms in the molecule resulting in little interpenetration between the solute molecules.

From the difference in solubility at two temperatures, the heat of solutions was calculated. For naphthalene in $(C_4F_9)_2O$ this was 8150 cal. per mole and in $(C_3F_7)_3N$ was 7850. This is compared with the ideal value of 4580. For *p*-nitrotoluene in $(C_4F_9)_2O$ this was 7320 and in $(C_3F_7)_3N$ was 8620. This is compared with the ideal value of 4010. The excess of these values above the ideal gives a rough measure of the heat of interpenetration.

As can be seen from the figures, there appears to be little difference in solubility of these substances in the fluorocarbon oxide or fluorocarbon nitride.

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[CONTRIBUTION 197, INSTITUTE FOR ATOMIC RESEARCH AND THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Conductances, Transference Numbers and Activity Coefficients of Aqueous Solutions of Some Rare Earth Halides at 25°[1]

BY F. H. SPEDDING AND I. S. YAFFE[2]

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The equivalent conductances, cation transference numbers and activity coefficients at 25° of aqueous solutions of $LaBr_3$, $PrBr_3$, $NdBr_3$, $GdBr_3$, $HoBr_3$, $ErBr_3$ and $GdCl_3$ have been determined for concentrations up to 0.1 *N*. Also the equivalent conductances of $NdCl_3$ have been redetermined. The Onsager law for conductance is obeyed for all halides studied up to a concentration of approximately 0.001 *N*. The transference numbers, determined by the moving boundary method, were found to be linear functions of the square root of the concentration; the slopes of these functions differed by a factor of approximately one-fifth from those predicted by the Onsager law. The activity coefficients, determined by the use of concentration cells with transference, were found to agree with those predicted by the Debye–Hückel law providing that the experimentally determined å. values were used to calculate the theoretical coefficients. All data reported are correlated with data on the rare earth chlorides previously reported.

Introduction

This paper is the fourth in a series concerning the electrolytic behavior of aqueous solutions of rare earth compounds. The earlier papers[3–5] have presented data on the conductances, transference numbers and activity coefficients of several rare earth chlorides. This paper extends this investigation to other rare earth halides, particularly the bromides, and attempts to correlate the data between the two series of halides. As discussed in the first article of this series,[3] such information should be of considerable value in the study of the various factors which enter into the modern theories of electrolytic behavior.

Experimental

Except as specifically discussed below, the experimental

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[1] Work was performed in the Ames Laboratory of the Atomic Energy Commission.

[2] Taken in part from the Ph.D. thesis submitted to the graduate faculty of Iowa State College, 1952.

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