Complexes of Urea and Symmetrical Tetraalkylammonium Halides[1]

Shuji Saito,[2] Melissa Lee, and Wen-Yang Wen

Contribution from the Department of Chemistry, Clark University, Worcester, Massachusetts 01610. *Received June 10, 1966*

Abstract: Various crystalline complexes of urea and symmetrical tetraalkylammonium halides (tetraethyl-, tetra-*n*-propyl-, tetra-*n*-butylammonium chlorides, bromides, and iodides) were prepared from aqueous solutions at room temperature. Crystals appeared as flat needles or plates depending upon the kind of complex and condition of crystallization. These complexes were analyzed and found to be either binary complexes of urea and a salt or ternary complexes containing water as the third component. Solubilities of urea in aqueous solutions containing these salts have been measured at 25°, and the phase diagrams of some ternary systems were determined. Stability of the crystalline complexes in connection with their possible structure is discussed.

Urea forms adducts with many straight-chain organic compounds such as *n*-paraffins, some *n*-olefins, *n*-carboxylic acids, ketones, and esters.[3] These adducts, which belong to a type of nonstoichiometric compounds, usually dissociate when exposed to water.[3] Urea also forms complex compounds (apparently stoichiometric) with alkaline salts, alkaline earth salts, and many other salts of metallic elements.[4] It is also reported to form complexes with certain unsymmetrical quaternary ammonium salts containing at least one relatively long hydrocarbon chain.[5] So far there seems to be no report on the crystalline complexes of urea and symmetrical tetraalkylammonium salts.

The symmetrical tetraalkylammonium salts are strong electrolytes, yet their large cations show hydrophobic properties in water in a way somewhat analogous to those of the dissolved hydrocarbons.[6] Interaction of hydrocarbons with urea is known to be rather different from that of urea with simple electrolytes such as alkaline halides.[7] It would be, therefore, of particular interest to study the interaction of urea with tetraalkylammonium salts.

In this paper we are reporting the preparation and characterization of various crystalline complexes formed by urea and symmetrical tetraalkylammonium halides from aqueous solutions. In addition, we have measured the solubilities of urea in aqueous solutions containing these salts at 25° and constructed the phase diagrams for some of the ternary systems.

Experimental Section

Materials. Tetraethyl-, tetra-*n*-propyl-, and tetra-*n*-butylammonium chlorides, bromides, and iodides were obtained from the Eastman Organic Chemicals Department of Distillation Products Industries except $(n\text{-}C_4H_9)_4NCl$. These compounds were purified and dried according to the procedure of Wen and Saito[6] for the bromides and that of Schiff and his co-workers for the chlorides.[8]

$(n\text{-}C_4H_9)_4NCl$ was prepared by the metathesis of a methanol solution of purified $(n\text{-}C_4H_9)_4NI$ with freshly prepared AgCl following the method of Unni and Schiff.[9] This salt, with mp 75°, was handled inside a drybox because of its hygroscopic nature. Melting points of several tetraalkylammonium halides are given in Table I in connection with the melting points of the complexes. Urea used was a Fisher certified reagent, mp 132°.

Preparation of Complexes. Urea and tetraalkylammonium salt were mixed in an appropriate ratio (to be discussed in the next section) and a quantity of water was added to dissolve the solid mixture. When the solution (6–20 *m* in urea concentration) was subjected to its natural evaporation in an open dish at room temperature, crystalline complexes appeared as flat needles or plates depending upon the kind of complex and condition of crystallization. These crystals were collected by filtration, cut to smaller pieces, and pressed between filter papers to remove the mother liquor, then powdered and dried for 30 min in a room at a relative humidity of 30–50% at 25°. This drying procedure is, of course, imperfect and some water may be still "trapped" in crystals without being incorporated into the crystal structure. Calibration of the drying procedure with complexes known to be anhydrous led us to use a value of 0.5% of total weight as the amount of "trapped" water still remaining in the powdered crystals.

Methods of Analysis. Compositions of the complexes were determined by two methods: the "direct" analysis and the Schreinemakers "wet residue" method. In the "direct" analysis, we determined the amount of water in the crystals by heat drying under reduced pressure or by Karl Fischer titration, the amount of salt by the gravimetric analysis of the halide with silver nitrate, and the amount of urea by the difference in weight. In the Schreinemakers "wet residue" method[10] we prepared mixtures of various proportions of the solid components with water and agitated them in a thermostat at 25° until equilibrium was established. The liquid phase was separated from the wet crystals and both were weighed and analyzed. The compositions thus obtained for saturated solution and the wet residue were plotted on a triangular diagram such as Figure 1. If points 1, 2, 3, etc., are a series of points arrived at in this manner for the compositions of saturated solutions and points 1′, 2′, 3′, etc., are the compositions of the corresponding wet residues, a tie line drawn between any corresponding pair of points 1 and 1′, 2 and 2′, 3 and 3′, etc., must pass, on extension past 1′, 2′, 3′, etc., through the composition of the solid complex.

Results

I. Crystalline Complexes and Phase Diagrams.

Bu_4NBr–Urea–Water. Results of applying the Schreinemakers "wet residue" method to this ternary

---

[1] Presented before the Division of Colloid and Surface Chemistry, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, Abstracts, p 24I.

[2] Momotani Juntenkan. Ltd., Ichioka 5, Minatoku, Osaka, Japan.

[3] L. C. Fetterly, "Non-Stoichiometric Compounds," L. Mandelcorn, Ed., Academic Press Inc., New York, N. Y., 1964, pp 491–567.

[4] I. Schaacke, *Naturwissenschaften*, **26**, 411 (1938); W. G. McGavock, J. M. Bryant, and W. W. Wendlandt, *Science*, **123**, 897 (1956); C. S. Pande and M. P. Bhatnager, *Z. Physik. Chem.* (Leipzig), **204**, 183 (1955); P. S. Gentile and L. H. Talley, *J. Am. Chem. Soc.*, **79**, 4296 (1957).

[5] A. W. Weitkamp, J. W. Arkis, and G. W. Fint, U. S. Patent 2,676,955 (April 1954); W. R. Price, Jr., and R. E. Norris, Belgian Patent 634,578 (Nov 1963).

[6] W. Y. Wen and S. Saito, *J. Phys. Chem.*, **68**, 2639 (1964); H. S. Frank and W. Y. Wen, *Discussions Faraday Soc.*, **24**, 133 (1957).

[7] D. B. Wetlaufer, S. K. Malik, L. Stoller, and R. L. Coffin, *J. Am. Chem. Soc.*, **86**, 508 (1964); (b) V. E. Bower and R. A. Robinson, *J. Phys. Chem.*, **67**, 1524 (1963).

[8] A. K. R. Unni, L. Elias, and H. I. Schiff, *ibid.*, **67**, 1216 (1963).

[9] A. K. R. Unni, Ph.D. Thesis, McGill University, Montreal, Canada, 1958.

[10] See, for example, S. H. Maron and C. H. Prutton, "Principles of Physical Chemistry," 3rd ed, Macmillan Co., New York, N. Y., 1958, p 417.

Table I. Some Characteristics of the Crystalline Complexes Formed by Urea and Symmetrical Tetraalkylammonium Halides

Complex	Crystal form, all triclinic	Stoichiometric composition in mole ratio	Mp, °C, of the complex	Mp, °C, of the pure R_4NX
Bu_4NCl–urea	Flat needle	1:6	137–141	75
Bu_4NBr–urea	1. Plate	1:2	117 (p)[a] 133 (c)[b]	119
	2. Flat needle	1:6	135–137 (p) 139 (c)	
Bu_4NI–urea	Flat needle	1:6	114–117 (p) 127 (c)	146
Pr_4NCl–urea	1. Flat needle	1:2	158–162	230
	2. Plate	1:3	132–135 (p) 147–149 (c)	
Pr_4NBr–urea	Flat needle	1:2	131–135	>250
Pr_4NBr–urea–water	Plate	1:3:1	73–80 (p) 117 (c)	>250
Pr_4NI–urea–water	Plate	1:3:1	87–90 (p) 98 (c)	>250
Et_4NCl–urea–water	Flat needle	1:1:0.8	80–82 (p) 90 (c)	>250
Et_4NBr–urea	Flat needle	1:2.5	100–105 (p) 115–118 (c)	>250
Et_4NBr–urea–water	Flat needle	1:1:0.8	50–52 (p) 75 (c)	>250

[a] p, premelting point. [b] c, clearing point.

system are shown in the triangular diagram of Figure 1. Point A represents the solubility of Bu_4NBr in water and point B that of urea in water at 25°. Curve ABC gives the compositions of saturated solutions containing both urea and Bu_4NBr. As shown in the plot, the "wet residue" method indicates the presence of two complexes: complexes D and E. Complex D contains Bu_4NBr and urea in a mole ratio of 1:2 while complex E contains them in a mole ratio of 1:6 and both complexes contain no water. The existence of these two complexes was also confirmed by the "direct" analysis. In the "direct" analysis we prepared a number of aqueous solutions containing urea and Bu_4NBr in various mole ratios and determined the mole ratio of urea to Bu_4NBr in the complexes formed. Figure 2 shows the plot of this mole ratio in crystalline complexes against that in the solution before crystallization. As can be seen from the plot, the mole ratio of urea to Bu_4NBr in complexes is either 2 or 6 in spite of the fact that the solutions were made up in widely different mole ratios. Closer observation reveals that these mole ratios in the crystalline complexes actually depend upon the composition of the liquid solution in which crystallization takes place. This is apparently due to a slight inclusion of the mother liquor into the crystalline complexes. The most probably correct mole ratio in a complex is, therefore, taken to be that obtained from the solution which has the same mole ratio as that of the crystals. Thus the most nearly correct composition of a complex is obtained by reading the intersection of the mole ratio plot with a straight line drawn from the origin with a slope of unity. (The straight line is not shown in the figure.) Crystal forms and melting points of these complexes are given in Table I.

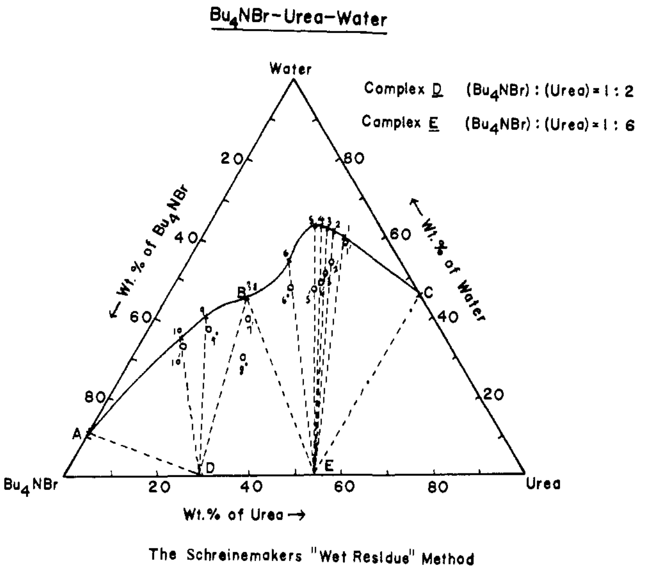

Figure 1. Triangular diagram for the ternary system, Bu_4NBr–urea–water, at 25° by the Schreinemakers "wet residue" method.

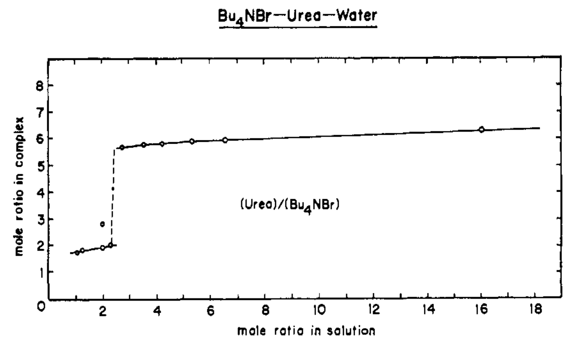

Figure 2. Mole ratio of urea to Bu_4NBr in the crystalline complex plotted against that in the initial solution before crystallization.

Pr_4NBr-Urea-Water. Results of the "wet residue" method and the "direct" analysis method for this ternary system are given in Figures 3 and 4, respectively. Both methods indicate the existence of two complexes:

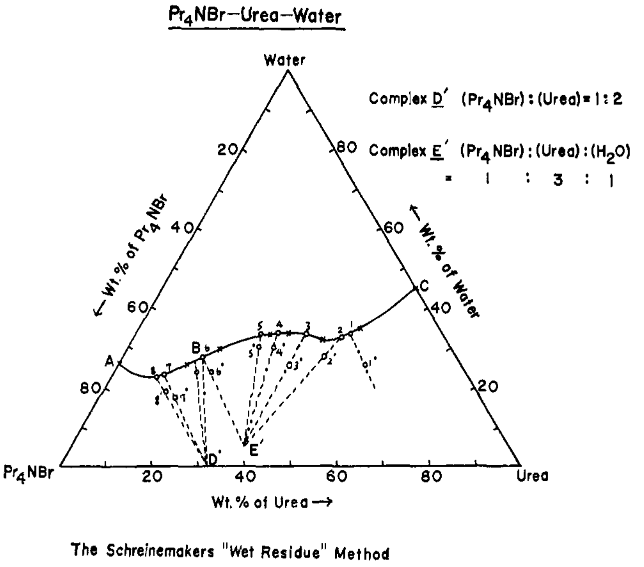

Figure 3. Triangular diagram for the ternary system, Pr_4NBr–urea–water, at 25° by the Schreinemakers "wet residue" method.

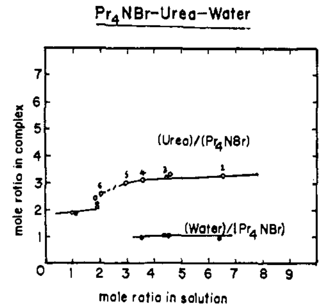

Figure 4. Mole ratio of urea to Pr_4NBr in the crystalline complex plotted against that in the initial solution before crystallization.

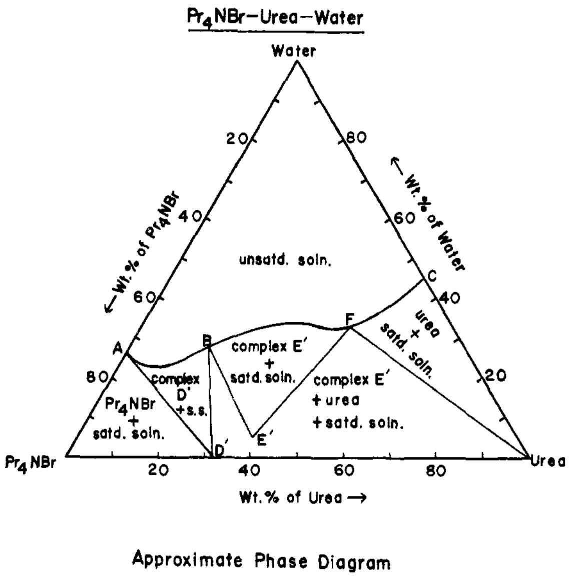

Figure 5. Approximate phase diagram of the ternary system, Pr_4NBr–urea–water, at 25°.

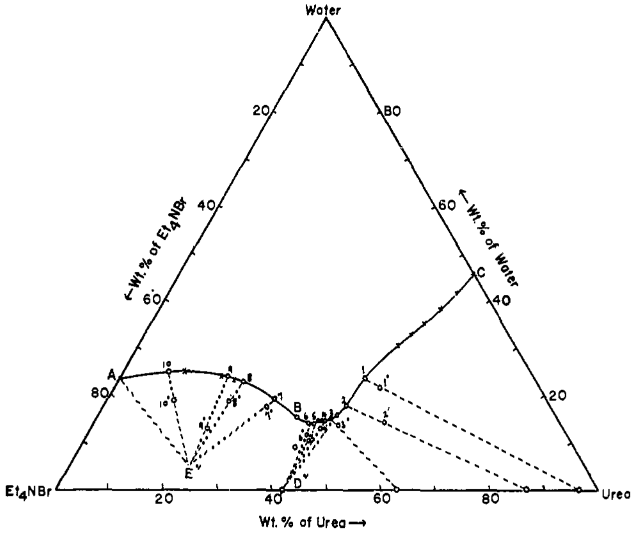

Figure 6. Triangular diagram for the ternary system, Et_4NBr–urea–water, at 25° by the Schreinemakers "wet residue" method.

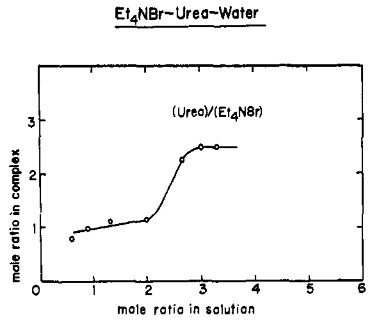

Figure 7. Mole ratio of urea to Et_4NBr in the crystalline complex plotted against that in the initial solution before crystallization.

complex D′ and complex E′. Complex D′ contains Pr_4NBr, urea, and water in a mole ratio of 1:3:1. Crystal forms and melting points of these complexes are given in Table I. The water content in complex E′ was determined by the drying method as well as by the Karl Fischer titration method. Complex E′ became opaque when dried in a desiccator over P_2O_5 under reduced pressure. The originally transparent and colorless crystals turned opaque even when the weight loss was as little as 0.5%. An increase in the melting point was observed when the complex was thoroughly dried. When the dried complex was allowed to absorb moisture back from the air, its melting point decreased to the original value. The approximate phase diagram for the ternary system at 25° is given in Figure 5.

Et_4NBr–Urea–Water. Figures 6 and 7 show results obtained for this ternary system. Both methods indicate the existence of two complexes: complex D″ and complex E″. Complex D″ contains Et_4NBr and urea in a mole ratio of 1:2.5 while complex E″ contains Et_4NBr, urea, and water in a mole ratio of 1:1:0.8. (Water content given here is an approximate value.) Both complexes have substantially lower melting ranges than the corresponding complexes formed by the larger tetraalkylammonium bromides indicating their low stability (see Table I).

Bu_4NCl–Urea and Bu_4NI–Urea. Both of the binary complexes were found to contain salt and urea in a mole ratio of 1:6 by the "direct" method. The mole ratio of 1:6 was obtained for the Bu_4NI–urea complex by extrapolation. The mole ratio line in Figure 8 (showing a mole ratio of around 1:7) was extrapolated to a lower mole ratio region and its intersection with a straight

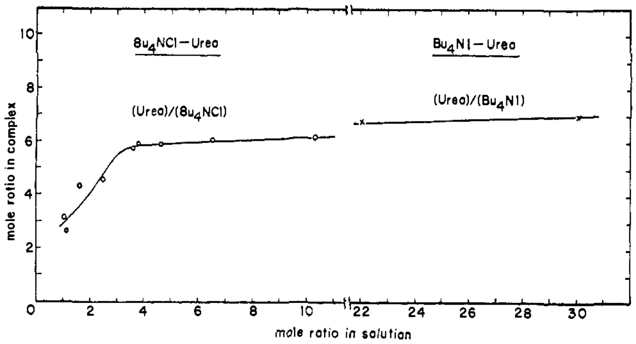

Figure 8. Mole ratio of urea to salt in the crystalline complex plotted against that in the initial solution before crystallization; salt: Bu_4NCl and Bu_4NI.

line, drawn from the origin with a slope of unity, was found to give 1:6 mole ratio. The reason for the rather high mole ratios of urea to Bu_4NI in solutions as indicated in the figure is the low solubility of Bu_4NI in water, and we could obtain crystals only from solutions with high urea concentrations. Both complexes contain no water and showed no change of melting points with drying. The crystal forms and melting points are given in Table I.

Pr_4NCl–Urea. Pr_4NCl and urea form two kinds of binary complexes with the salt to urea mole ratio of 1:2 and 1:3 as shown in Figure 9a and Table I.

Pr_4NI–Urea–Water. Pr_4NI forms a ternary complex with urea and water in a mole ratio of 1:3:1. Properties of this complex are found to be similar to those of the Pr_4NBr–urea–water complex described above. (See Figure 9b and Table I also.)

Et_4NCl–Urea–Water. Et_4NCl forms a ternary complex with urea and water in a mole ratio of 1:1:0.8 as shown in Figure 9c in analogy to the ternary complex of Et_4NBr–urea–water (water content is approximate).

Bu_4NBr–Urea. In addition to the room temperature preparation of the binary complexes mentioned earlier, we carried out the complex formation at 3°. It was found that Bu_4NBr forms two complexes with urea in exactly the same compositions as those formed at room temperature (1:2 and 1:6 for the mole ratio of salt to urea). When the salt solution contained enough water as well as urea at 3°, there existed a possibility of forming a clathrate hydrate, $Bu_4NBr \cdot 32.8H_2O$, mp 12.5°, in addition to the Bu_4NBr–urea complexes. But no clathrate hydrate was found to form when enough urea was dissolved in the solution. We have found also that thiourea and tetraalkylammonium salts form similar crystalline complexes from aqueous solutions. These are now under investigation.

II. Solubilities of Urea in Aqueous Solutions Containing Tetraalkylammonium Salts at 25°. The solubility of urea in pure water at 25° is 19.86 *m*. We have studied the change of solubility of urea in water when tetraalkylammonium salts were added. The solubility of urea is expressed in molality, *i.e.*, number of moles of urea per 1000 g of water in the ternary system. The results obtained are given in Table II. Any number shown with an asterisk as a superscript expresses the remaining urea concentration in the solution from which the crystalline complex has separated out. In this sense the numbers with asterisks are not solubilities of urea and are given in the table to indicate the formation of a crystalline complex.

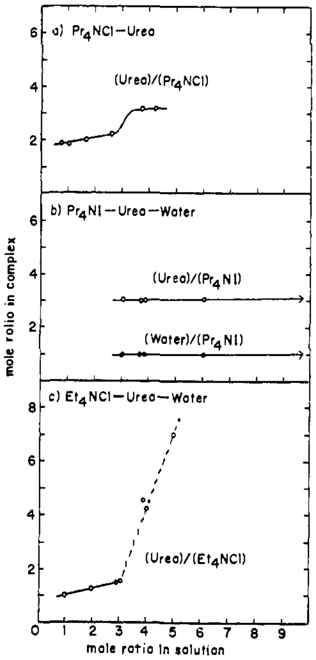

Figure 9. Mole ratio of urea to salt in the crystalline complex plotted against that in the initial solution before crystallization; (a) Pr_4NCl, (b) Pr_4NI, and (c) Et_4NCl.

Table II. Solubilities of Urea in Aqueous Solutions Containing Tetraalkylammonium Salts at 25°[a] (moles per 1000 g of water)

Bu_4NCl	Urea	Bu_4NBr	Urea	Bu_4NI	Urea
0.092	19.98	0.042	20.04	0.054	19.98
0.142	20.02	0.074	19.99	0.111	20.26
0.186	19.44*	0.087	19.51*	0.212	17.09*
0.277	15.94*	0.223	11.96*	0.330	15.23*
Pr_4NCl	Urea	Pr_4NBr	Urea	Pr_4NI	Urea
0.126	20.03	0.168	20.07	0.214	20.38
0.709	20.49	0.772	21.23	0.327	20.80
0.997	20.40	1.569	22.52	0.484	20.61*
2.682	22.65	2.247	23.52	0.499	15.20*
4.254	22.60	2.479	22.71*		
		2.802	19.50*		
Et_4NCl	Urea	Et_4NBr	Urea	Et_4NI	Urea
0.244	20.31	0.303	20.47	0.219	20.29
0.618	20.84	0.878	21.35	0.534	20.94
1.093	21.59	1.047	21.69	0.828	21.53
1.856	22.59	1.060	21.63	1.625	22.43
		1.251	22.18	2.243	23.16
		1.953	23.89		
		3.360	26.30		
Me_4NCl	Urea	Me_4NBr	Urea	Me_4NI	Urea
0.518	20.34	0.533	20.58	0.288	20.40
0.998	20.73	1.580	21.59	0.830	21.38
1.774	21.35	2.722	22.69		

[a] An asterisk denotes the remaining urea concentration in the solution from which the crystalline complex has separated out. In this context those numbers with * are not solubilities of urea and are given here to indicate the formation of a crystalline complex.

The data of Table II are plotted in Figure 10 with the ordinate indicating the molality of urea and the abscissa denoting the molality of an added salt. As can

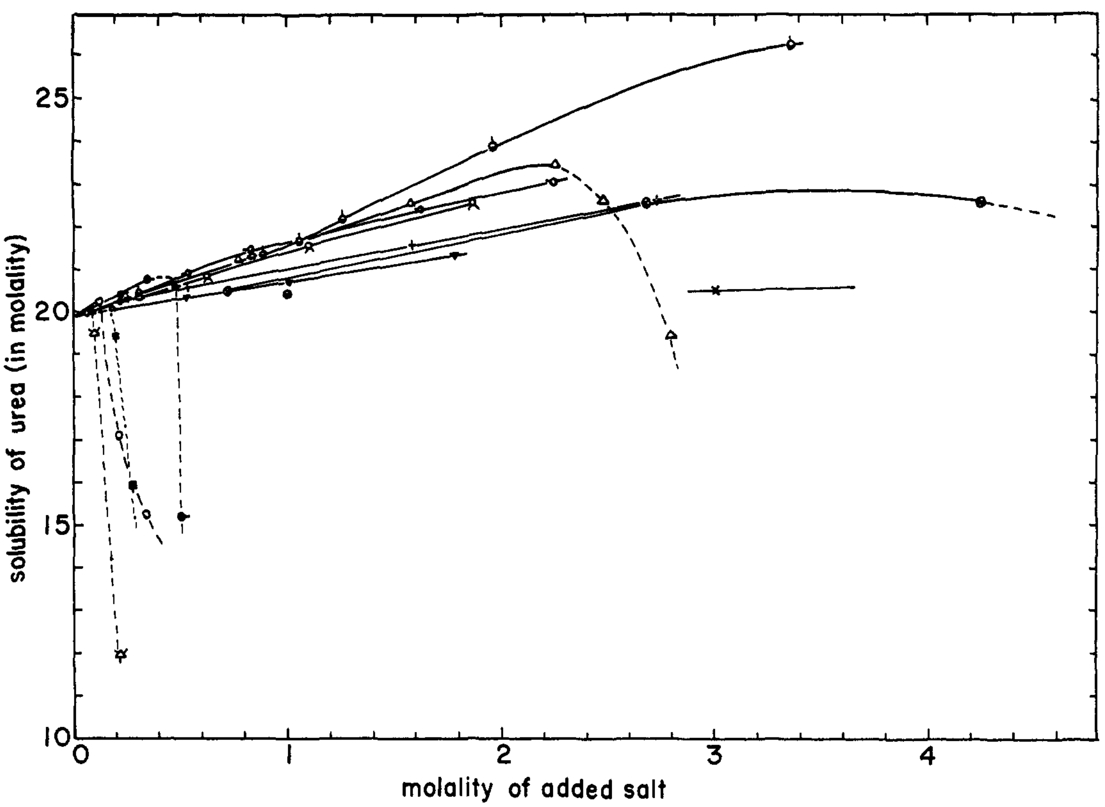

Figure 10. Solubility of urea in aqueous solutions plotted against the molality of an added tetraalkylammonium salt at 25°. Dotted lines indicate concentrations of urea in solutions when crystalline complexes formed: Bu_4NCl, ▼; Bu_4NBr, ☆; Bu_4NI, ○; Pr_4NCl, ⊗; Pr_4NBr, △; Pr_4NI, ●-; Et_4NCl, ♀; Et_4NBr, ◊; Et_4NI, -◑; Me_4NCl, ▼; Me_4NBr, +; Me_4NI, ○; NaCl, ×.

be seen from Figure 10, the solubility of urea generally increases with the addition of a tetraalkylammonium salt until the formation of a crystalline complex takes place. With the complex formation the concentration of urea decreases sharply with a further increase in the salt concentration.

In general, when the concentration of added tetraalkylammonium salts is too low to induce any crystalline complex formation, the iodides cause the greatest increase in the solubility of urea while the bromides cause the next greatest increase, and the chlorides the smallest increase. Among the salts with identical anion and different cations, tetrabutylammonium salts cause the greatest increase in the solubility of urea at the very low concentration range but bring about the complex formation at the lowest concentration in comparison with the corresponding tetrapropyl and tetraethylammonium halides. At moderate concentrations (2–4 *m*) Et_4NBr seems to cause the largest increase in the solubility of urea partly because this salt does not induce a complex formation until a rather high salt concentration. Tetramethylammonium halides also bring about an increase in urea but to a much lesser extent than the corresponding tetraethylammonium halides. Though relatively small these effects are still appreciable when compared to the effect of NaCl addition, reported to be very little.[7b]

Discussion

From the solubility measurements in aqueous solutions it seems to us that the tetraalkylammonium salts show a "salting-in" effect toward urea. The "salting-in" effect increases with the cationic and anionic size of the salts until it results in the crystalline complex formation. The strong "salting-in" effect should cause a considerable lowering of activity coefficients of urea and the salts. Since NaCl shows almost no "salting-in" effect toward urea our results seem to present an interesting contrast to the NaCl–urea–water system.[7b] The measurements of activity coefficients of urea and the salts employing the isopiestic comparison method would be a logical next step in the investigations of these systems.

Most of the crystalline complexes obtained showed rather wide ranges of melting temperatures. We characterized the melting of a complex by observing temperatures which indicate a start of melting (premelting point) and an end of melting (clearing point). These temperatures are usually different from the melting points of either component (urea or R_4NX) as shown in Table I. On examining Table I we noticed the fact that the melting temperatures for complexes of the type $Bu_4NX \cdot 6CO(NH_2)_2$ (where X represents Cl, Br, or I) having flat needle forms decrease in the order chloride > bromide > iodide, indicating the crystal lattice stability of the complexes to be the greatest for the chloride, next for the bromide, and the lowest for the iodide. The chloride complex has a melting temperature considerably higher than that of pure salt (75°) and even slightly higher than that of pure urea (132.7°). Pure Bu_4NCl is very hygroscopic, but its urea complex is not hygroscopic at all, indicating the ability of Bu_4NCl to bind urea more strongly than water. In the absence of any significant ion–dipole interaction between the large Bu_4N^+ ion and the urea molecule, the difference in melting temperatures of the salt–urea complexes under discussion seems to indicate the presence of some strong ion–dipole interaction between halide ions and urea molecules. Halide ion size should influence not only the strength of the ion–dipole interaction but also the spatial arrangement of the lattice which determines the crystal stability. Similar statements can be made about complexes $Pr_4NX \cdot 2CO(NH_2)_2$ (where X represents Cl or Br but not I) which do not contain water. Pure salts of Pr_4NBr and Pr_4NI are not hygroscopic but they can form complexes with urea which contain water, $Pr_4NX \cdot 3CO(NH_2)_2 \cdot H_2O$ (where X represents Br or I but not Cl). When these complexes are dried, the anhydrous 1:3 complexes remain which can reabsorb moisture and transform back to the original 1:3:1 complexes.

For the understanding of the crystal structure of these complexes one has to wait a detailed X-ray structural analysis. We may, however, say a few words about the structure of these crystalline complexes. The crystal structure of R_4NX–urea binary complexes is certainly not that of urea–*n*-paraffin hydrocarbon complexes in which urea molecules form a channel to accommodate the planar zigzag hydrocarbon molecule. The binary complexes are most likely to have cage structures in which a host component forms a cage-like network imprisoning a guest component. The host cages may be formed by urea molecules and halide ions, while R_4N^+ ions are the guest locating inside the appropriate cages. This kind of arrangement may be considered to be somewhat analogous to the clathrate hydrates formed by some tetra-*n*-butylammonium salts in which water molecules and anions form the mixed host and Bu_4N^+ ions the guest.[11] The structure will be more complicated for the ternary complexes of R_4NX–urea–water. Our speculation will place water molecules as part of the mixed host, hydrogen bonded to urea molecules and halide ions. R_4N^+ ions probably remain as the only guest in the clathrate structures.

Acknowledgments. This research was supported by the Public Health Service (Grant No. GM-11684) and the United States Department of the Interior, Office of Saline Water (Grant No. 14-01-0001-456).

---

(11) R. McMullan and G. A. Jeffrey, *J. Chem. Phys.*, 31, 1231 (1959); D. Feil and G. A. Jeffrey, *ibid.*, 35, 1863 (1961); R. K. McMullan, M. Bonamico, and G. A. Jeffrey, *ibid.*, 39, 3295 (1963).

Organometallic Electrochemistry. V. The Transition Series

Raymond E. Dessy,[1] R. Bruce King,[2] and Morgan Waldrop[3]

Contribution from the Departments of Chemistry, Virginia Polytechnic Institute, Blacksburg, Virginia, and the University of Georgia, Athens, Georgia, and the Research Laboratories of Phillips Petroleum Co., Bartlesville, Oklahoma.

Received May 23, 1966

Abstract: In a continuation of the report made in paper IV[4] of this series, 65 additional transition metal derived organometallics have been studied electrochemically in dimethoxyethane.

The organometallic electrochemistry of σ-bonded derivatives of groups IIb and IVa has been previously described.[5] The basic technique involves polarographic, cyclic triangular voltammetric, and controlled potential electrolytic studies on organometallic species dissolved in dimethoxyethane with Bu_4NClO_4 as supporting electrolyte. Coupled with ultraviolet spectroscopy considerable information can be obtained concerning the fate of the organometallic assembly RmQ, when an electron is added or removed. The symbol m represents a metal, M, and a less than normal number of valence positions. The present paper presents further findings in the transition metal derived materials, involving σ- or π-complexed derivatives. For convenience of discussion the compounds in the present study are numbered consecutively from paper IV of this series which discusses 65 other compounds.[4]

Experimental Section

The experimental details have been described previously.[4] All solutions for electrochemical studies were 2×10^{-3} *M*.

The compounds used were obtained largely from various projects currently active at the Mellon Institute, or from commercial sources when available. Where necessary, further purification was accomplished by standard methods, until a polarographically "clean" material was obtained.

Electron spin resonance spectra were obtained using a classical cell designed around a Pt counter electrode and a Hg test electrode, the two being separated by a large medium-fritted disk. The reference electrode (10^{-3} *M* $AgClO_4|Ag$) was placed as near the pool as possible. Transfer of the electrolyzed solutions to the 3-mm i.d. quartz esr cells was accomplished *via* and through appropriate arrangement of three Delmar O-ring valves, the normal Viton seat being replaced by Teflon and the barrel rings by low-temperature silicon rings. Evacuation of the esr cell and leads to the electrolysis cell, followed by isolation from the vacuum pump, allowed rapid transfer of the electrochemically generated species. The esr cell was attached to the electrolytic cell by an O-ringed (Viton) ball and socket joint. All solutions were 4×10^{-3} *M*. Where it appeared that hyperfine structure might be contained in a single absorption envelope, the esr spectra were measured at temperatures down to the freezing point of the solvent (−70°). The measurements were made with standard Varian equipment in the chemical laboratory, Phillips Petroleum Co.

---

(1) Department of Chemistry, Virginia Polytechnic Institute.

(2) Department of Chemistry, University of Georgia.

(3) Phillips Petroleum Co.

(4) R. E. Dessy, *et al.*, *J. Am. Chem. Soc.*, 88, 471 (1966).

(5) R. E. Dessy, *et al.*, *ibid.*, 88, 453, 460, 467 (1966).