

and Fig. 1). The titrations were carried out over a twenty-fold variation in the total metal chelate concentration, in order to determine the presence of polymeric species.

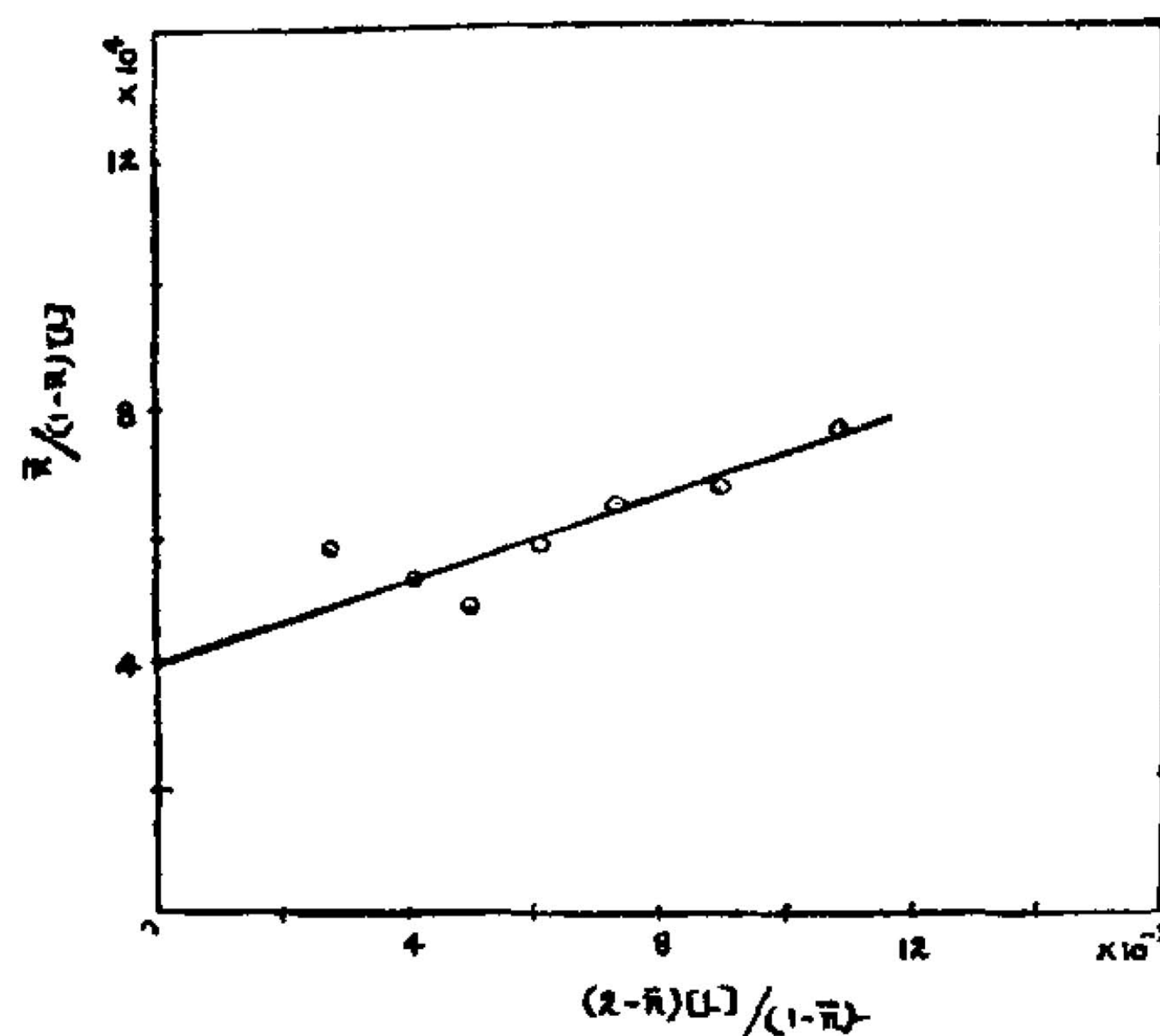


FIG. 1. Uranyl ion-thiosalicylic acid system.

$\mu = 0.1 \text{ M (NaClO}_4\text{)}$   $T = 30^\circ \pm 0.1^\circ \text{ C}$

Plot of  $\bar{n}/(1-\bar{n}) [L]$  versus  $(2-\bar{n}) [L]/(1-\bar{n})$

$$\text{Slope} = \frac{K_{ML_1} K_{ML_2}}{K_{ML_1} + K_{ML_2}} = 3.235 \times 10^8$$

$$\text{Intercept} = K_{ML_1} = 4.000 \times 10^4$$

### COMPLEXES OF URANYL ION WITH SOME AMINO AND MERCAPTO ACIDS

SYSTEMATIC aqueous pH titrations at  $30^\circ \pm 0.1^\circ \text{ C}$ . and  $\mu 0.1 \text{ M (NaClO}_4\text{)}$  on systems of uranyl ion—cysteine; methionine; N-acetyl glycine and thiosalicylic acids have been carried out by us with a view to determine the composition(s) and stability constant(s) of complex(es) formed. The chemicals used were all of AnalaR grades. The pH meter (Universal Pye; cat. 10085) with a built-in calomel glass electrode was used and the recorded pH values were accurate to  $\pm 0.02$ . Data of pH  $> 3.5$  (hydrolysis) were not used in the calculations. Due to the low solubility of thiosalicylic acid in water, a 50% dioxan-water mixture was used for that system only. Dissociation constants of the ligand acids were determined by the conventional method<sup>1</sup> for amino-acids and by slope and intercept method due to Irving and Rossotti<sup>2</sup> for other acid ligands. Values of  $\bar{n}$  and pL were calculated from the pH titration curves by the method adopted by Albert<sup>3</sup> for amino-acids and that by Irving and Rossotti<sup>2</sup> for other systems. Values of the stability constants of the metal complexes were evaluated from the slope and intercept<sup>4</sup> by least squares treatment (Table I

We conclude from our results that :

- (i) 1 : 1 complexes were formed with cysteine and N-acetyl glycine ;
- (ii) 1 : 1 and 1 : 2 complexes were formed with methionine and thiosalicylic acids ;
- (iii) absence of polymeric species of the chelates was indicated by the observed decreasing  $K_{ML}$  values with increasing total metal chelate concentration ( $5 \times 10^{-4} \text{ M}$  to  $1 \times 10^{-2} \text{ M}$ );
- (iv) both amino and carboxylic groups are involved in co-ordination to uranyl ion with further stabilization by S atom in the case of cysteine and without stabilization by S in the case of methionine as evidenced from the order of stability constants (Table);

TABLE I

Equilibrium constants of systems of uranyl ion with some amino and mercapto acids

$\mu = 0.1 \text{ M (NaClO}_4\text{)}$

$T = 30^\circ \pm 0.1^\circ \text{ C}$

System	Dissociation constant of ligand			Stability constant of complex		
	pK <sub>COOH</sub>	pK <sub>SH</sub>	pK <sub>NH<sub>3</sub><sup>+</sup></sub>	Log K <sub>ML<sub>1</sub></sub>	Log K <sub>ML<sub>2</sub></sub>	
1. Uranyl ion-cysteine	..	1.65	8.27	10.66	9.04	..
2. Uranyl ion-methionine	..	2.12	..	9.05	7.45	6.30
3. Uranyl ion-N-acetyl glycine	..	3.65	..	..	3.30	..
4. Uranyl ion-thiosalicylic acid	..	5.10	..	..	4.60	3.91



- (v) a complex involving only the COOH group and not involving the nitrogen atom was formed in uranyl - N-acetyl glycine system as evident from the stability value being comparable to that of complexes of uranyl ion with simple carboxylic acids<sup>5,6</sup>; and
- (vi) the -SH group of thiosalicylic acid is probably involved in co-ordination to uranyl ion in addition to -COOH group as evidenced by the higher stability value of UO<sub>2</sub>-thiosalicylic acid system than uranyl-N-acetyl glycine and development of red colouration. Our results agree with the earlier work of Kumar and co-workers<sup>7</sup> who reported only the composition of the complexes of uranyl ion-thiosalicylic acid to be 1:1 and 1:2.

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Dept. of Physical Chemistry,  
University of Madras,  
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A. RAGHAVAN.  
M. SANTAPPA.

1. Greenstein, J. P. and Winitz, M., *Chemistry of the Amino-Acids*, 1961, 1, 476.
2. Irving, H. M. and Rossotti, H. S., *J. Chem. Soc.*, 1954, p. 2904; *Ibid.*, 1953, p. 3397.
3. Albert, A., *Biochem. J.*, 1952, 50, 693.
4. Rossotti, F. J. C. and Rossotti, H. S., *Acta Chem. Scand.*, 1955, 9, 1166.
5. Ramamoorthy, S. and Santappa, M., *Bull. Chem. Soc., Japan*, 1969, 42, 411.
6. —, Raghavan, A. and Santappa, M., *J. Inorg. Nucl. Chem.*, 1969, 31, 1765.
7. Kumar, A. N., Nigam, H. L. and Katyal, M., *Bull. Chem. Soc., Japan*, 1967, 40, 788.