ON THE MOLECULAR VOLUME OF UREA IN COMPLEX IONS.

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Complex salts which contain six molecules of urea co-ordinating with various central metallic atoms in their cations were recently prepared by Okuda and Fujikawa(1), P. Pfeiffer(2), and G. A. Barbieri(3)(4). The present author has studied the molecular volume of urea in complex ions of the complex salts given by the former authors, in order to know

(1) *J. Chem. Soc. Japan*, **40** (1919), 404.
(2) P. Pfeiffer, *Ber.*, **36** (1903), 1926.
(3) Univ. Ferrara, *Atti. accad. Lincei*, **22** (1913), 867; *C. B.*, **1913**, II, 1034; *C.A.*, **7** (1913), 3937.
(4) Univ. Ferrara, *Atti. accad. Lincei*, **24** (1915), 916; *C.B.*, **1916**, I, 924; *C.A.* **9** (1915), 2852.

whether organic molecules contained in a complex ion as "Ligand" generally hold or not the same molecular volume as those in free state.

The following six complex salts were thus used in this study:

$[Ca(ur)_6{}^*]Br_2$[1], $[Ca(ur)_6]I_2$[1], $[Cr(ur)_6]Cl_3 \cdot 3H_2O$[2], $[Fe(ur)_6]Cl_3 \cdot 3H_2O$[3], $[Al(ur)_6]I_3$[4], $[Al(ur)_6](ClO_4)_3$[4].

Experimentals.

(I) **Specific Gravity Determination.** The determination of the specific gravities of the complex salts mentioned above was performed by the pycnometer method, benzene being used as displacement liquid, for these complex salts are all easily soluble in water. The calculation was made by the following formula:

$$d = \frac{a \cdot s_1}{a+b-c},$$

where a is the weight of the complex salt taken, b the weight of the pycnometer filled with benzene, c the weight of the pycnometer charged with the complex salt and benzene, and s_1 the density of benzene. The results of the observations are given in Table 1.

Table 1.

Molecular formula	Molecular weight	Density D_4^{20}	Molecular volume
C_6H_6	—	0.8778	—
$[Ca(ur)_6]Br_2$	560.20	1.6495	339.62
$[Ca(ur)_6]I_2$	655.20	1.8941	345.91
$[Cr(ur)_6]Cl_3 \cdot 3H_2O$	572.71	1.4774	387.65
$[Fe(ur)_6]Cl_3 \cdot 3H_2O$	576.54	1.5014	384.00
$[Al(ur)_6]I_3$	768.01	1.9973	384.52
$[Al(ur)_6](ClO_4)_3$	685.62	1.7245	397.56
$CO(NH_2)_2$	60.05	1.3289	45.19

(II) **Calculation of Molecular Volume of Urea in Complex Ions.** (1) $[Ca(ur)_6]Br_2$ and $[Ca(ur)_6]I_2$. As shown in Table 2, the molecular volume of urea calculated from the iodide is in good accordance with its value in the free state, but the value obtained from the bromide is somewhat larger than the former.

* The symbol ur represents the molecular formula of urea, $CO(NH_2)_2$.

Table 2.

Salt	$[M(ur)_6]X_2$		MX_2		Molecular volume of urea in complex ion
	D_4^{20}	Molecular volume	D_4^{25}	Molecular volume	
$[Ca(ur)_6]Br_2$	1.6495	339.62	3.352[5]	59.64	46.66
$[Ca(ur)_6]I_2$	1.8941	345.91	3.956[5]	74.29	45.27

(2) $[Cr(ur)_6]Cl_3$ and $[Fe(ur)_6]Cl_3$. These two complex salts contain trivalent metallic central atoms, and the calculated values of molecular volume of urea are practically equal in both cases and do not differ very much from the theoretical within the limit of observation errors, Table 3.

Table 3.

Salt	$[M(ur)_6]X_3 \cdot 3H_2O$		MX_3		Volume of $(ur)_6 \cdot 3H_2O$	Molecular volume of H_2O[7]	Molecular volume of urea[8]
	D_4^{20}	Molecular volume	D_4^{25}	Molecular volume			
$[Cr(ur)_6]Cl_3 \cdot 3H_2O$	1.4774	387.65	2.784[6]	56.89	330.76	19.87	46.10
$[Fe(ur)_6]Cl_3 \cdot 3H_2O$	1.5014	384.00	2.898[6]	55.97	328.03	18.96	45.65

Each of these salts contains three molecules of water of crystallisation, and the author tried also to calculate the molecular volume of water in these complex salts. Formerly W. Biltz obtained 14.4 as the mean molecular volume of water in various complex ions, but the values found by the present author are 19.87 and 18.96[7]. Therefore, it may be said that water molecules existing outside a complex ion show a nearly normal but considerably larger value than that obtained by Biltz for water as "Ligand" in complex ions.

(3) $[Al(ur)_6]I_3$ and $[Al(ur)_6](ClO_4)_3$. From the iodide, a nearly normal value for the molecular volume of urea was again obtained, Table 4.

(5) Baxter and Brink, *J. Am. Chem. Soc.*, **30** (1908), 46; Ruff and Plato, *Ber.*, **32** (1902), 1577.

(6) W. Biltz and Birk, *Z. anorg. Chem.*, **134** (1924), 125.

(7) In this case the calculation was done by taking the normal value, 45.15 for the molecular volume of urea.

(8) In this case the calculation was done by taking the normal value, 18.05 at 20°C. for the molecular volume of water.

Table 4.

Salt	$[Al(ur)_6]I_3$		AlI_3		Molecular volume of urea
	D_4^{20}	Molecular volume	D_4^{20}	Molecular volume	
$[Al(ur)_6]I_3$	1.9973	384.52	3.98	102.5(9)	46.98

In order to calculate this value from the perchlorate, the molecular volume of anhydrous aluminium perchlorate must be found by an indirect way, because its density is yet unknown. For this reason the author chose the two hydrated salts, $[Al(H_2O)_6](ClO_4)_3$ and $[Al(H_2O)_6](ClO_4)_3 \cdot 3H_2O$, for the purpose of calculation of the molecular volume of anhydrous aluminium, Table 5.

Table 5.

Salt	D_4^{20}	Molecular volume	Volume of water (as H_2O, in complex ion = 14.4 and crystalline water = 19.42)			Molecular volume of $Al(ClO_4)_3$
			In complex ion	Water of cryst.	Total	
$[Al(H_2O)_6](ClO_4)_3$	2.1678	199.95	86.4	—	86.4	113.55
$[Al(H_2O)_6](ClO_4)_3 \cdot 3H_2O$	1.9260	253.10	86.4	58.26	144.66	108.44

The mean value 111.00 thus obtained was used for the further calculation of the molecular volume of urea in the aluminium-urea-complex salt.

Table 6.

Salt	D_4^{20}	Molecular volume	Molecular volume of $Al(ClO_4)_3$	Molecular volume of urea
$[Al(ur)_6](ClO_4)_3$	1.7245	397.56	111.00	47.76

The value given in Table 6 is somewhat larger than those obtained from other urea-complex salts. But considering that the last case involves very possibly certain errors in result, because the calculation has been done in a roundabout way, it may perhaps be concluded that the molecular volume of urea does not deviate from its normal value also in the perchlorate.

(9) Biltz and co-worker, *Z. anorg. Chem.*, **121** (1922), 257.

Summary

(1) The molecular volume of urea, which is contained in complex ions of various metallic complex salts, was determined. The average value thus obtained was found nearly equal to the theoretical.

(2) The molecular volume of water which exists as the water of crystallisation in some urea metallic complex salts was also calculated, and found normal, while Biltz gives distinctly smaller values for water contained in complex ions as "Ligand".

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