pending upon the concentration of reagents used, temperature, time of heating and finally upon the concentration of hydrogen sulfide formed in the reaction. The reaction is not productive of a quantitative yield of thio-urea.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF LELAND STANFORD JUNIOR UNIVERSITY.]

THE ALKYL AMINES AS SOLVENTS.

BY HOWARD MCKEE ELSEY.

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That primary amines are ionizing solvents has been shown by the work of Gibbs[1] and others, and by analogy we would expect that a salt soluble in ammonia would be less soluble in methylamine, still less soluble in ethylamine and dimethylamine, and perhaps insoluble in propylamine and trimethylamine. Indeed Shinn[2] found potassium iodide, a salt very soluble in liquid ammonia and fairly soluble in methylamine, to be entirely insoluble in ethylamine, the next higher ammono alcohol. From this, it would seem that the higher amines would be very poor solvents for inorganic substances.

The salts used in the present solubility determinations were of the ordinary commercial variety, dried as thoroughly as was possible without danger of decomposition. Excepting in a very few cases those compounds only were taken from which all the water was known to have been removed.

The ethyl-, methyl-, propyl- and isopropylamines used as solvents were water-free imported samples. To ensure their remaining dry, they were stored over metallic sodium. The dimethyl and trimethylamines were purchased as the water solutions. They were recovered as the water-free substances by distilling from a flask through an inverted condenser and then a soda-lime tube and finally condensing in a glass container cooled by a liquid ammonia bath. Several pieces of freshly cut sodium were added to the container to remove the last traces of moisture present and to absorb any that might later be introduced. Some difficulty was encountered in preventing loss of the amine by leakage through the stopcock of the container. The value of the amines as organic solvents is shown by the ease with which they dissolved any lubricant which was placed on the stopcock; and it was finally found necessary to keep the tube, holding the stock of amine, in an ice-bath while working, and to seal the stopcock off at night.

Since the lower amines are gases under operating conditions the solubility determinations were made in hermetically sealed glass tubes. For

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[1] Gibbs, THIS JOURNAL, 28, 1395 (1906).

[2] Shinn, *J. Phys. Chem.*, 11, 537 (1907).

this purpose a glass tube was closed at one end, a small amount of substance introduced and the tube placed in an ammonia bath. Solvent was then distilled in and the upper end of the tube sealed off. If, after the temperature rose to room temperature and after agitation, no marked solvent action could be observed, the tube was cooled with liquid ammonia to precipitate, if possible, any dissolved material. In most cases these solutions have very high temperature coefficients, and the change from room temperature to —33.5° is often sufficient to cause crystallization at once from a solution which is by no means saturated at the higher temperature.

In later experiments, these straight tubes were replaced by 2-legged tubes in which it was much easier to judge the relative solubilities of the different salts. These tubes were filled in the same way, but after the solvent had been added the tube was constricted at the neck, evacuated and sealed off. Unless the air was removed in this way, distillation from one arm to the other was very slow.

After filling and sealing, the tubes were allowed to stand for several days, being frequently agitated to ensure the attainment of equilibrium. The clear solution was then decanted over into the shorter leg and the long leg was placed in an ice-bath. Due to the difference in temperature, the solvent was distilled out of the second leg and the solubility of the compound could be determined roughly by the amount of residue remaining

This separation of the solute by distilling off the solvent could not be accomplished in all cases on account of the exceedingly high viscosity of concentrated solutions in the amines. Ammonia and the amines as a class have very low viscosities, being much more mobile than water. But even dilute solutions in ammonia and the amines are markedly more viscous, while concentrated solutions in them are apt to have the consistency of the thickest of molasses.

One of the most striking properties of the amines is the ease with which they enter the molecular structure of compounds as amine of crystallization. These aminates usually form immediately on contact of the cold liquid with the solute, causing the salt to swell up into a bulky mass. Often this aminate is very soluble at room temperatures and on removing the tube from the bath it quickly goes into solution. In other cases, the aminate is insoluble or only slightly soluble at room temperature and it remains as a solid phase. As a rule the addition product is sufficiently soluble to go over slowly to a crystalline structure, the crystals often attaining considerable size.

Since the chemically pure amines are very expensive and our supply of them was somewhat limited, the solubility tubes were of necessity too small to afford quantitative results. However, it is believed that our results are accurate within the limits of error of the method used. The salts are classified as being very soluble, moderately soluble, slightly soluble, or insoluble. A salt is classed as being very slightly soluble where no appreciable residue is left in the second leg and yet where there is some evidence of solubility such as color in the solution.

The solubilities of the different salts in the several amines are tabulated below. For comparison, the measurements of Franklin and Kraus[1] in liquid ammonia and of Gibbs[2] in methylamine are included in the table. The determinations taken from Gibbs' paper are marked thus, *. The following abbreviations are used in the table, very soluble, *v;* moderately soluble, *m;* slightly soluble, *s;* and insoluble, *i.*
A indicates the formation of an aminate on contact of the solvent and solute, the solubility of this aminate being shown by one of the letters above. R indicates marked reaction between solute and solvent.

Table I.—Solubilities of Salts in Amines.

Solvent. Solute.	NH_3.	CH_3NH_2.	$C_2H_5NH_2$.	$C_3H_7NH_2$.	CH_3 $CHNH_2$ CH_3	$(CH_3)_2NH$	$(CH_3)_3N$
AgBr	*m*	..	*v*	..	..	..	..
AgI	*v*	*v*	*v*	..	..	*v*	A *i*
$AgNO_3$	*v*	*v**	*v*	*v*	*m*	*v*	..
Ag_2SO_3	..	*s*	*s*	..	..	..	..
Ag_2SO_4	*i*	A *i*	A *i*	..	..	..	..
$BaBr_2$	..	..	*v*	..	..	*s*	..
$BaCl_2$	*i*	..	*s*	..	..	..	..
$Ba(ClO_3)_2$[a]	..	..	*m*	..	..	..	..
BaI_2	*s*	A *v*	A *v*	A *v*	A *m*	A *v*	A *s*
$Ba(NO_3)_2$	*m*	*s*	*s*	..	..	*s*	*s*
$Ba(SCN)_2$	*v*	*v*	*v*	..	*m*	*m*	*i*
$BiBr_3$	*v*	..	*m*	..	..	*v*	..
$BiCl_3$	*m*	A *m*	..	..	..	..	..
BiI_3	*s*	A *v*	*v*	..	..	*v*	*s*
Bi_2S_3	*i*	*s*	*s*	..	..	..	..
Br_2[b]	..	*v*	R *v*	..	..	R *v*	..
CaC_2	..	*i*	*i*	..	..	..	..
CaI_2	..	..	A *v*	..	..	*v*	..
$Ca(NO)_3$	*v*	*m*	*v*	..	..	*i*	*i*
$CdBr_2$	..	..	*s*	..	..	A *m*	..
$Cd(CN)_2$	..	..	*m*	..	..	*m*	..

[a] A solution of $Ba(ClO_3)_2$ in $C_2H_5NH_2$ is unlike most of the solutions in these solvents in that it has a very low temperature coefficient of solubility.

[b] Bromine reacts with the dimethylamine with the evolution of heat to form a very soluble crystalline compound. With methylamine and ethylamine, the reaction is much more violent and there is formed in addition to a soluble crystalline product, a black residue.

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[1] *Am. Chem. J*, 20, 820 (1897).

[1] *Loc. cit.*

TABLE I (*continued*).

Solvent. Solute.	NH_3.	CH_3NH_2.	$C_2H_5NH_2$.	$C_3H_7NH_2$.	$CH_3 \diagup CHNH_2 \diagdown CH_3$.	$(CH_3)_2NH$.	$(CH_3)_3N$.
CdI_2[c]	*s*	..	A *m*	..	..	*v*	*m*
$Cr_2(SO_4)_3$	..	*i*	*i*	..	..	..	..
$CuCl$	*s*	R*	A *m*	..	..	..	..
$CuCl_2$	*i*	..	A *m*	..	..	..	..
$CuHAsO_3$	*i*	*s*	*s*	..	..	..	..
CuI[d]	*v*	..	*v*	..	..	..	..
CuS	*i*	*s*	*s*	..	..	..	*i*
$CuSCN$	..	*v*	*v*	..	..	..	..
$CuSO_4$[e]	*i*	*i**	A *i*	..	..	..	..
Fe	*i*	..	*i*	..	..	..	..
$FeCl_3$	..	..	A *s*	..	..	..	..
FeI_2	..	..	A *i*	..	..	*m*	..
$Fe_2(SO_4)_3$	*i*	A *i*	*i*	..	..	..	..
$Hg(CN)_2$	*v*	*v**	..	..	..	*v*	..
$Hg(CON)_2$[f]	*v*	..	R	..	..	..	..
HgI	*v*	..	*m*	..	..	..	..
HgI_2	*v*	*v**	*v*	..	..	*v*	*m*
HgS	*i*	..	*i*	..	..	..	..
$Hg(SCN)_2$	*v*	*s*	*m*	..	..	..	*s*
I[g]	*m*	*v*	*v*	..	..	*v*	*s*
$KAg(CN)_2$	..	..	*s*	..	..	*s*	..
KCN	..	..	*s*	..	..	*s*	..
$K_4Fe(CN)_6$	*i*	..	*s*	..	..	..	..
KI	*v*	..	*s*	*s*	*i*	*s*	*i*
$KMnO_4$	*v*	..	R	..	..	..	..
KNO_3	*v*	*s*	*s*	..	..	..	..
K_2PtCl_4	..	..	*s*	..	..	*s*	..
K_2PtCl_6	..	*s*	*s*	..	..	..	..
$KSCN$	*v*	*v*	*m*	..	..	..	..
$LiCl$	*s*	*v**	A *v*	..	..	*m*	..

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[c] A saturated solution of CdI_2 in $(CH_3)_2NH$ is a fair conductor of the electric current at 20°.

[d] CuI is very soluble, forming a blue solution in $C_2H_5NH_2$. If metallic copper is placed in this solution, the blue color is discharged, due possibly to the reduction of Cu^{++} to Cu^{+}, the cupric salt being present as an impurity.

[e] The blue aminate formed is the only one observed which did not, on standing, become noticeably crystalline in character.

[f] $Hg(CON)_2$ reacts and is reduced to metallic mercury and other products which are soluble.

[g] Iodine is extremely soluble in all the amines tested, with the exception of trimethylamine. On standing, the deep color of the solution fades in color. One solution of iodine in dimethylamine had a resistance of 80 ohms between sealed-in electrodes. The resistance increased to 100 ohms after the solution had become colorless. Iodine is only slightly soluble in trimethylamine but, after some weeks, colorless crystals separate from this solution.

TABLE I (*continued*).

Solvent. / Solute.	NH_3	CH_3NH_2	$C_2H_5NH_2$	$C_3H_7NH_2$	$\overset{CHNH_2}{CH_3\diagup\diagdown CH_3}$	$(CH_3)_2NH$	$(CH_3)_3N$
$LiIO_3$	..	..	*i*	..	..	..	..
MgI_2	*v*	..	A *v*	..	..	..	..
$Mg(NO_3)_2$	*v*	..	..	..	..	A *s*	..
$NaBr$	*v*	..	*s*	..	..	*s*	..
$Na_2C_4H_4O_4$	..	..	*i*	..	..	..	..
$NaClO_3$	*v*	*m*	*s*	..	..	*s*	..
NaI	*v*	..	..	..	..	..	..
NaN_3	..	..	*s*	..	..	..	..
$NaNO_3$	*v*	*v**	..	*s*	*s*	*s*	*s*
Na_2SeO_4	..	*s*	..	..	..	..	..
$NiCl_2$	*i*	..	A *i*	..	..	..	..
$Ni(CN)_2$	..	..	*s*	..	..	*s*	..
$Ni(SCN)_2$	..	..	*v*	A *m*	..	..	..
$NiSO_4$	*i*	*i*	*i*	..	..	..	..
P (red)	*i*	*s*	*s*	..	..	..	*i*
P (yellow)[h]	*m*	*m*	*v*	..	..	..	..
$PbBr_2$	*m*	..	A *v*	..	..	*m*	..
PbI_2[i]	*v*	A *s*	A *m*	A *m*	*m*	A *s*	A *s*
$Pb(SCN)_2$	..	A *v*	A *m*	..	..	..	*m*
$PtCl_2$	*s*	..	*m*	..	..	..	..
PtI_2	..	..	*m*	..	..	*s*	..
S	*m*	*v*	*v*	..	..	..	*s*
SbI_3	R	..	*v*	..	..	*v*	*i*
Se[j]	*m*	..	*s*	..	..	..	..
SnI_4	..	A *i*	A *v*	..	..	*m*	..
$SrBr_2$	..	..	A *v*	..	..	..	..
$SrCl_2$	*i*	..	*m*	..	..	..	..
SrI_2	..	..	*v*	..	..	A *v*	..
$Sr(NO_3)_2$	*v*	*v*	A *s*	..	..	..	..
Te	..	..	*i*	..	..	..	..
TlI	..	..	*i*	..	..	..	..
$TlNO_3$	*m*	*v*	*m*	*m*	*m*	*m*	*s*
Tl_2SO_4	..	..	*i*	..	..	..	..
$UrO_2(C_2H_3O_2)_2$[k]	..	*s*	*m*	..	..	..	..
$UrO_2(NO_3)_2$	..	..	*i*	..	..	..	*i*
ZnS	..	*i*	*i*	..	..	..	..

[h] Yellow phosphorus is soluble in ethylamine and methylamine, forming almost colorless solutions; but on standing the red modification, which is only slightly soluble, separates.

[i] PbI_2 turns white on contact with the amines. By heating the tubes very gently, the original yellow color returns, indicating that the amine of crystallization has been removed. On cooling, the PbI_2 again turns white

[j] Se in $C_2H_5NH_2$ turns from red to black in color but without visible increase in volume.

[k] A solution of $UrO_2(C_2H_3O_2)_2$ gelatinizes on standing for some days.

The action of the sulfides of the alkali and alkaline earth metals in these amines is interesting. Samples of the commercial variety of these salts when treated with the amines give yellow solutions very similar to a dilute solution of sulfur. The residual salts, which previously were a dirty yellow in color, are reduced to a pure white color and a granular condition. It is suggested that any free sulfur present in the sulfides is dissolved and the polysulfides thus reduced to the normal sulfides. This explanation, if correct, indicates a possible method of purifying these compounds.

Summary.

The results of this study show that the simpler primary and secondary amines at room temperatures are fair solvents for many salts. However, the solubilities have high temperature coefficients and at the boiling-point of liquid ammonia but very few salts are perceptibly soluble in any of the amines.

The work outlined in this paper was done at the suggestion and under the direction of Professor E. C. Franklin, and I wish to thank him for his kind advice and assistance.

UNIVERSITY OF KANSAS,
LAWRENCE, KANSAS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY.]

ORGANIC MOLECULAR COMPOUNDS. II.

BY JAMES F. NORRIS AND DOROTHY M. TIBBETTS.

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It was shown some time ago[1] that tetraphenyl-ethylene dichloride, $(C_6H_5)_2CCl.ClC(C_6H_5)_2$, forms well characterized molecular compounds with chloroform and carbon tetrachloride. The existence of these addition-products led to a study of substances of similar and related structures, and it was discovered that organic compounds of certain types possess to a high degree the power to form molecular compounds.[2] Among the substances studied were substitution-products of tetraphenyl-ethylene. Of these *p*-tetrabromo-tetraphenyl-ethylene, $(BrC_6H_4)_2C = C(C_6H_4Br)_2$, was noteworthy as it formed well crystallized compounds with acetone, methylethyl ketone, ether, carbon tetrachloride, ethyl acetate, and benzene.

As a result of an attempt to interpret the facts discovered and the endeavor to guide future work an hypothesis was devised. A large number of molecular compounds, both inorganic and organic, have been described, but no adequate explanation of their structure based on our present views of valence has been proposed. The subject is an important one, and it

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[1] Norris, Thomas and Brown, *Ber.*, 43, 2940 (1910).

[2] Norris, THIS JOURNAL, 38, 702 (1916).