Hence the conclusion that B was a compound is further indicated.

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Solubility of Potassium Halides in Fused Acetamide

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A chief drawback with fused inorganic salts is the necessity of maintaining a high operating temperature. Fused acetamide has been shown by several investigators[1,2] to exhibit good solvent properties for electrolytes. Acetamide melts at 80° and boils at 222°. Its dielectric constant is 60.6 at 94°.[3] Undoubtedly its strong solvent power for salts is attributed principally to its high dielectric constant.

Jander and Winkler[3] have utilized fused acetamide as a reaction medium for several inorganic reactions. Wallace and Bruins[4] have reported that potassium halide–acetamide solutions make excellent cell electrolytes for thermal salt cells. (A thermal salt cell produces electrical energy of long duration on application of heat. The electrolyte of this batter is solid and nonconducting at ordinary temperatures, but when external heat is applied, the solid melts and becomes conducting.) Recently, the electrical conductance and viscosity of potassium halide salts in dilute acetamide solutions have been measured.[5] Unfortunately, a search of the literature reveals that there are no quantitative solubility and heat of solution data for potassium halide salts in fused acetamide.

Consequently, in this work, the solubilities of potassium halide salts in acetamide have been measured as a function of temperature between 80 and 130°. From these solubility data, experimental heats of solution were also calculated. The order of decreasing solubility in fused acetamide, KI > KBr > KCl, has the same order as that found for these halides in water and *N*-methylacetamide.

Experimental Section

Apparatus.—A 500-ml Pyrex tube was fitted with a glass stopper, a 0.1° calibrated thermometer, and a glass stirrer. The stirrer was bent into a ring at its lower end. It was moved up and down vigorously during each solubility determination. This whole apparatus was clamped in position in a large electric oven. Titrations were made by a 50-ml Teflon-tipped buret.

(1) **Acetamide.**—Analytical grade acetamide crystals (Mallinckrodt Chemical) were further purified by recrystallization in pure benzene. The resulting solvent (mp 80.0–80.5°) had a mean specific conductance of 8.5×10^{-6} ohm^{-1} cm^{-1} at 94°.

(2) **Halides.**—Analytical grade KI, KBr, and KCl (Mallinckrodt Chemical) were recrystallized from distilled water and fused.

(3) **Standardized Solutions.**—Standard 0.100 *N* silver nitrate and 0.119 *N* potassium thiocyanate solutions were prepared. A saturated solution of ferric ammonium sulfate, made to 0.3 *N* acidity with nitric acid, served as the indicator for the titrations.

Procedure.—Purified acetamide containing an excess of the solid potassium salt in the Pyrex tube was heated to the desired temperature and allowed to equilibrate. All solubility measurements were made with the tube held in a silicone oil bath maintained at a constant temperature to within 0.1°. Aliquot portions of the supernatant liquid were drawn off with a pipet at the same temperature and were placed in a 250-ml erlenmeyer flask. The solution was then weighed, dissolved in water, and titrated according to the Volhard titration method.[6]

Results and Discussion

In Table I are presented the solubilities in grams of potassium halide salt in 100 g of acetamide. The solubility of each solution was corrected for loss of acetamide by weighing the sample before and after each determination, and the data represent averages of duplicate or triplicate determinations. For KCl, the solubility ranged from 2.45 g at 80° to 2.74 g at 130°; for KBr, 10.3 g at 80° to 11.6 g at 130°; and for KI, 32.3 g at 80° to 33.6 g at 130°. It is noted that KI is much more soluble in acetamide than either KBr or KCl.

TABLE I
SOLUBILITY OF POTASSIUM HALIDE SALTS IN MOLTEN ACETAMIDE

KCl		KBr		KI	
Temp, °C	Solubility, g/100 g of acetamide	Temp, °C	Solubility, g/100 g of acetamide	Temp, °C	Solubility, g/100 g of acetamide
80	2.45	81	10.3	80	32.3
86	2.52	90	10.5	85	32.5
103	2.58	100	10.8	97	32.8
115	2.62	110	11.0	118	33.2
120	2.68	120	11.2	130	33.6
130	2.74	130	11.3		

The series of decreasing solubilities in molten acetamide, KI > KBr > KCl, has the same order as that found for these halides in *N*-methylacetamide[7] and water.[8] The position of the iodide ion in this series shows that it is highly solvated in fused acetamide. Our solubility data can also be represented as a function of temperature by the following: for KCl, $\log s = 9.50 \times 10^{-4}t + 0.313$; for KBr, $\log s = 9.40 \times 10^{-4}t + 0.937$; and for KI, $\log s = 3.33 \times 10^{-4}t + 1.484$, where s is solubility, in grams per 100 g of molten acetamide, and t is temperature.

Heats of solution in the temperature range between 80 and 130° were determined from the van't Hoff equation

$$\frac{\mathrm{d} \ln m}{\mathrm{d}(1/T)} = \frac{\Delta H_{\mathrm{soln}}}{R}$$

where m is molality, in moles per 1000 g of acetamide, T is the absolute temperature, R is the gas constant,

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and ΔH_{soln} is the heat of solution per mole. In these computations, ΔH is assumed to be constant and activity coefficients of potassium halides approach unity.[9] Figure 1 gives the best least-squares fit of the solubility data plotted as ln (molality) against the reciprocal of the absolute temperature.

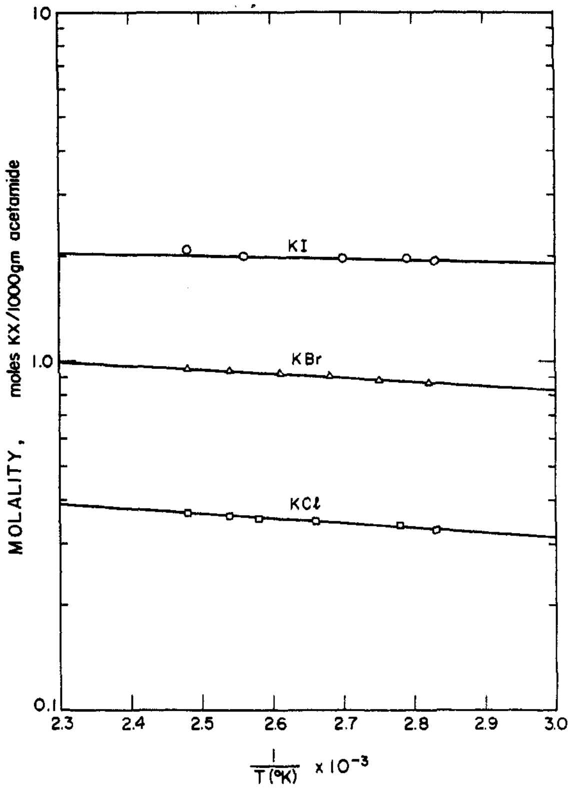

Figure 1.—Plot of ln (molality) of potassium halide salts in fused acetamide against reciprocal temperature.

The heats of solution of potassium halides in fused acetamide are 631, 544, and 163 cal/mol for KCl, KBr, and KI, respectively. The order of the observed heats of solution is in the reverse order of the corresponding heats of solution of these salts in water.[8] These data indicate that the much larger potassium halide solubilities in water correspond to smaller heats of solution. In formamide at 25° the corresponding heats of solution, as given by Held and Criss,[10] are 2220 cal/mol for KI, 820 cal/mol for KCl, and 230 cal/mol for KBr.

In essence, the facts that potassium halide salts are readily soluble and that the acetamide has a high[11] dipole moment of 3.7 D suggest that considerable solvation occurs. From these results and others,[12] acetamide should be rated as an unusually good electrolytic solvent for inorganic salts and their reactions, particularly over the elevated temperature range between 80 and 130°.

Acknowledgment.—This work was supported in part by the Stanford University Center for Materials Research.

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The Electronic Structure of *N,N'*-Bis[pentaammineruthenium(II,III)]-pyrazine(5+)

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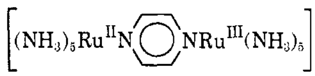
Creutz and Taube[1] have reported the synthesis of the complex *N,N'*-bis[pentaammineruthenium(II,III)] pentakis(*p*-toluenesulfonate) trihydrate to which they assigned the cation structure as



Very rapid electron transfer was reported to occur converting the Ru(II) to Ru(III) and the Ru(III) indicated above to Ru(II). They interpreted a band at 1570 mμ in the near-ir spectrum of the above complex as arising from an electron-exchange transition, which they described as [2,3] → [3,2]* and, from the energy of this transition, they calculated a rate of electron exchange of 3×10^9 sec^{-1}. In a complex molecule of this sort, the near-ir transition could arise from some other source, *vide infra*, so we have considered several alternative possibilities for the bonding in this complex: (a) Creutz and Taube's structures with electron exchange slow on the nmr time scale, (b) Creutz and Taube's structures with rapid electron exchange, (c) two Ru(III)'s bridged by a pyrazine radical anion, (d) a molecular orbital description in which the metal ion and pyrazine-filled π mo's are mixed and the unpaired electron is mainly but symmetrically distributed over the two cations, and (e) a similar mo scheme in which the interaction is essentially with the π* mo's of pyrazine. It should be realized that both (d) and (e) could be occurring simultaneously, and our conclusion is related to which one dominates the energy level ordering.

In an attempt to shed further light on the electronic structure of this most interesting system, we have studied the isotropic ^{1}H nuclear magnetic resonance shifts of this complex. Other than the solvent and anion resonances, we observed three peaks shifted downfield from internal TMS. The results are given in Table I. The assignments are based on the line widths and comparison with the isotropic spectra of the pentaammine halides of Ru(III).[2] The area of the cis ammine resonance is much larger than any of the other resonances, and this aids in its identification.

The structures described under (a) above can be eliminated on the basis of the observed spectrum since, for slow electron exchange, we would expect to see six separate resonances. The ammonias on the ruthenium(II) would be expected to be sharper than those observed and easy to detect.

Next, we shall consider the possibility of having a bridging radical anion (c) in which the electron is in an empty π* ligand orbital. The value of the ^{1}H hyperfine coupling constant for the pyrazine anion is

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