

## Triazines as Adsorption Indicators (Argentometric Titration of halides)

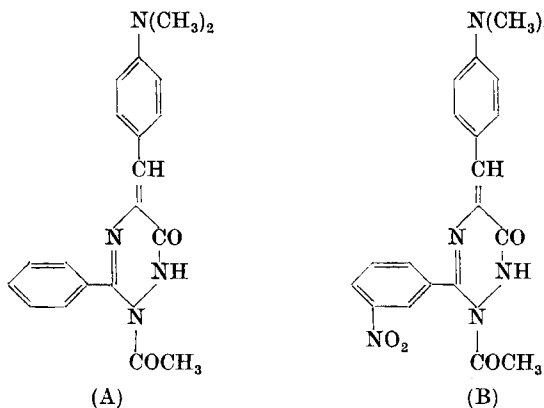
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### Summary

The use of triazines as adsorption indicators in argentometric titration of Chloride, Bromide and Iodide has been studied. Detail experimental procedures with two typical triazines are described and the results obtained are discussed in the light of the existing theories of adsorption indicators.

In this communication the use of a series of new adsorption indicators, the triazines in the argentometric titration of halides is described. The triazines used were (A) 2-acetyl 1:2:5 tetrahydro-6-oxo-5-p-dimethylaminobenzylidene-3-phenyl 1:2:4 triazine, and (B) 2-acetyl 1:2:5 tetrahydro-6-oxo-5-p-dimethylaminobenzylidene-3-m-nitro-phenyl 1:2:4 triazine, both giving deep yellow solutions in ethanol.

The triazines were prepared according to S. K. GANDHI<sup>1)</sup>. The relevant hydrazides are prepared from oxazol-5-ones by standard methods and then treating hydrazides with acetic acid and acetic anhydride (acetylation) and heating over a water-bath for 1½ hrs. On cooling triazine (A) separates out due to cyclisation of the hydrazides which is further purified. The com-



<sup>1)</sup> S. K. GANDHI, D. phil. Thesis, University of Allahabad (1963).

pound (B) is prepared as Nitrohydrazide from corresponding nitro-oxazolones and nitrotriazine separates out from nitrohydrazide likewise as described earlier. The triazines have red crystals with M. Ps (A) 213–214 °C, (B) 170–171 °C respectively and have the structures (see p. 10).

The absorption maxima of the above two triazines is (A) 460 m $\mu$  and (B) 480 m $\mu$  and adsorbability differs as  $A > B$ .

## Experimental

**Reagents:** All the reagents used were of analytical reagent grade (B. D. H.) A 0.2% of the triazine solutions in ethanol was used as indicator. For every 10 ml of the solution titrated 3–4 drops of the indicator were used.

### 1. Titration of chloride ions against silver ions

With 0.05 N solutions the end points are quite sharp. Coagulation starts before the end point and suspension has a slight pink color, however, at the end point there is a sharp color change from light to deep pink color of precipitate. With 0.01 N solutions titrations gives most sharp end points as the coagulation is near the end point. With 0.005 N solutions end points are not so sharp as the coagulation of the precipitate takes place after much shaking. Titrations are not possible with further dilute solutions. Titrations are reversible in some cases. Titrations are possible in neutral medium only. It has been observed that at 0.01 N concentration the titration is most suitably carried out.

### 2. Titration of bromide ions against silver ions

With 0.05 N solution the coagulation starts slightly before the end point and suspension has a light pink color but there is a sharp color change from light pink color to deep pink color of the precipitate at the end point. The sharp end points are obtained at 0.01 N solution and coagulation is complete at the end point and supernatant liquid is clear. With 0.005 N solution much shaking is required for complete precipitation. With dilute solutions titrations are reversible. Titrations are possible in neutral medium only. The best concentration for titration of bromide is 0.01 N solutions.

### 3. Titration of Iodide ions against silver ions

With 0.05 N solutions the coagulation of the precipitate begins before the end point, complete coagulation takes place at the end point leaving a clear supernatant solution. The color of the precipitate is pink-yellow and end points are sharper than the chloride and bromide titrations. With 0.01 N solutions titration is good and a sharp end point is obtained and with 0.005 N solution titration can be satisfactorily carried out though much shaking is required. Titration is reversible in some cases and is possible in neutral medium only. The best concentration observed for the titrations is 0.01 N solutions.

FAJANS<sup>2)3)</sup> explains the working of adsorption indicators as a result of secondary adsorption of the dye ions on the charged polar precipitate which

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<sup>2)</sup> K. FAJANS and O. HASSEL, *Z. electrochem. angew. physik. chem.* **29**, 495 (1923); cf. *Z. analyt. Chem.* **64**, 351 (1924).

<sup>3)</sup> K. FAJANS, *Die chemische Analyse*, Bd. **33**, 161–207 (1935).

Table 1  
Compound (A)

Vol. and concentration of solution titrated	Drops of Indicator	Vol. and Conc. of AgNO <sub>3</sub> soln.	Color change at the end point	Detailed conditions
10 ml of 0.05 N KCl	3—4	9.98 ml of 0.05 N	light pink → deep pink precipitate	Color change is sharp at the end point, coagulation starts before the end point. Titration is reversible
10 ml of 0.01 N KCl	3—4	10 ml of 0.01 N	light pink susp. → deep pink precipitate	End point is sharp and coagulation is near the end point
10 ml of 0.005 N KCl	3	10.08 ml of 0.005 N	light pink susp. → deep pink precipitate	Precipitation is complete after the end point, much shaking is required
10 ml of 0.05 N KBr	3	9.98 ml of 0.05 N	light pink → deep pink precipitate	End point is sharp, suspension is light pink, titration is reversible, coagulation starts before the end point is reached
10 ml of 0.01 N KBr	3—4	10 ml of 0.01 N	light pink susp. → deep pink precipitate	End is very sharp and color change is also sharp over the precipitate, shaking is required for complete precipitation. Titration reversible
10 ml of 0.005 N KBr	3	10.04 ml of 0.005 N	light pink susp. → deep pink precipitate	End is after the actual end point, much shaking is required
10 ml of 0.05 N KI	3—4	9.96 ml of 0.05 N	light pink → Pink-yellow precipitate	Precipitation is complete at the end point sharp, supernatant soln. clear. Titration is reversible
10 ml of 0.01 N KI	3	10.02 ml of 0.01 N	light pink yellow → deep Pink-yellow precipitate	Precipitation starts near the end point and is complete after the addition of one more drop of AgNO <sub>3</sub> , supernatant liquid is clear. Titration reversible
10 ml of 0.005 N KI	3	10 ml of 0.005 N	light pink yellow → deep pink-yellow precipitate	Precipitate settles at once at the end point, much shaking is required. Titration reversible

Table 2  
Compound (B)

Vol. and concentration of solution titrated	Drops of Indicator	Vol. and Conc. of $\text{AgNO}_3$ soln.	Color change at the end point	Detailed conditions
10 ml of 0.05 N KCl	3-4	9.98 ml of 0.05 N	light pink $\rightarrow$ Pink precipitate	End point good, color change at the precipitate during coagulation
10 ml of 0.01 N KCl	3	9.96 ml of 0.01 N	light pink susp. $\rightarrow$ Pink precipitate	Precipitation starts before the end point and is complete near the end point (one drop earlier). Titration is reversible
10 ml of 0.005 N KCl	3-4	10.04 ml of 0.005 N	light pink susp. $\rightarrow$ Pink precipitate	Much shaking is required and coagulation is complete after the end point. Titration reversible but end point not sharp
10 ml of 0.05 N KBr	4	9.98 ml of 0.05 N	Pink susp. $\rightarrow$ Pink precipitate	Soln. becomes turbid near the end point. Titration reversible. End point good
10 ml of 0.01 N KBr	3-4	10 ml of 0.01 N	light pink susp. $\rightarrow$ pink precipitate	Coagulation is complete at the end point. Titration reversible. Precipitate settles at once
10 ml of 0.005 N KBr	3-4	10.02 ml of 0.005 N	Pink susp. $\rightarrow$ deep Pink-yellow precipitate	Coagulation is complete after the end point. Supernatant liquid clear. Titration reversible. Much shaking is required
10 ml of 0.05 N KI	3-4	0.06 ml of 0.05 N	Pink $\rightarrow$ deep Pink-yellow precipitate	Supernatant liquid clear. End point good
10 ml of 0.01 N KI	3	10 ml of 0.01 N	Pink susp. $\rightarrow$ Pink-yellow precipitate	Precipitation complete at the end point. Soln becomes turbid near the end point. Color change on the precipitate. Titration reversible
10 ml of 0.005 N KI	3	10.02 ml of 0.005 N	Pink susp. $\rightarrow$ Pink-yellow precipitate	Precipitation is complete after the end point. Much shaking is required. Supernatant liquid clear

is accompanied by intense change of color. KOLTHOFF<sup>4)</sup><sup>5)</sup> extends his ideas of exchange adsorption and MEHROTRA<sup>6)</sup><sup>7)</sup><sup>8)</sup> has emphasized the process of chemisorption. It appears that in the present case strong adsorption of triazines on the charged polar precipitate takes place through forces which are mostly chemical in nature and the sharp color change is due to the pronounced deformation of the electron system of the adsorbed ions near the points of equivalence. Further work on the isolation of the chemisorped compounds and the establishment of their chemical formula is in progress.

Thanks are due to Dr. S. K. GANDHI for preparing and supplying the triazine compounds.

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<sup>4)</sup> I. M. KOLTHOFF and W. D. LARSON, J. Amer. chem. Soc. **56**, 1881 (1934). cf. Z. analyt. Chem. **103**, 207 (1935).

<sup>5)</sup> I. M. KOLTHOFF, Chem. Rev. **16**, 87 (1937).

<sup>6)</sup> R. C. MEHROTRA, Analyt. chim. Acta **3**, 78 (1949); cf. Z. analyt. Chem. **130**, 437 (1949/50).

<sup>7)</sup> R. C. MEHROTHA, Adsorption indicators in precipitation titrations, University of Allahabad Studies, Chem. Sec. (1948).

<sup>8)</sup> B. D. H., Adsorption Indicators (1961).

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