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STUDIES ON AMINE HYDROTHIOCYANATES. II. SOLUBILITIES AND HEATS OF SOLUTION IN SOME ORGANIC SOLVENTS

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ABSTRACT

The solubilities of piperidine hydrothiocyanate, piperazine monohydrothiocyanate, ethylenediamine dihydrothiocyanate, and propylenediamine dihydrothiocyanate in some or all of the solvents methanol, ethanol, and acetone have been determined. Linear regression analysis of the solubility data indicates a good fit in each case to the equation $\ln S = (A/T) + B$. Heats of solution have been calculated from the linear relationships.

INTRODUCTION

Since hydrothiocyanic (rhodanic) acid is a strong acid, it forms a variety of stable amine salts. These amine hydrothiocyanates have a number of interesting properties which are currently being investigated in this laboratory. In our previous work, it was found that they provide useful molten salt synthetic media for preparing thiocyanate complexes [1], also, these compounds function as solid acid catalysts in deamination reactions [2,3]. However, basic physical and chemical data are lacking for these compounds. Accordingly, we have begun a series of investigations on some of the most useful properties of several of these salts. This report describes the results of studies on the solubility of some of these compounds in organic solvents.

EXPERIMENTAL

Preparation of compounds

The amine hydrothiocyanates were prepared by the method of Mathes et al. [4]. Prior to use, the liquid amines were dried by refluxing over solid sodium hydroxide pellets for several hours and distilled from the base. Reagent grade NH_4SCN was used without further purification.

Piperidine hydrothiocyanate (pipHSCN) was prepared by heating 0.5 mole of piperidine with 0.5 mole of NH_4SCN which was added in small portions with constant stirring. After the addition of NH_2SCN was complete, the mixture was heated at 85°C for 2 h. After cooling, the product was removed by filtration and recrystallized twice from acetone and washed with cold acetone. The white product melts at 92—94°C.

Ethylenediamine dihydrothiocyanate, en(HSCN)$_2$, was prepared by heating 0.5 mole of ethylenediamine with 1.0 mole of NH_4SCN added in small portions. After the addition was complete, the mixture was heated at 125°C for 15 min to expel ammonia. After cooling, the product was recrystallized twice from ethanol and washed with cold ethanol. The white solid melts at 144—145°C.

The dihydrothiocyanate of 1,3-propylenediamine was prepared by heating 0.5 mole of the amine with 1.0 mole of NH_4SCN using the same procedure as in the preparation of en(HSCN)$_2$. The product was recrystallized twice from acetone and washed with cold acetone. The product melts at 109—111°C.

Since piperazine is a solid, a different procedure was followed in the preparation of the monohydrothiocyanate of that amine. A solution of 1.0 mole of piperazine in 100 ml of benzene was prepared. The mixture was placed in a flask fitted with a reflux condenser and the flask was placed in an oil bath at 100°C; to this mixture was added 1.0 mole of NH_4SCN in small portions. The piperazine monohydrothiocyanate is not soluble in benzene and collects as a solid precipitate. The solid was collected by filtration and was recrystallized twice from water and washed with cold water. The product melts at 166—168°C.

Carbon, hydrogen, and nitrogen analyses were performed by Microanalysis, Inc., of Wilmington, Delaware. Table 1 shows the analytical data for the amine hydrothiocyanates used in this work.

Solubility determinations

The solubilities of the amine hydrothiocyanates were determined in selected combinations with methanol, ethanol, and acetone. Freshly opened bottles of spectral grade solvents were used. Flasks containing the solvents were suspended in a constant temperature bath and an excess of the amine hydrothiocyanate was added. After allowing the solutions to stand for several hours to equilibrate, 10 ml aliquots of the saturated solutions were removed and added to 25 ml of water acidified with HNO_3. The thiocyanate was precipitated by adding a solution of $AgNO_3$ and the solid AgSCN was removed by filtration. From the weight of AgSCN obtained, the solubility

TABLE 1

Analytical data for the amine hydrothiocyanates

Compound	%C		%H		%N	
	Calc.	Found	Calc.	Found	Calc.	Found
pipHSCN	49.96	50.46	8.41	8.18	19.41	19.18
pipzHSCN	41.35	41.92	7.65	7.58	28.92	28.85
en(HSCN)$_2$	26.95	27.09	5.67	5.75	31.41	31.50
pn(HSCN)$_2$	31.23	31.50	6.30	6.12	29.12	29.04

TABLE 2

Solubilities of amine hydrothiocyanates

Compound	Solvent	Solubility (mol l^{-1})			
		25° C	30° C	35° C	40° C
pipHSCN	CH_3OH	2.772	3.707	4.231	5.386
pipHSCN	C_2H_5OH	1.400	1.703	2.039	2.341
pipHSCN	$(CH_3)_2CO$	0.920	1.067	1.456	1.989
pipzHSCN	CH_3OH	0.265	0.298	0.367	0.431
pipzHSCN	C_2H_5OH	0.045	0.054	0.066	0.075
en(HSCN)$_2$	C_2H_5OH	0.211	0.221	0.246	0.265
pn(HSCN)$_2$	CH_3OH	4.863	5.162	5.620	5.852
pn(HSCN)$_2$	C_2H_5OH	1.140	1.309	1.372	1.618

of the amine hydrothiocyanate was calculated. Solubilities were determined at 25, 30, 35, and 40° C in each case.

RESULTS AND DISCUSSION

The solubilities of the amine hydrothiocyanates in the solvents are shown in Table 2. An increase in solubility with increasing temperature is seen in every case. All of the amine hydrothiocyanates show solubilities which decrease in the order methanol > ethanol > acetone. This is expected on the basis of the ion solvating ability of the solvents. The solubilities of en(HSCN)$_2$ and pipzHSCN in acetone are so low that reproducible values could not be obtained.

Using a linear regression analysis, the solubilities shown in Table 2 were fitted to a linear equation of the form

$$\ln S = (A/T) + B \qquad (1)$$

where S is the solubility, T is the absolute temperature, and A and B are constants. In general, a good linear fit of the data was obtained for each solute/solvent pair, and from the slopes of the linear relationships the heat of solution, ΔH, was obtained. These parameters are shown in Table 3 for the systems studied.

The data shown in Table 3 indicate that the dissolution processes are all endothermic, but that the heat absorbed is greatest for dissolution in acetone, the solvent of poorest ion solvating ability. This trend is similar to that for ammonium halides and ammonium thiocyanate [5]. The solubilities of the amine hydrothiocyanates in the organic solvents are fairly high, undoubtedly because of the large sizes of the ions. The resulting low lattice energy of the solid and the favorable interaction of the large ions with organic molecules by the hard—soft interaction principle causes the solubility to be substantial.

We are currently investigating other solution and physical characteristics of the amine hydrothiocyanates.

TABLE 3

Regression analysis parameters for eqn. (1) and heats of solution

Solute/solvent	*A*	*B*	Corr. coeff.	Δ*H* (kJ mol^{-1})[a]
pipHSCN/CH_3OH	—3709	13.52	0.996	30.8
pipHSCN/C_2H_5OH	—4528	15.10	0.982	37.7
pipHSCN/CH_3OH	—5646	18.71	0.999	46.9
pipzHSCN/CH_3OH	—3107	9.08	0.994	25.8
pipzHSCN/C_2H_5OH	—3230	7.74	0.997	30.0
en$(HSCN)_2$/C_2H_5OH	—1468	3.36	0.990	12.2
pn$(HSCN)_2$/CH_3OH	—1198	5.60	0.982	9.96
pn$(HSCN)_2$/C_2H_5OH	—2040	6.98	0.980	16.9

[a] Estimated error is about 3—4%.

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