Role of Urea in Chemical Separation

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INTRODUCTION

UREA[1] is an important laboratory and industrial chemical of today. In laboratory it is used as a starting material in many organic syntheses. It is also employed to remove nitrous acid in many organic reactions and to control diazotization. It is a good antioxidant. In industry urea has varied applications. Its extensive use as a fertilizer on account of its high nitrogen content is well-known. It forms condensation products with formaldehyde, ammonium thiocyanate and many polybasic acids to give plastics. In textile printing, it is used to improve fastness and intensity of the colour. It improves abrasion resistance, hardness and water-resistance of shellac films.

In 1939, Bengen[2], a German chemist, found that when a saturated aqueous solution of urea was shaken with a straight-chain organic compound such as a hydrocarbon, an alcohol or an acid, a crystalline adduct was readily formed. However it was only after the end of the World War II that this discovery came to be extensively studied and it has now led to an entirely new application of urea in the field of organic chemical separations.

Urea forms crystalline needle-shaped complexes with alcohols[3], esters, ethers, aldehydes, ketones and organic acids, provided the carbon chain has a minimum length of six carbon atoms and is unbranched or slightly branched. Combinations with branched chain and cyclic compounds have not been possible. The halogen[5], sulphur and various oxygen derivatives form entirely similar complexes if the carbon chain is linear. Compounds with a side methyl group form urea complexes if the chain is of

about twenty carbon atoms. The complex formation also depends on the nature of the substituent and the position of the methyl group.

Urea also forms complexes with inorganic substances such as $NaCl^5$ [a] NaBr, H_3PO_4, H_2O_2 and $CrCl_3$[6]. The exceedingly stable hexa-urea chromic chloride with the co-ordination number of Cr completely satisfied by urea is a fair, although a very slow, tanning agent.

This important property of urea to form complexes selectively, has been utilized in the segregation of fatty acids, alcohols, esters and hydrocarbons. Many[7] other uses also have been developed. The nature of the complex has been extensively studied. A brief review of the work done in these fields is presented here.

Conditions of Complex formation :--

In this study of selective complex formation and separation of organic compounds by urea, Bengen and Shlenk[8] pointed out that the process of separation can be based on their reactivity or non-reactivity towards urea. Bengen had used aqueous solution of urea, however later[9] workers have used absolute methanol, methyl isobutyl ketone, isooctane, ethanol, normal hexane and methylated spirit[11] as solvents.

The formation of urea complexes depends on the kind of solvent, concentration of urea and temperature[3b, 12]. Since no definite stoichiometric relationship has been noticed between the amount of urea and the compound in the complex formed, the proportion of the two is not fixed. In the case of fatty acids and hydrocarbons, molar

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ratios from 1:1 to 1:14 (organic com-
pound to urea) have been reported and
with esters the molar ratio[16] has varied
between 1:9 and 1:14. In some cases
the ratio has been as high as 1:18.

. Absolute methyl alcohol is widely
used and has been found satisfactory.
Generally too much solvent decreases
the yields of urea adducts[12], and if too
less a quantity is used, the organic sub-
stances get occluded on the surface of
the urea complexes and intensive wash-
ing is then necessary. For washing pur-
poses the solvent used must be at the
same temperature at which the urea
complexes are formed, or it should be
a few degrees below the reaction tem-
perature. It is then possible to obtain
a sufficiently pure complex in good yield
and free from any excess urea and or-
ganic substance. The concentration of
urea solution is also an important factor.
It is common to use a saturated solu-
tion of urea.

The formation of complexes is an
equilibrium[31b,12] reaction which is affect-
ed by a change in temperature. Lower
temperature favours the precipitation of
the unsaturated part of the organic mix-
ture in the form of orea complexes, while
high temperature lowers the stability of
the complex.

These complexes are formed with
heat liberation of about 1.6 Kg.Cal. per
methylene group. Thus, in the forma-
tion of urea-n-hexadecane, 23.0 Kg.Cal.
of heat per mole of n-hexadecane are
liberated and the complex contains
eleven molecules of urea. Zimmers-
chied[5,12] et al, have developed a carori-
metric method to measure the rise in
temperature and to determine thereby
the moles of n-alkane reacting with urea.

Technique of Preparing Urea
   Complexes :—

There is no definite method available
at present, which will quantitatively

separate the saturated and the mono-
unsaturated compounds from the poly
unsaturated compounds of a mixture. A
general technique is given below.

The organic substance is dissolved in
absolute methanol, containing a suitable
quantity of urea. The proportion in
which the methanol and urea are to be
taken depends upon the organic mixture.
Witnauer [3a] et al have suggested a pro-
portion of 1:3:20 (organic substance:
urea:methanol). The solution is warmed
and allowed to stand overnight. Needle-
like crystals are formed, which are
separated by suction filtration. If the
filtrate is kept overnight at a lower tem-
perature at 15°C or 0°C, an additional
yield of complex is obtained.

After filtration, the complex is washed
and dried in a vacuum desiccator to
constant weight. It is very easily decom-
posed in excess of water. Sometimes a
little concentrated hydrochloric acid
added to water helps its decomposition.
The organic substance is separated and
can be extracted by ethyl ether or
petroleum ether.

Physical Nature of Urea Complexes :—

The urea adducts can scarcely be con-
sidered as salts formed by the weakly
basic urea with the linear compound
behaving as an acid. Moreover the
complexes formed by various organic
molecules are all alike in form i.e., crys-
talline needles of varying shapes. They
are dissociated very easily by the addi-
tion of water. The water dissolves the
urea and the organic substance floats
on the surface of water. These facts do
not support a chemical combination[3a,12]
between the urea and n-alkane molecules.

The complexes are formed with evo-
lution of about 1.6 Kg.Cal. of heat per
methylene group—a value of the same
order as the heat of adsorption of hydro-
carbons upon solid surfaces. On com-
paring this adduct formation with several
other physical transformations, Zim-

merschied, et al, have concluded that the n-alkane chains penetrate the urea lattice, within which they are held by forces which may be similar to those in adsorption and have therefore classed urea adduct formation as an adsorption phenomenon.

Knight[3a] et al, observed a linear relationship between dissociation temperature of the complex and the total number of carbon atoms. This is in agreement with the structure of the complexes. The urea molecules form a spiral around the organic molecule which is thus trapped inside, and is held by secondary valence forces. The amount of energy to break the association depends on the chain length, the van der Waals forces increasing regularly with each methylene group.

Smith[4] made an X-ray investigation of the urea complexes. Complete Wissenberg data were taken for a single crystal of cetane urea and 1:10-dibromodecane urea complex. Powder patterns were also taken of urea complexes of C_{10} to C_{50} hydrocarbons and many alcohols, acids and esters. All gave essentially identical powder patterns. The unit cell is hexagonal where $a = 8.24$Å, $C = 11.0$Å space group $C6_1^2$ with six urea molecules per unit Cell. The spiral structure of the complex was confirmed. Spirals of hydrogen bonds between the O and NH_2 groups of adjacent urea molecules account for the stability of the structure. The shorter N-H-O bonds are about 2.93 Å in length and are planar with the urea molecule. The longer H bonds are about 3.03 Å.

Fergusson[13] referred to urea complexes as forming helices probably by head to tail hydrogen bonding and the entrapped substances are held in the centre channels. These complexes have melting-points close to the melting-point of urea, have dissociation temperatures which vary directly with the vapour pressure of the enclosed molecule and are decomposed by heat or by dissolving in solvents of urea.

Redlich[3b] et al, studied the molar ratio, weight ratio (urea/reactant) and the heat evolved during the decomposition of urea complexes of many acids, alcohols and esters. The molar ratio in which the complexes are bound is a function of the amount of urea and amount of solvent. Knight[3a] et al, studied the urea complexes of the cis and trans forms of oleic acid, their methyl esters and oleyl and elaidyl alcohols and found that the molar ratio is the same in the case of cis and trans isomers.

In their physical nature, these urea complexes find similarity with the addition compounds of cholic acids[13] and quinol complexes in which desoxycholic acid or resorcinol form crystalline stable compounds with various types of substances.

Application of Urea in various separations :—

As already stated the n-alkanes form urea complexes. The longer the chain of carbon atoms the more stable are the urea adducts and more readily are they formed. Only one double bond in the chain does not prevent the formation of the complex. As the number of double bonds increases the tendency to form urea complexes decreases. Thus, oleic or elaidic acids form urea complexes but not the linoleic and linolenic acids. This gives an easy means of separating the polyunsaturated fatty acids and other substances from the saturated and mono-unsaturated substances. The trans 9:10-octadecanoic acid has a slightly higher tendency to form complexes than the cis form. The following illustrative examples of separations are given.

1. Segregation of Fatty Acids :—

   (a) Various pairs of fatty acids :—

Shlenk and Holman[14] were able to separate the following fatty acid mixtures on a laboratory scale in good yield and purity. (1) Lauric and stearic, (2) Lauric and linoleic, (3) Oleic and stearic, (4) Linoleic and stearic, (5) Oleic and linoleic, (6) Linoleic and linolenic, (7) Stearic and β eleaosteric, (8) Oleic and β eleaosteric. The saturated acids formed urea complexes preferentially over the unsaturated or the other saturated acids with lower number of carbon atoms. In the case of linoleic and linolenic acids, the first was separated from the second in a good yield. Linoleic acid forms a urea complex only in a concentrated solution of urea in methanol.

(b) *Linoleic acid*[15,16,17] :—Corn oil fatty acids were subjected to urea adduct formation in successive crops, which mainly removed the saturated and oleic acids. The raffinate fatty acids were fractionated. The linoleic acid obtained was of 95% purity, with 3% oleic acid and an I.V. of 176.2. The yield was 50%.

(c) *Linolenic acid*[17,18]:—From the perilla oil fatty acids, linolenic acid of 87% purity and having 6% linoleic acid was obtained. Linseed oil fatty acids yielded a concentrate with iodine value of 228.0 (80%).

Mehta, *et al*,[18] have fractionated linseed oil fatty acids, using solid urea, aqueous urea and urea in methanol. The raffinate fatty acids had iodine values of 234.0, 192.3 and 233.0.

(d) *Oleic acid*[15] :—Brown grease fatty acids were subjected to solvent crystallization at 0°C. The raffinate fatty acids were treated with urea in order to remove the remaining saturated acids. Fractional distillation of the raffinate gave oleic acid of 95% purity. By this method a low-linoleic oleic acid is obtained. Swern, *et al*, have done the separation of olive oil, corn oil and rape oil fatty acids. They have obtained 99%

pure oleic acid which is free from linoleic acid.

(e) *Erucic acid*[19] :—By urea separation of rape oil fatty acids, erucic acid of I.V. 74.5 and m.p. 29°C was obtained.

2. **Separation of fatty acids from Glycerides[20] :—**

Ringmonti and Ricco studied the separation of olive oil glycerides and fatty acids by using a large excess of urea. Oils with high f.f.a. content. gave better results than oils with low f.f.a. content.

3. **Separation of fatty alcohols[21,3,3a] :—**

Fairly pure oleyl alcohol was obtained by urea adduct separation of the fractionated sardine and calmury oil alcohols. Also from cottonseed and poppy seed oil—alcohols were separated: cetyl, oley and linoleyl alcohols in good purity.

4. **Separation of hydrocarbons and petroleum fractions[4,5,12,9] :—**

Since hydrocarbons with carbon chain up to 50 carbon atoms form urea complexes, while isoparaffin, cyclohexane, and hydrocarbons from the aromatic class do not there is a potential scope in utilizing urea to remove straight chain alkanes and alkenes from petroleum oil.

5. **Separation of esters[10] :—**

The remarkable difference between the normal and branched chain fatty acids and hydrocarbons in forming urea adducts is also noticed in esters. Stable crystalline adducts were obtained from ethyl tetradecanoate, decanoate, octanoate and crotonate. Among esters of dicarboxylic acids diethyl succinate, adipate, azelate and sebacate gave urea complexes readily. It has also been possible to separate diethyl adipate

from its mixture with methyl salicylate and ethyl crotonate.

6. Improvement of drying oils[22] :—

The technique employed is- similar to that of segregating linoleic and linolenic acids. Soyabean oil on account of the substantial amount of saturated acids and oleic acid dries slowly. These acids were, therefore, removed from soyabean oil fatty acids by extractive crystallization with urea. The iodine value of soyabean oil fatty acids was 132.0 and of methyl esters was 139.0. After removal of the saturated and oleic acids by urea-adduct formation, the iodine values were increased to 177.0 and 175.0 respectively. The latter having increased unsaturation were converted to triglycerides by carefully reacting with glycerol triacetate in presence of sodium methoxide. By the same method methyl esters of linseed oil and dehydrated castor oil fatty acids were converted to triglycerides. The films of these synthetic oils were compared with those of alkali refined natural linseed oil and it was found that the synthetic oil was equal to or slightly better than linseed oil although not so good as dehydrated castor oil. Tall oil by the same method was inproved as a drying oil.

7. Sterols and their addition products[23] :—

Sterols are separated from mixtures through their addition compounds with urea or inorganic salts. Cholesterol was obtained in 72.6% purity from wool fat alcohols. Further reaction with urea and urea hydrochloride gave cholesterol in 94.4% purity.

8. Stabilization of fatty acids against oxidation[14] :—

The free acids and the urea complexes behave differently with respect to auto-xidation. The urea complexes of soyabean oil fatty acids did not develop rancidity on standing in air for several weeks. Several 10 gram portions of complexes and a 40. grams lot of fatty acids were kept open to atmosphere and their peroxide values determined periodically. The results showed that fatty acids in complexes did not form oxidation products. The oxygen uptakes of linoleic and linolenic acids were also measured against their urea complexes. The complexes absorbed periodically negligible amounts of oxygen.

Swern[24], et al, confirm the spatial position of the hydroxy groups in the high melting 9:10-dihydroxy stearic acid as on opposite sides of the carbon chain as it does not form urea complex. The low melting 9:10-dihydroxy stearic acid readily forms urea complex in quantitative yield. The presence of oxirane keto or hydroxyl groups along the chain does not prevent formation of the complex. Catravas and G. Knafo[25] tried the precipitation of oxidised linseed oil and, castor oil fatty acids by urea. The urea complexes did not remove much of the oxidised acids from the non-oxidised. The same workers oxidised methyl oleate and methyl linoleate in presence of ultra-violet light below 30°C. The product was subsequently treated with urea and they were able to separate the polymerised product from the original. Ribas and Gilcurbera[26] compared the urea adducts of stearic, oleic, and adipic acids with those of 12-hydroxy stearic, ricinoleic and the cork acids as felonic, felogenic, floinic and floinilic. They found that the presence of hydroxy groups in the centre of the chain does not prevent the formation of a urea complex.

Crystalline Complexes of Thiourea :—

In analogy with urea thiourea[4] also forms crystalline complexes with cyclohexane, triptane and certain branched chain and compact molecules. The mode of formation and their behaviour are similar to those of urea complexes in many respects.

The arrangement of the thiourea molecules is similar to that of the urea molecules in the urea complex. The larger radius of the sulphur atoms results in a larger channel into which cyclohexane, hexachloroethane, triptane fit well. The X-ray powder patterns of the urea and thiourea complexes are different from those of simple urea or thiourea.

CONCLUSION

Urea has thus become another new tool in the hand of the chemist. It has opened new fields of research—especially for the physical and the organic chemist. Applications for separation in different directions will continue to increase. In a few years to come, urea-adduct formation and separation may rank as an independent laboratory operation like low temperature crystallization.

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