when in competition with OH in the same molecule. (6) The C—H bond does not readily break at room temperature to form dissociatively adsorbed hydrocarbons. (7) Chemisorption of oxygen does produce the V=O species.

This behavior pattern suggests that in the catalytic interaction of alcohols, aldehydes, or ketones with vanadium surfaces attachment of the reacting complex to the surface is more likely to be through an oxygen atom than a carbon atom.

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OAK RIDGE, TENNESSEE 37830

Solubility of Cerium Trifluoride in Molten Mixtures of Lithium, Beryllium, and Thorium Fluorides[1,2]

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The solubility of CeF_3 in eight $LiF–BeF_2–ThF_4$ and four $LiF–ThF_4$ mixtures was determined between 600 and 800° by radiochemical and wet chemical methods. Sintered copper filter sticks were used to remove filtered samples of the molten fluoride mixtures that were saturated with CeF_3 tagged with ^{144}Ce. The data are represented by straight lines in log (solubility) *vs.* $1/T$ plots, the slopes of which gave heats of solution. These data, together with published values for the solubility of CeF_3 in $LiF–BeF_2$ mixtures, permitted formulation of relationships between solubility and solvent composition that could be rationalized in terms of charge and size of the ions involved.

Introduction

The molten salt reactor experiment has been in operation at Oak Ridge National Laboratory for several years and has fully demonstrated the feasibility of the molten fluoride reactor concept. The initial fuel loading for the reactor had the composition 65 mol % LiF-29 mol % BeF_2-5 mol % ZrF_4-0.9 mol % UF_4. Attention is now being directed to development of molten salt breeder reactors. Although the fuel composition for these reactors has not been fixed, the solvent for the fissionable species is expected to be a mixture of LiF, BeF_2, and ThF_4. A phase diagram for this system[4] was developed at ORNL about 10 years ago. Interest in the solubility of CeF_3 in such mixtures results, in part, from the fact that rare earth trifluorides will be produced by the fission process. In a molten salt breeder reactor the concentration of these fission products is expected to be maintained far below their solubility limit by continuously processing the fuel. The principal reason for the present interest in CeF_3 solubility is that PuF_3 may be one of the fissionable species used for the initial fueling of molten salt breeder reactors. A comparison of data on the solubility of CeF_3[5] and PuF_3[6] in $LiF–BeF_2$ mixtures (Figure 1) suggests that CeF_3 can serve as a convenient stand-in for PuF_3 in a systematic study of solubility behavior in the system $LiF–BeF_2–ThF_4$. A limited number of PuF_3 solubility measurements may be made in the future to confirm predictions based on the CeF_3 results. A description of the technique used in this investigation and part of the data reported here were included in an ORNL report.[7]

Experimental Section

The reaction vessel used (Figure 2) was a welded cylindrical nickel container with an internal diameter of 1.5 in. and a depth of 6.5 in. A 7-in. secion of 0.5-in. i.d. nickel pipe was welded to the lid and was closed at the top with a stainless steel ball valve having an internal clearance of 0.5 in. An additional opening in the lid accommodated a thermocouple well of 0.25-in. thin-wall nickel tubing closed at the lower end which extended to within 0.125 in. of the bottom. The remaining lid opening held a 0.25-in. dip leg of heavy-wall nickel tubing extending to within 0.25 in. of the vessel bottom to facilitate agitation and purification of the melt by admitting gases beneath the melt surface.

The vessel was mounted vertically in a 3-in. tube furnace whose temperature was regulated by means of a chromel–alumel thermocouple placed between the furnace wall and the vessel and by a high-sensitivity bucking-circuit controller. Melt temperatures were determined by means of a second chromel–alumel thermocouple in the thermocouple well and a Leeds and Northrup Type K-2 potentiometer.

Copper filter sticks of the type shown in Figure 2 were used to take filtered samples of the molten fluoride mixtures. The sintered copper filter material had a nominal pore size of 0.0004 in. The 0.125-in. tubing of these filter sticks slipped through a Teflon gland made to fit a 0.5-in. Swagelok tubing connector. A length of soft rubber tubing which fitted over the free end of

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

(2) Paper presented before the Division of Nuclear Chemistry and Technology at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969.

(3) Oak Ridge Associated Universities summer participant from St. Cloud State College, St. Cloud, Minn.

(4) R. E. Thoma, H. Insley, H. A. Friedman, and C. F. Weaver, *J. Phys. Chem.*, **64**, 865 (1960).

(5) W. T. Ward, R. A. Strehlow, W. R. Grimes, and G. M. Watson, "Solubility Relations among Rare Earth Fluorides in Selected Molten Fluoride Solvents," Report ORNL-2749, Oak Ridge National Laboratory, Oak Ridge, Tenn., Oct 1959.

(6) C. J. Barton, *J. Phys. Chem.*, **64**, 306 (1960).

(7) J. A. Fredricksen, L. O. Gilpatrick, and C. J. Barton, "Solubility of Cerium Trifluoride in Molten Mixtures of LiF, BeF_2, and ThF_4," Report ORNL-TM-2335, Oak Ridge National Laboratory, Oak Ridge, Tenn., Jan 1969.

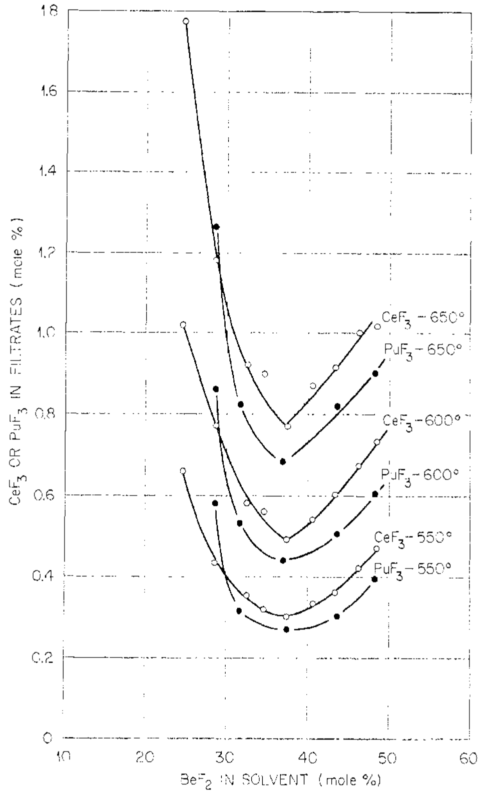

Figure 1.—Comparison of CeF_3 and PuF_3 solubility in LiF–BeF_2 solvents.

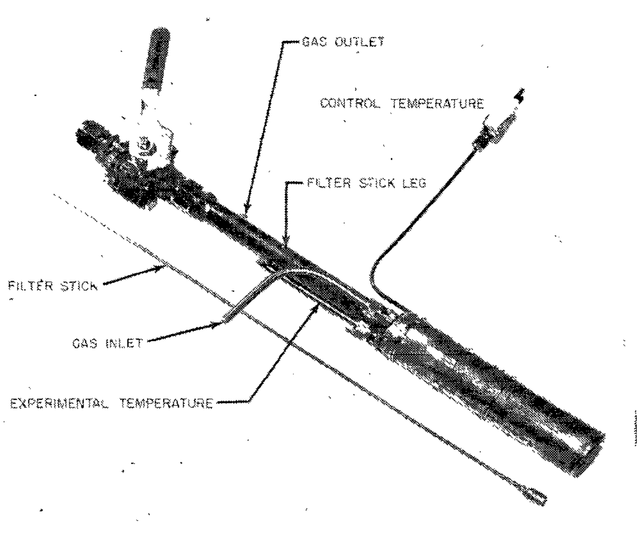

Figure 2.—Fused-salt vessel and filter stick for solubility measurements.

the filter stick could be connected to either a vacuum pump or a helium source.

Some of the solvent mixtures had been previously purified by other ORNL workers and others were prepared by suitable additions to the purified mixtures. All received a purification treatment after melting consisting of sparging with an H_2–HF mixture followed by H_2 alone to reduce NiF_2 introduced by the HF treatment. Tagged CeF_3 was prepared by mixing 10 mCi of ^{144}Ce with 308 g of hydrated cerium chloride, precipitating CeF_3 by addition of ammonium bifluoride, followed by filtering, washing, and drying.

After the purification procedure was completed, the mixture containing sufficient CeF_3 to exceed the expected maximum solubility was allowed to equilibrate for about 1 hr with a slow flow of helium agitating the melt. A sample of the saturated melt was withdrawn by means of the copper filter stick. After cooling to room temperature, the filter was cut open in a glove box and the salt was removed and ground. Fifty-milligram portions were weighed and placed in plastic vials for counting on a sodium iodide crystal attached to a multichannel analyzer. The sample counts were converted into CeF_3 percentages by mixing accurately weighed amounts of the tagged CeF_3 with

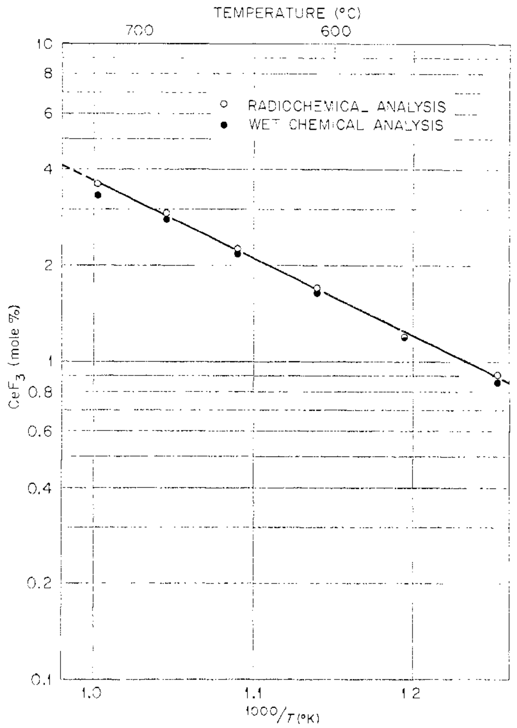

Figure 3.—Solubility of CeF_3 in 72 mol % LiF–16 mol % BeF_2–12 mol % ThF_4.

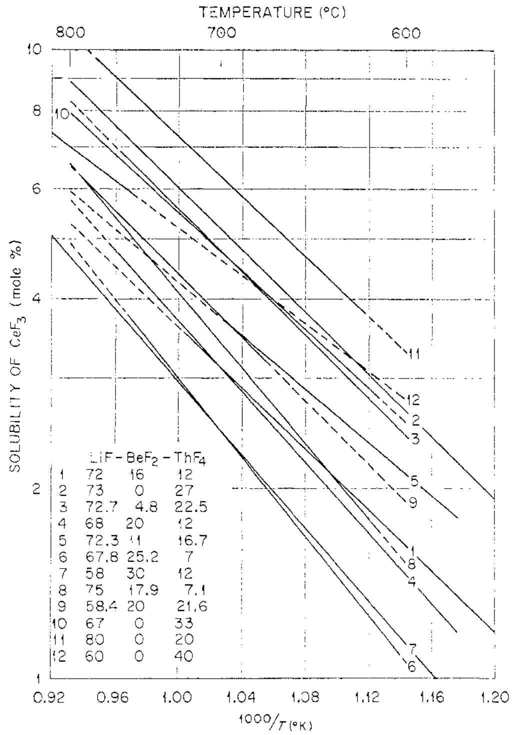

Figure 4.—Best-value plots of the solubility of CeF_3 in LiF–ThF_4 and LiF–BeF_2–ThF_4 solvents.

TABLE I

SOLUBILITIES AND APPARENT HEATS OF SOLUTION OF CeF_3 IN MIXTURES OF LiF, BeF_2, AND ThF_4

Mixture no.	Salt compn, mol %			CeF_3 solubility and std error of fit (95% confidence level), mol %		Apparent heat of soln and std dev, cal/mol	u = [Th]/[Th + Be]	b = [free LiF], mol %
	LiF	BeF_2	ThF_4	600°	800°			
1	72	16	12	1.62 ± 0.03	(5.28)[a] ± 0.11	11,070 ± 220	0.428	+4
2	73	0	27	2.65 ± 0.05	8.90 ± 0.18	11,360 ± 260	1.000	(−7)[d]
3	72.7	4.8	22.5	22.43 ± 0.05	(8.25)[a] ± 0.17	11,470 ± 390	0.824	(−4)[d]
4	68	20	12	1.45 ± 0.03	(5.78)[a] ± 0.12	12,890 ± 400	0.375	(−8)[d]
5	72.3	11.0	16.7	2.10 ± 0.04	(5.93)[a] ± 0.12	9,670 ± 560	0.603	0
6	67.8	25.2	7.0	(1.06)[b] ± 0.02	(4.92)[a] ± 0.10	14,440 ± 650	0.217	(−4)[d]
7	58	30	12	1.13 ± 0.02	4.43 ± 0.10	13,650 ± 550	0.286	(−38)[d]
8	75	17.9	7.1	(1.52)[b] ± 0.03	(6.59)[a] ± 0.13	13,720 ± 350	0.284	+18
9	58.4	20.0	21.6	(1.90)[b] ± 0.04	6.50 ± 0.14	11,570 ± 750	0.519	(−46)[d]
10	67	0	33	(2.54)[b] ± 0.05	7.91 ± 0.17	10,660 ± 600	1.000	(−32)[d]
11	80	0	20	(3.30)[b] ± 0.07	(10.07)[a] ± 0.21	10,840 ± 410	1.000	+20
12	60	0	40	(2.77)[b] ± 0.06	7.00 ± 0.14	11,210 ± 640	1.000	(−60)[d]
13	66.7	33.3	0	(0.60)[c]	(3.7)[c]	17,500	0.0	0
14	72.7	27.3	0	(0.95)[c]	(5.7)[c]	16,700	0.0	+18

[a] Extrapolated from our values to higher temperature. [b] Extrapolated from our values to lower temperature. [c] Interpolated from literature values[5] and extrapolated to 800°. [d] Negative values of "free" LiF correspond to excess BeF_2 and/or ThF_4 over Li_2BeF_4 and/or Li_3ThF_7, *i.e.*, to acidic compositions in the sense of the Lewis acid–base concept. In this acidic range CeF_3 solubility changes little with composition (see Figures 1 and 5).

sufficient salt solute to give a 50-mg total and counting these standards with the same geometry used for the samples.

Portions of each sample were also submitted for wet chemical analysis by members of the ORNL Analytical Chemistry Division.

Results

A plot of the data obtained with one solvent is presented in Figure 3 in terms of mole per cent CeF_3 *vs.* the reciprocal of the absolute temperature. Figure 4 shows the best-value plots for most of the solvents studied to date, including eight LiF–BeF_2–ThF_4 mixtures and three LiF–ThF_4 binary mixtures. The data are summarized in Table I together with apparent heats of solution. Also included in Table I are data derived from earlier work at this laboratory.[5] A plot of the data for the LiF–ThF_4 solvents (Figure 5) shows the relation between CeF_3 solubility and solvent composition in the range of solvent compositions that could be conveniently studied. Data[5] on the solubility of CeF_3 in LiF–BeF_2 mixtures at one temperature are shown for comparison. The value for the solubility of CeF_3 in LiF at 800° was obtained from the LiF–CeF_3 phase diagram studied earlier at this laboratory.[8] It was necessary to extrapolate data from the phase diagram below the eutectic temperature (755°) in order to obtain the hypothetical solubility at 700 and 600°.

Discussion

Figure 3 shows that there was very good agreement between the radiochemical results and the wet chemical analyses in this experiment (mixture no. 1, Table I). The agreement was not always this good and the intercomparison often resulted in rechecking both types of analyses. The application of a least-squares computer program to both types of data gave the best-value plots shown in Figure 4 and the solubility values listed in Table I, together with the calculated standard error of fit of the data at the 95% confidence level. The standard deviation of the heat of solution in Table I is a measure of the uncertainty in the slope of the lines in Figure 4 which shows the temperature range of the measurements. In applying least-squares analyses to the data from the various experiments, we excluded solubility values where the solvent was obviously not saturated and measurements were made below the liquidus temperature of the solvent. This procedure reduced the number of useful data points to 8 or 9 for several experiments.

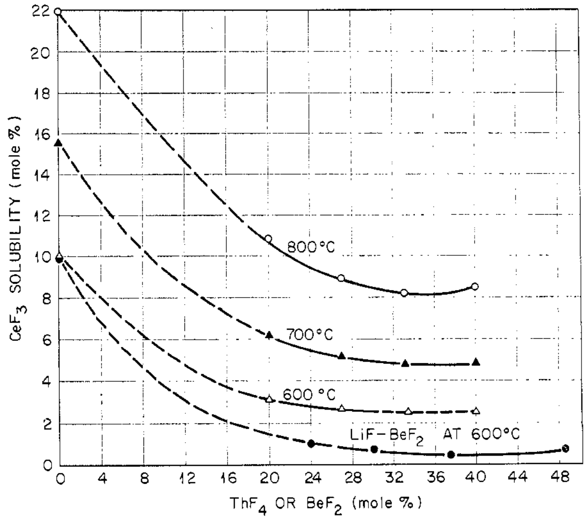

Figure 5.—Solubility of CeF_3 in LiF–ThF_4 and LiF–BeF_2 mixtures.

Preliminary attempts[7] to relate the solubility of CeF_3 in LiF–BeF_2–ThF_4 mixtures to solvent composition gave unsatisfactory results. We demonstrate here that the molar ratio of ThF_4 to BeF_2 is the dominant factor for the binary and ternary mixtures listed in Table I. The smooth lines of Figure 6 (where the compositions in Table I are identified by mixture number) show the nearly linear dependence of the solubility of CeF_3 $\{s = 100[\mathrm{Ce}]/[\mathrm{Ce} + \mathrm{Li} + \mathrm{Be} +$

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(8) C. J. Barton, *et al.*, "Phase Diagrams of Nuclear Reactor Materials," R. E. Thoma, Ed., Report ORNL-2548, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1959.

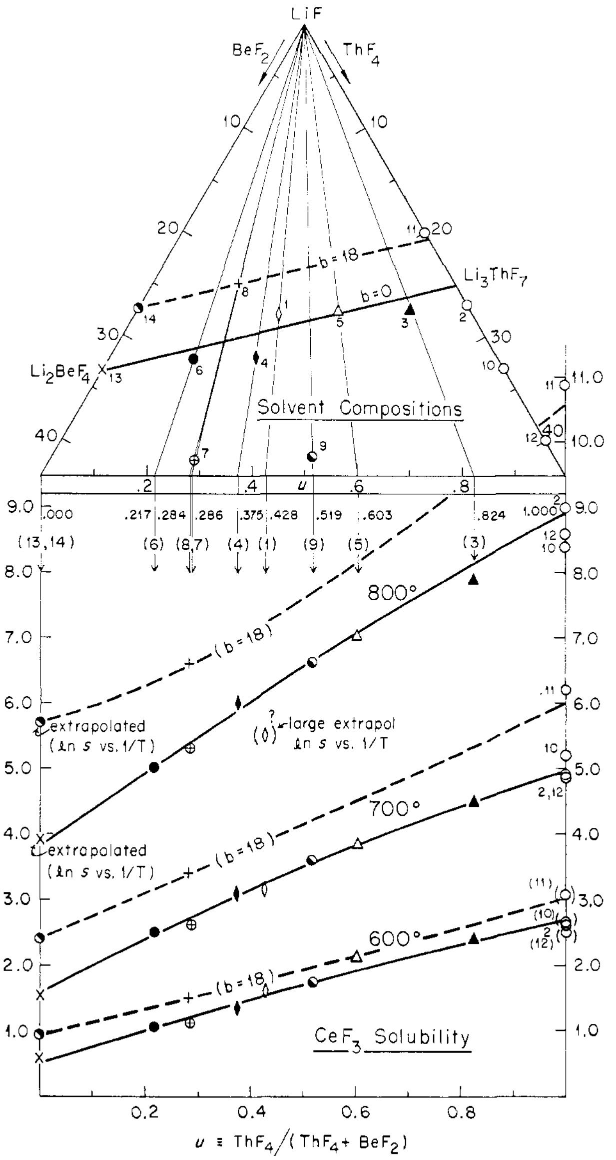

Figure 6.—Correlation of CeF_3 solubility with solvent composition. Smooth lines depict solubility for compositions with $b = [LiF - 2BeF_2 - 3ThF_4] \leq 0$ (no "free" LiF). Dotted lines show solubility for $b = 18$ (18 mol % "free" LiF).

Th]} on u (= [Th]/[Th + Be]) in accordance with the equations

$$s(600°) = 0.50 + 2.60u - 0.40u^2$$

$$s(700°) = 1.60 + 4.23u - 0.88u^2$$

$$s(800°) = 3.80 + 5.80u - 0.80u^2$$

The only significant deviation among the ternary mixtures, $\Delta s = +0.30$, $+0.70$, and $+1.20$ mol % CeF_3 at 600, 700, and 800°, respectively, occurred for mixture 8, 75.0 mol % LiF–17.9 mol % BeF_2–7.1 mol % ThF_4, with a "free" LiF content, $b = [LiF - 2BeF_2 - 3ThF_4]$, of 18 mol %. This definition of b represents the algebraic form for the assumption made here that BeF_2 exists in the molten mixtures as BeF_4^{2-} and ThF_4 as ThF_7^{3-} ions. This assumption has proved useful to other investigators at this laboratory. The significance of b as a secondary parameter is further demonstrated by the similarity of the Δs values listed above with $\Delta s = +0.40$, $+0.80$, and $+1.70$ mol % CeF_3 at 600, 700, and 800° for binary mixture 14, 72.7 mol % LiF–27.3 mol % BeF_2, having the same "free" LiF content, $b = 18$ mol %.

An attempt is made here to rationalize the observed dependence of the CeF_3 solubility in mixtures of LiF, BeF_2, and ThF_4 on solvent composition. The dependence reflects the significance of the greater availability of F^- ions for interaction with Ce^{3+} in melts richer in LiF. The significance of such interaction was indicated by the considerable, negative deviation from ideality in the LiF–CeF_3 phase diagram.[8] Values, measured or extrapolated, for the CeF_3 concentrations of the CeF_3 liquidus at 600–800° *exceed* those estimated from the known entropy of fusion of CeF_3 (7.62 cal deg^{-1} mol^{-1} at the melting point of CeF_3) by factors of 4–2. On the other hand, in LiF–BeF_2 mixtures containing 25–50 mol % BeF_2, the solubility is very much *smaller* than ideal. This positive deviation from ideality can be attributed to the much weaker interionic forces between the singly charged Li^+ ions and the relatively large BeF_4^{2-} anions (*cf.* also the low melting points in the LiF–BeF_2 system) as compared with the forces between the triply charged Ce^{3+} and the relatively small F^- ions. Although molten Li_3ThF_7 is assumed here to contain even larger complex anions, ThF_7^{3-}, the solubility of CeF_3 in this solvent is intermediate between that in LiF and Li_2BeF_4. This apparent anomaly can be attributed to the fact that the Ce^{3+} ion, with a charge-to-size ratio, or "ionic potential," $z/r \cong 3$, competes much more successfully with Th^{4+} ($z/r \cong 4$) than with Be^{2+} ($z/r \cong 6$) for interaction with F^- ions.

Several ternary compositions have negative values of "free" LiF, but they fit the correlation shown in the bottom part of Figure 6. This may be explained by reference to Figure 5 which shows comparatively little change in CeF_3 solubility in LiF–ThF_4 mixtures in the range 25–40 mol % ThF_4 and only slightly greater change in LiF–BeF_2 solvents in the 33–40 mol % range where negative values of "free" LiF are calculated for the binary solvents. The small change in CeF_3 solubility in this range may be contrasted with the steeply ascending curves for both binary solvents containing "free" LiF as previously defined and with the large difference in solubility in LiF–BeF_2 solvents and that in LiF–ThF_4 compositions.

Finally, we compare apparent heats of solutions of CeF_3, ΔH_{soln}, in the various solvents (Table I). Those given for LiF–BeF_2 mixtures, approximately 17 kcal/mol, exceed considerably the heat of fusion of CeF_3, ΔH_{fusion}, which may be estimated from the value[9] 13.2 kcal at the melting point as 10–12 kcal for temperatures of 600–800°. On the other hand, on substitution of ThF_4 for BeF_2 (Figure 7) the heat of solution drops to the vicinity of the heat of fusion, *i.e.*, 11 kcal, in line with the considerations of the preceding paragraph on

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(9) K. K. Kelley, Bureau of Mines Bulletin 584, U. S. Government Printing Office, Washington, D. C., 1960, p 54; A. U. Christensen, unpublished work.

the smaller deviation from ideality. A smooth curve fits the data for the ternary mixtures except for mixtures 1 and 5, Table I. The calculated heats of solution for these solvents appear to be rather low. It should be noted that if the indicated error in solubility at the high temperature is in one direction and the error at the low end of the range has the opposite sign, a considerable change in the apparent heat of solution would result.

The values shown in Figure 7 for the heat of solution of CeF_3 in the two LiF–BeF_2 mixtures listed in Table I are higher than those calculated for LiF–BeF_2 solvents with higher BeF_2 concentrations[5] and are much greater than more recent values[10] for the heats of solution of NdF_3 and SmF_3 in LiF–BeF_2 (66–34 mol %), 11.5 and 10.5 kcal/mol, respectively. Consequently, the shape of the curve in the low-ThF_4 end of Figure 7 is not firmly established.

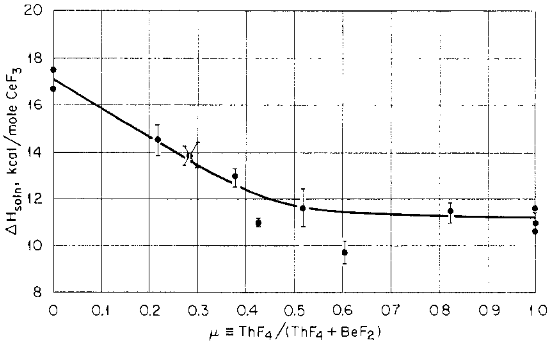

Figure 7.—Correlation of apparent heat of solution with solvent composition.

Acknowledgment.—The authors thank J. H. Shaffer and coworkers for supplying purified solvent compositions and members of the ORNL Analytical Chemistry Division under the supervision of W. R. Laing and L. J. Brady for performing wet chemical analyses.

[10] F. A. Doss, F. F. Blankenship, and J. H. Shaffer, Report ORNL-4119, Oak Ridge National Laboratory, Oak Ridge, Tenn., July 1967, p 144.

CONTRIBUTION FROM ROCKETDYNE, A DIVISION OF NORTH AMERICAN ROCKWELL CORPORATION, CANOGA PARK, CALIFORNIA 91304

Chlorine Monofluoride. Reactions with Sulfur Oxides

BY CARL J. SCHACK AND RICHARD D. WILSON

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The reactions of ClF with SOF_2, SO_2, and SO_3 are reported. These reactions produce SOF_4, $ClSO_2F$, and $ClOSO_2F$, respectively, in excellent yields. New characterization data for $ClOSO_2F$ are presented and some of its reactions are described. The interaction of ClF with HSO_3F and HSO_3Cl is also reported.

Introduction

Chlorine monofluoride has been shown to react in a variety of ways. For example, it can function as either a Lewis acid[1] forming the ClF_2^- anion or a Lewis base[2] forming the Cl_2F^+ cation. In addition, it can act as a chlorinating agent,[3,4] a fluorinating agent,[5] or a chlorofluorinating material. The latter form of reaction can be either catalyzed[6,7] or uncatalyzed.[8] Our interest in the chemistry of ClF prompted an examination of the course of its reaction with a series of sulfur–oxygen-containing compounds.

Experimental Section

Apparatus.—Reactions were conducted in stainless steel cylinders and the products were separated and purified using a stainless steel–Teflon FEP (polyfluoroethylenepropylene) vacuum line. Pressures were measured by means of a Heise Bourdon-tube type pressure gauge. Infrared spectra were taken on Perkin-Elmer Infracords 137 and 337 using 5-cm path length stainless steel or Kel-F cells fitted with AgCl windows. The ^{19}F nmr spectra were obtained using a Varian Associates high-resolution nmr spectrometer operating at 56.4 Mc. Samples were sealed in Kel-F tubes and $CFCl_3$ was employed as the external standard. Mass spectral data were obtained with a CEC 21-103C mass spectrometer with the inlet system operating at room temperature and employing an ionization voltage of 70 V. A Hanovia 100-W utility lamp (Catalog No. 30620) was used for the photolysis.

Materials.—Chlorine monofluoride was prepared by heating an equimolar mixture of Cl_2 and ClF_3 to 150° for several hours in a stainless steel cylinder. Thionyl fluoride was made from thionyl chloride and NaF in acetonitrile.[9] Sulfur dioxide (Matheson Co.) and sulfur trioxide (Baker and Adamson) were commercial materials and were purified by removal of impurities not condensable at $-196°$. Fluorosulfonic (Baker and Adamson) and chlorosulfonic (Eastman) acids were used as received. Cesium fluoride and potassium fluoride were fused and then powdered in a drybox prior to use. In all cases the chlorine monofluoride was purified immediately before use by vacuum fractionation through a U trap cooled to $-142°$.

Reaction of ClF with Thionyl Fluoride.—Thionyl fluoride (102 cm^3, 4.55 mmol) and ClF (211 cm^3, 9.42 mmol) were successively condensed at $-196°$ into a prepassivated 30-ml cylinder. The cylinder was then allowed to warm from $-78°$ to

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[1] K. O. Christe and J. P. Guertin, *Inorg. Chem.*, **4**, 1785 (1965).
[2] K. O. Christe and W. Sawodny, *ibid.*, **8**, 212 (1969).
[3] C. J. Schack, *ibid.*, **6**, 1938 (1967).
[4] D. Pilipovich and C. J. Schack, *ibid.*, **7**, 386 (1968).
[5] K. Dehnicke, *Angew. Chem.*, **76**, 385 (1964).
[6] C. J. Schack and W. Maya, *J. Am. Chem. Soc.*, **91**, 2902 (1969).
[7] C. J. Schack, R. D. Wilson, J. S. Muirhead, and S. N. Cohz, *ibid.*, **91**, 2907 (1969).
[8] W. K. R. Musgrave, *Advan. Fluorine Chem.*, **1**, 18 (1960).
[9] F. A. Fawcett, C. W. Tullock, and D. D. Coffmann, *J. Am. Chem. Soc.*, **84**, 4275 (1962).