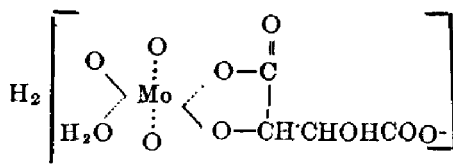


PHYSICO-CHEMICAL STUDIES OF COMPLEX FORMATION
BETWEEN MOLYBDIC AND TARTARIC ACIDS. PART II.
STUDIES ON THE OPTICAL ROTATION PROPERTIES
OF MOLYBDOTARTARIC ACID COMPLEX IN PRESENCE
OF DIFFERENT BASES, ACIDS AND ALCOHOLS

By ANIL BHUSAN BISWAS

The stability of complex molybdotartaric acid in different pH and in solutions containing suitable organic acids, alcohols and phenols which are expected to form similar co-ordination complex as tartaric acid, has been examined by measuring optical rotatory power. The change of the rotation values of such complex solution has been associated mainly with the preferential formation of the undissociated acid or its ions between pH limits 1.0 and 4.2 and the complex breaks beyond that on either side. The relative affinities of oxalic, malonic, succinic, citric and malic acids for complex formation with molybdic acid in solution containing tartaric acid are calculated from optical rotation values.

In Part I of the series (*J. Indian Chem. Soc.*, 1945, 22, 351) the cause of enhanced rotation exhibited by a solution of *d*-tartaric acid in presence of molybdic acid, has been ascribed to the formation of a co-ordination complex compound,



The normal molybdate ion (MoO_4^{2-}) is known to be unstable in acidic medium and so it readily co-ordinates with other similar ions to form polymolybdates or with the tartrate ion when present in the solution, to form molybdotartrate complex. But the molybdate ion is stable in neutral or alkaline solutions and hence in these systems, the complex compound formation cannot be expected.

If to a solution containing molybdotartrate complex another inactive organic acid, whose anion also is capable of forming a co-ordination complex with molybdate ion, is added, a new equilibrium condition will be attained; the concentration of the two complex compounds from the two organic acids will depend on their relative affinities for molybdate ion, and thus it may be possible to compare, from changes in optical rotation values, the relative affinities of different co-ordinating substances.

Another factor which affects the stability of complex in cases where the groups occupy two co-ordination points, as indicated in the present case, is the length of the closed chain. Five-membered ring is more easily formed than higher ones as can be tested by adding substances which can form closed chain compounds of higher order.

In the present investigation, we have studied (1) the stability of molybdotartrate complex at different pH adjusted by adding strong and weak bases and

also by strong and weak acids which have little tendency for complex formation ; (2) the relative affinity of tartaric acid for complex formation with molybdc acid in presence of similar organic hydroxy-acids or phenols and alcohols which also can form similar complexes ; and (3) the relative tendency of molybdc acid to form five or more membered closed chain compounds.

EXPERIMENTAL

The influence of the following substances on the optical rotation values of molybdotartaric acid complex in solution has been observed, the rotations having been measured similarly as described in Part I using a 0.54 dm. tube at 25°.

(a) Bases	Caustic soda and ammonia
(b) Acids	HCl, H ₂ SO ₄ , CH ₃ COOH and mono-, di-, and tri-chloroacetic acids
(c) Dibasic carboxylic acids	Oxalic, malonic and succinic acids
(d) Hydroxy-acids	Citric and malic acids
(e) Phenols and alcohols	Catechol, salicylic acid and glycerol.

Action of Bases like NaOH and NH₄OH.

The neutralisation of a solution containing 0.0252M-molybdc acid (calculated as MoO₃) and 0.0252M-H₂T (tartaric acid) with 0.838N-NaOH (representative of a strong base) and 0.873N-NH₄OH (representative of a weak base) has been followed to see whether the nature of the base has any influence on the rotation values or in rotation-neutralisation curves at any stage. The results are presented in Tables IA and IB.

TABLE IA

$\frac{\text{NaOH}}{\text{H}_2\text{T}}$	Observed rotations at wave-lengths			
	690 μ .	578 μ .	516 μ .	436 μ .
0.00	+0.44	+0.53	+0.62	+1.16
0.53	+0.52	+0.65	+0.75	+1.43
1.59	+0.71	+0.80	+1.01	+2.05
2.12	+0.62	+0.76	+0.87	+1.74
3.44	+0.14	+0.20	+0.22	+0.37
4.24	+0.07	+0.11	+0.13	+0.24

TABLE IB

$\frac{\text{NH}_4\text{OH}}{\text{H}_2\text{T}}$	Observed rotations at wave-lengths			
	690 μ .	578 μ .	546 μ .	436 μ .
0.55	+0.53	+0.67	+0.74	+1.44
1.65	+0.70	+0.91	+1.02	+2.06
2.21	+0.80	+0.77	+0.88	+1.75
3.59	+0.11	+0.14	+0.16	+0.30
4.32	+0.05	+0.06	+0.10	+0.18

The behaviour of pure tartaric acid solution during similar neutralisation with NaOH has also been examined and the results are represented in Table II.

TABLE II

Titration of 0.0988M-H₂T solution with N/2-NaOH.

$\frac{\text{NaOH}}{\text{H}_2\text{T}}$	Observed rotations at wave-lengths			
	690 μ .	578 μ .	546 μ .	436 μ .
0.00	+0.12	+0.13	+0.15	+0.20
0.84	+0.18	+0.19	+0.22	+0.32
1.69	+0.23	+0.26	+0.32	+0.50
2.10	+0.25	+0.32	+0.35	+0.55
2.94	+0.26	+0.32	+0.36	+0.55

The Action of HCl, H₂SO₄, Acetic acid and its three Chloro-acids.

These acids are of widely different strengths and their relative influences on a complex acid solution are noted in Tables IIIA and IIIB below.

TABLE III A

Influence of H₂SO₄ and HCl on a solution containing 0.0252M-MoO₃ + 0.0252 M-H₂T.

Conc. of the acid.	pH.	Observed rotations at wave-lengths			
		690 $\mu\mu$.	578 $\mu\mu$.	546 $\mu\mu$.	436 $\mu\mu$.
		H ₂ SO ₄			
0.00M	1.99	+0.44	+0.54	+0.62	+1.18
0.03	1.31	+0.34	+0.44	+0.52	+0.98
0.06	0.86	+0.26	+0.36	+0.42	+0.78
0.09	0.80	+0.23	+0.26	+0.32	+0.62
0.15	0.63	+0.20	+0.23	+0.27	+0.53
		HCl			
0.00M	1.99	+0.44	+0.54	+0.62	+1.20
0.01	1.70	+0.38	+0.50	+0.58	+1.14
0.04	1.27	+0.34	+0.43	+0.56	+0.96
0.09	0.84	+0.26	+0.34	+0.42	+0.80
0.19	0.65	+0.21	+0.25	+0.29	+0.59

TABLE III B

Influence of acetic acid and its three chloro-acids on the optical rotation of a solution containing 0.0241M-MoO₃ + 0.0241M-H₂T.

Conc. of acid.	pH.	Observed rotations at wave-lengths			
		690 $\mu\mu$.	578 $\mu\mu$.	546 $\mu\mu$.	436 $\mu\mu$.
		Acetic acid. $K=1.8 \times 10^{-5}$			
0.00M	2.02	+0.41	+0.50	+0.60	+1.11
0.12	1.98	+0.40	+0.48	+0.59	+1.10
0.97	1.91	+0.38	+0.46	+0.56	+1.05
2.15	1.85	+0.35	+0.42	+0.51	+0.98
		Monochloroacetic acid $K=1.6 \times 10^{-5}$.			
0.00	2.02	+0.41	+0.50	+0.60	+1.11
0.19	1.73	+0.37	+0.44	+0.54	+1.03
0.25	1.62	+0.35	+0.42	+0.50	+1.00
0.92	1.40	+0.34	+0.40	+0.49	+0.95
		Dichloroacetic acid. $K=5 \times 10^{-5}$.			
0.00	2.02	+0.41	+0.50	+0.60	+1.15
0.10	1.37	+0.34	+0.41	+0.47	+0.95
0.18	*1.23	+0.30	+0.36	+0.41	+0.83
0.32	*1.17	+0.30	+0.35	+0.42	+0.82
0.38	*1.10	+0.30	+0.35	+0.41	+0.81
		Trichloroacetic acid. $K=3 \times 10^{-1}$			
0.00	2.02	+0.41	+0.50	+0.60	+1.15
0.08	1.35	+0.32	+0.40	+0.45	+0.89
0.14	*1.21	+0.30	+0.37	+0.41	+0.82
0.21	*1.01	+0.29	+0.36	+0.41	+0.81
0.27	0.86	+0.26	+0.30	+0.35	+0.69
0.30	0.70	+0.21	+0.27	+0.32	+0.61

Influence of Oxalic, Malonic and Succinic Acids.

The complex formation between molybdic and oxalic acids has been reported by Rosenheim (*Z. anorg. Chem.*, 1896, 11, 225) and Spittle and Wardlaw (*J. Chem. Soc.*, 1931, 1748). The results on the addition of the above acids in increasing amounts to a solution containing 0.0261*M*-MoO₃+0.0261*M*-H₂T, are shown in Table IV.

TABLE IV
Rotations at wave lengths

Conc. of acid.	<i>pH</i> .	690 μ .		578 μ .		546 μ .		436 μ .	
		Obs.	Corrected for <i>pH</i>	Obs.	Corrected for <i>pH</i>	Obs.	Corrected for <i>pH</i>	Obs.	Corrected for <i>pH</i>
Oxalic acid.									
0.00 <i>M</i>	1.94	+0.48	—	+0.59	—	+0.66	—	+1.30	—
0.0070	1.92	+0.39	+0.39	+0.50	+0.50	+0.57	+0.57	+1.10	+1.11
0.0138	1.87	+0.30	+0.31	+0.39	+0.40	+0.45	+0.46	+0.90	+0.93
0.0268	1.80	+0.20	+0.22	+0.23	+0.25	+0.29	+0.32	+0.51	+0.59
0.0393	1.70	+0.12	+0.15	+0.15	+0.19	+0.10	—	+0.34	+0.42
Malonic acid.									
0.00	1.94	+0.48	—	+0.59	—	+0.66	—	+1.30	—
0.0065	1.92	+0.47	—	+0.58	—	+0.65	—	+1.28	—
0.0247	1.88	+0.45	—	+0.55	—	+0.62	—	+1.25	—
0.0616	1.86	+0.41	+0.42	+0.50	+0.51	+0.57	+0.59	+1.13	+1.16
Succinic acid.									
0.00	1.94	+0.48	—	+0.59	—	+0.66	—	+1.30	—
0.0094	1.92	+0.46	—	+0.58	—	+0.65	—	+1.27	—
0.0182	1.91	+0.45	—	+0.56	—	+0.63	—	+1.25	—
0.0700	1.89	+0.43	0.44	+0.55	+0.56	+0.62	+0.63	+1.21	+1.22

In the above tables the optical rotation values under the head "obs" are observed rotations after the addition of the respective acids, and under the head "corrected for *pH*" are the rotation values after correction for the partial diminution of rotation caused by increase of [H⁺]. This aspect is dealt with later on.

Influence of Organic Hydroxy-acids like Malic and Citric Acids.

Due to their similarity in structure with tartaric acid, they are expected to form complexes readily with molybdic acid. Darmois and collaborators (*Compt. rend.*, 1925, 180, 921; 1924, 179, 629; 1924, 178, 2183) and Travers and Malaprade (*Bull. Soc. chim.*, 1926, 39, 1408) observed complex formation between molybdic and malic acids. In the present case we have used inactive malic acid so that the resulting complex becomes optically inactive. The influence of the two acids in increasing amounts on a solution containing 0.0219*M*-MoO₃+0.0219*M*-H₂T has been studied as represented in Table V.

TABLE V

Conc. of acid.	pH.	Rotations at wave-lengths							
		690 $\mu\mu$		578 $\mu\mu$		546 $\mu\mu$		436 $\mu\mu$	
		Obs.	Corrected for pH	Obs.	Corrected for pH	Obs.	Corrected for pH	Obs.	Corrected for pH
Malic acid.									
0.00M	2.09	+0.37	—	+0.46	—	+0.52	—	+1.06	—
0.0112	2.00	+0.31	+0.32	+0.40	+0.42	+0.45	+0.47	+0.86	+0.92
0.0280	1.92	+0.26	+0.28	+0.36	+0.39	+0.41	+0.45	+0.75	+0.82
0.0561	1.83	+0.23	+0.27	+0.28	+0.33	+0.32	+0.38	+0.60	+0.71
0.0841	1.76	+0.21	+0.25	+0.24	+0.30	+0.28	+0.35	+0.54	+0.67
Citric acid.									
0.00	2.09	+0.37	—	+0.46	—	+0.52	—	+1.06	—
0.0055	1.89	+0.32	+0.33	+0.39	+0.41	+0.44	+0.45	+0.90	+0.94
0.0111	1.76	+0.24	+0.28	+0.27	+0.33	+0.31	+0.36	+0.59	+0.72
0.0330	1.72	+0.13	+0.20	+0.19	+0.26	+0.23	+0.31	+0.43	+0.58
0.0550	1.70	—	—	+0.17	—	+0.20	—	+0.39	—

Influence of Catechol, Salicylic acid and Glycerol.

The above are often known to form compounds similar to tartaric acid as exhibited by enhanced conductivity and $[H^+]$ (Holleman, "Organic Chemistry", 1925, p.275). The affinities are compared with that of tartaric acid in a solution containing 0.0219M-MoO₃ and 0.0219M-H₂T and the results are noted in Table VI.

TABLE VI

Conc.	pH	Observed rotations at wave-lengths.			
		690 $\mu\mu$.	578 $\mu\mu$.	546 $\mu\mu$.	436 $\mu\mu$.
Catechol.					
0.00M	2.09	+0.37	+0.46	+0.52	+1.06
0.08	2.07	+0.36	+0.46	+0.51	+1.03
0.15	2.04	+0.35	+0.44	+0.50	+1.02
Salicylic acid.					
0.00	2.09	+0.37	+0.46	+0.52	+1.06
0.08	2.07	+0.36	+0.44	+0.51	+1.05
0.20	2.00	+0.34	+0.41	+0.47	+0.98
Glycerol.					
0.00	2.09	+0.37	+0.46	+0.52	+1.06
0.15	2.07	+0.37	+0.46	+0.52	+1.04
0.30	2.06	+0.35	+0.45	+0.50	+1.02

DISCUSSION

The Action of NaOH and NH₄OH.

The action of the two bases are more or less similar in affecting the rotation values of the complex acid solution. The rotation values first increases during neutralisation and passes through a maximum followed by rapid decrease until it reaches a steady value which is the same as that given by pure H₂T solution

under similar conditions. From the p_H -rotation curves (not shown) it appears that the maxima at all concentrations of the complex acids, are always near p_H 4.2 and the minima of steady rotations are reached at p_H 7.0.

Britton and Jackson (*J. Chem. Soc.*, 1934, 1035) interpreted the region, where rotation values increase, to be due to the increasing formation of the complex, the maximum complex formation occurred near p_H 4.0, when tartaric acid was $3/4$ neutralised. There is no justification for such assumptions. We have advanced here a more reasonable interpretation to co-ordinate all the observed facts better looking into the parallel behaviour of the active component, viz, H_2T under similar conditions. We have seen in Table III similar to the observations of Vle's and Vellinger (*Compt. rend.*, 1925, 180, 742) and Britton and Jackson (*J. Chem. Soc.*, 1934, 978) that the rotation value of a tartaric acid solution gradually increases during neutralisation with NaOH and ultimately a steady value is attained. This phenomenon is associated with the different molecular rotatory powers of H_2T (non-ionised tartaric acid), HT' (acid tartrate ion) and T'' (tartrate ion) which are of increasingly higher order; a steady value is reached when tartaric acid is completely dissociated containing T'' ion in solution responsible for the observed steady value. Similar phenomenon operates during the neutralisation of the complex acid solutions.

The non-ionised complex acid $H_2[MoO_3T, H_2O]$ and its two ions $H[MoO_3T, H_2O]$ and $[MoO_3T, H_2O]''$ have rotatory powers of increasingly higher order and hence the rotation values increased during neutralisation due to the formation of the stronger rotatory complex ions more and more by progressive ionisations. But beyond p_H 4.2, $[MoO_3T, H_2O]''$ ion is unstable and begins to dissociate into its components; the rotation values rapidly fall due to large difference between rotatory powers of the complex ion and T'' ion. This dissociation becomes complete near p_H 7.0, when rotations observed are due to T'' ion only. This is in accordance with our expectations indicated before, that MoO_4'' is stable in neutral or alkaline medium and hence in such systems it will freely ionise in the solution unco-ordinated with tartrate or similar organic anions.

If we assume that the complex anion of the molybdotartaric acid does not decompose at or before p_H 4.2 and the complex acid remains completely ionised at this p_H , then in a system free of uncombined H_2T the observed maximum rotation value at this p_H may be ascribed to the complex ion $[MoO_3T, H_2O]''$ only and hence the molecular rotation of this ion can be determined thus: the rotation values observed under the stated conditions are

$$\alpha_{690\mu\mu}^{25^\circ} = +0.30; \quad \alpha_{578\mu\mu}^{25^\circ} = +0.38; \quad \alpha_{546\mu\mu}^{25^\circ} = +0.43; \quad \alpha_{436\mu\mu}^{25^\circ} = +0.91$$

for a concentration of $1.061 \times 10^{-2} M$ of $[MoO_3T, H_2O]''$. Therefore the molecular rotation values at respective wave-lengths are 28.28, 35.82, 40.53 and 85.76 for 0.54 dm. length at 25° .

The Action of HCl, H₂SO₄, Acetic acid, etc.

While the increase of rotation values of a complex solution with the addition of alkali is caused by the formation of stronger rotatory ions of the complex acid,

conversely the decrease of *pH* in such systems should diminish the rotation values by the repression of ionisation when less rotatory molecules or ions will be formed. When strong acids like H₂SO₄, HCl are added to a solution containing the complex acid and its ions, the rotation values decrease continuously. Provided the complex does not break at low *pH*, it is expected that there will be a definite *pH* value (depending on the ionisation constant of the complex acid) below which the acid will remain completely unionised, the rotation value will then remain steady. But this steady region could not be revealed with H₂SO₄ or HCl, probably the complex acid is unstable in their presence at low *pH* value.

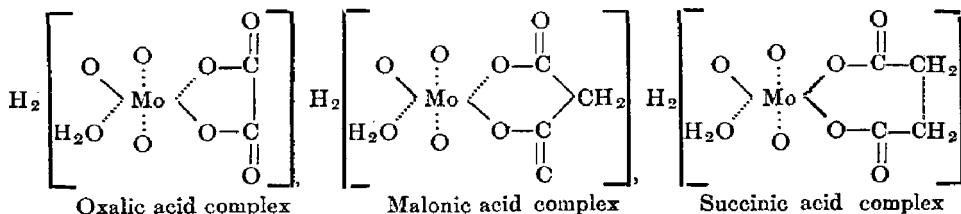
The influence of acids like acetic acid and its three chloro-acids, whose strengths are of gradually increasing order (*K* = 1.8 × 10⁻⁵ to 3 × 10⁻¹), on the complex solution has been studied alternatively. Acetic acid and monochloroacetic acid are probably weak to suppress completely the ionisation of the complex acid. But the desired region is revealed in the case of di- and trichloroacetic acids where the rotation values remained constant even when the *pH* dropped from 1.20 to 1.00. But with trichloroacetic acid the rotation values diminished below *pH* 1.0. If we assume again that the complex acid in solution remains completely unionised between *pH* 1.2 and 1.0, the molecular rotation of unionised acid can be determined from rotation values observed under the stated conditions thus :

$$\alpha_{690\mu\mu}^{25^\circ} = +0.30; \quad \alpha_{578\mu\mu}^{25^\circ} = +0.38, \quad \alpha_{548\mu\mu}^{25^\circ} = +0.41, \quad \alpha_{436\mu\mu}^{25^\circ} = 0.82$$

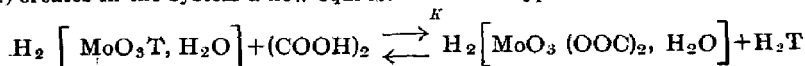
are the observed rotation values when the concentration of the complex acid is 1.987 × 10⁻²*M*. The molecular rotation values at respective wave-lengths are 15.09, 18.11, 20.63 and 41.25 for a 0.54 dm. tube at 25°.

The Action of Oxalic acid, etc.

While oxalic acid causes rapid decrease in rotation values (Table IV) with increasing concentration, the other two acids, viz. malonic and succinic acids, have little influence in affecting the rotation of a molybdotartaric acid solution ; probably in the latter cases, if they are to form a co-ordination complex, the length of the closed chain increases from 5 members in the case of tartaric and oxalic acids, to 6 and 7 respectively for malonic and succinic acids as shown below and thereby the affinity for combination is weakened.



The presence of oxalic acid in a solution of molybdotartaric acid complex (MoT) creates in the system a new equilibrium of the type.



If the applicability of Mass Law in such a complex system is assumed, the value of the equilibrium constant (K) will be given by

$$K = \frac{[\text{Oxalato complex}] \times [\text{H}_2\text{T}]}{[\text{Tartrate complex}] \times [(\text{COOH})_2]} = \frac{[\text{MoOx}] [\text{H}_2\text{T}]}{[\text{MoT}] [\text{Ox}]}$$

The oxalato complex is optically inactive and so the observed rotations at any stage in presence of oxalic acid are due to (MoT) and uncombined H_2T . The diminution of rotation is due to the proportional transformation of MoT to MoOx. It is now possible to determine the value of K from the data in Table IV. A typical calculation is shown below.

In the starting solution the concentration of molybdotartaric acid, *i.e.* [MoT], as calculated from the equations given in Part I, is 0.0215M and $[\text{H}_2\text{T}]$ is equal to (0.0261 - 0.0215). If x be the amount (in molarity) of MoT decomposed by the addition of 0.007M oxalic acid (Ox), then x will also be equal to the concentration of the new oxalato complex, *i.e.*, [MoOx] and an equivalent amount of H_2T will be liberated in the solution. Then

$$K = \frac{x \times [\text{H}_2\text{T} + x]}{[\text{MoT} - x] [\text{Ox} - x]}$$

Now the observed rotation = (original concentration of MoT - x) \times molecular rotation of MoT + (original conc. of H_2T + x) \times molecular rotation of H_2T .

The molecular rotations of MoT and H_2T for a 0.54 dm. polarimeter tube at the 4 wave-lengths in question are taken from the values given in Part I.

Then $0.39 = (0.0215 - x) \times 22.4 + (0.0046 + x) \times 1.01$ (for wave-length 690 μ)

$$x = 0.0048$$

$$\text{and } K = \frac{[\text{MoOx}] \cdot [\text{H}_2\text{T}]}{[\text{MoT}][\text{Ox}]} = \frac{(0.0048) \times (0.0046 + 0.0048)}{(0.0215 - 0.0048)(0.0070 - 0.0048)} = 1.23$$

similarly the values of K are calculated from other data and represented in Table VII.

It will be noticed that along with the diminution in rotation values by the addition of oxalic acid, the pH of the system also decreases and obviously this is also partly responsible for the diminution of optical rotation. With reference to Table III B for dichloroacetic acid, the proportional decrease of rotation for a certain pH drop is known; thus the observed rotation values in Tables IV and V are corrected for the rotation that the solution in question would give if there were no change from the original pH caused by the addition of foreign substances. These corrected values are noted in respective tables and only those are used for determining K . Similarly the following equilibrium constants K_1 , K_2 , K_3 and K_4 are also determined from recorded data in Tables IV and V

$$K_1 = \frac{[\text{MoO}_3 \cdot \text{Malonic}] [\text{H}_2\text{T}]_{\text{free}}}{[\text{MoT}] [\text{Malonic acid}]_{\text{free}}}, \quad K_2 = \frac{[\text{MoO}_3 \cdot \text{Succinic}] [\text{H}_2\text{T}]_{\text{free}}}{[\text{MoT}] [\text{Succinic acid}]_{\text{free}}}$$

$$K_3 = \frac{[\text{MoO}_3 \cdot \text{Malic}] [\text{H}_2\text{T}]_{\text{free}}}{[\text{MoT}] [\text{Malic acid}]_{\text{free}}}; \quad K_4 = \frac{[\text{MoO}_3 \cdot \text{Citric}] [\text{H}_2\text{T}]_{\text{free}}}{[\text{MoT}] [\text{Citric acid}]_{\text{free}}}$$

TABLE VII

Acid	Oxalic	Citric	Malic	Malonic	Succinic
Mean of relative equilibrium constants 13×10^{12}			153	86	16.5	2.67	1.17

From the above table an idea about the comparative affinities, relative to tartaric acid, of different acids for complex formation with molybdc acid is obtained. While oxalic acid has more affinity than tartaric acid, citric acid has got slightly less and malic acid has still less affinity. The affinities of the other two acids, viz., malonic and succinic acids are much smaller.

Referring to Table VI, phenols, phenolic acid and alcohols appear to have negligible affinities for complex formation in presence of tartaric acid.

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PHYSICO-CHEMICAL STUDIES OF COMPLEX FORMATION BETWEEN
MOLYBDIC AND TARTARIC ACIDS. PART III. ULTRAMICROSCOPIC
STUDIES ON THE CHANGE OF PARTICLE NUMBER AND
CATAPHORETIC VELOCITY OF MOLYBDIC ACID SOL
PARTICLES DURING COMPLEX FORMATION

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That an appreciable portion of molybdc acid in its sol is present as true solution and also the presence of tartaric acid in the sol transforms the colloidal particles into solution, have been shown by counting the number of particles per c.c. with an ultramicroscope. The cataphoretic velocity of molybdc acid sol particles, either alone or in presence of tartaric acid at different pH has been studied and the results discussed.

The work of Dumanskii and collaborators (*J. Russ. Phys. Chem. Soc.*, 1928, 60, 1053; *Kolloid Z.*, 1929, 48, 49) indicated the existence of a "colloidal complex" when tartaric acid (H_2T) was added to a sodium tungstate solution. This can be advantageously tested if we start with a colloidal solution and follow with a ultramicroscope the change of particle number taking place with the addition of an organic acid.

We started with a molybdc acid sol in which an appreciable percentage of the acid was present as true solution and the sol particles were found to be negatively charged. Dhar and collaborator (*J. Indian Chem. Soc.*, 1943, 20, 282) assumed the likely existence of an equilibrium of the type

