

Distribution Studies of Halides and Thiocyanate Ions in Aqueous Acetone Media

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The distribution of halides and thiocyanate ions have been reported in aqueous acetone media using an anion exchanger-Amberlite IRA-400 (20-40 mesh) in nitrate form. The change in affinity sequence with percentage of acetone in solution have been derived from the distribution data. Binary separations of these ions have been reported in 10% aqueous acetone media using differential elution technique.

INTRODUCTION

Separation of halide ions have been reported in aqueous medium by De Geiso *et al.*¹ This separation has been given also by Rieman III and Walton². Radioactive halogens have been separated by Berger *et al.*³ on Dowex 1 × 10 with cellulose as binder. Though a few separations have been reported for anions in non-aqueous and mixed solvents, yet no separation of halides have been reported in aqueous acetone media. In this communication distribution data for halides and thiocyanate ions have been procured and on its basis affinity sequence of these ions have been obtained. Binary separations of these ions have also been reported in 10% acetonic solvents.

EXPERIMENTAL

All halides and thiocyanate have been obtained as their potassium salts, which were all A.R. reagents. Acetone used was also an A.R. reagent, but it was distilled once. All aqueous acetone solutions were prepared by mixing acetone and double distilled water on volume to volume basis.

Distribution data was obtained by batch technique following the relationship given below:

$$K_D = \frac{\text{meq of ion/dry gm of the resin}}{\text{meq of ion/ml of the solution}}$$

Determination of anions: Chloride and bromide were estimated titrimetrically against silver nitrate solution using potassium chromate-dichromate mixture and eosin solutions respectively as indicators. Iodide and thiocyanate ions were estimated by Volhard's method using 50% nitric acid followed by ferric alum as indicator.

Separation studies: Separation studies were carried out by using column technique with an influent volume (20 ml) consisting of 10 ml each of the anion solutions (0.02 M). Column length of 20 ml and a flow rate of 2 ml/min/cm² was maintained throughout. Each time 20 ml fractions of the effluent solution was collected and titrated for the presence of concerned anion. The elution of chloride and bromide ions were done with 0.1 M ammonium nitrate in 10% (v/v) aqueous acetone solutions, while iodide and thocyanate ions were eluted with 2.0 M ammonium nitrate in 10% (v/v) aqueous acetone solution. All separations were carried out in a binary combinations using the following pairs of ions:



The distribution coefficients, which gave the maximum possible difference for the ions concerned were used in separations studies. Thus at ionic concentrations 0.02 M and 10% (v/v) aqueous acetone solutions were used for all separation studies.

RESULTS AND DISCUSSION

The results obtained for distribution coefficients of the 4 anions are given in Table 1. The separations have been shown in Fig. 1 for $\text{Cl}^- - \text{I}^-$ and $\text{Br}^- - \text{I}^-$. It

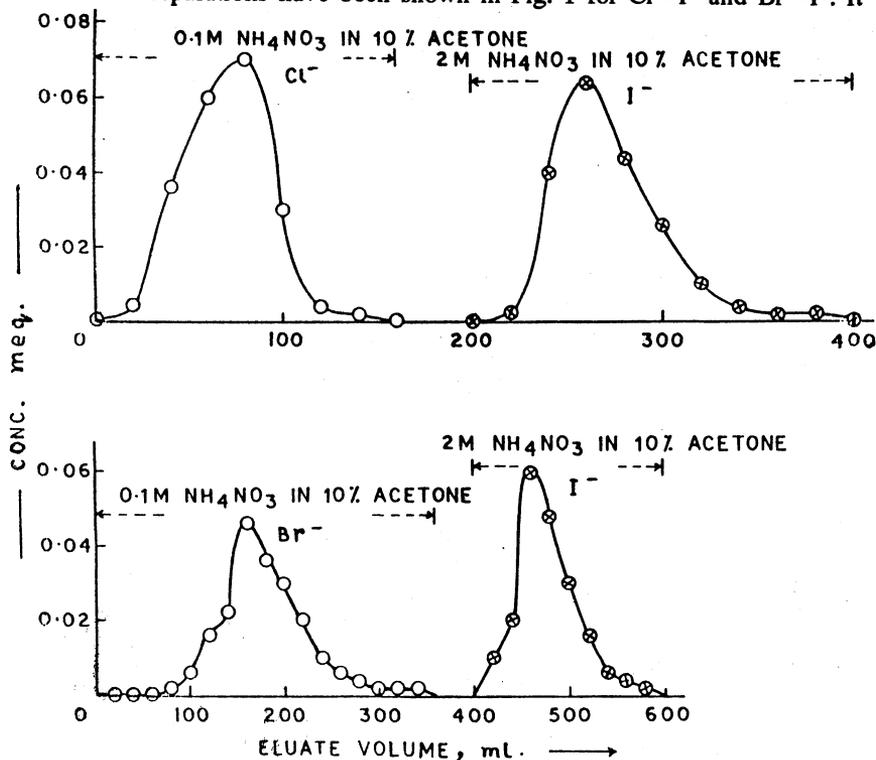


Fig. 1

appears that 0.02 M ionic concentration for Cl^- - CNS^- and Br^- - CNS^- was good for all concerned ions. Only the solvent consisting of 10% (v/v) aqueous acetone gave the high distribution coefficients for all the ions concerned.

TABLE 1
DISTRIBUTION COEFFICIENTS IN AQUEOUS ACETONE SOLUTIONS

Anion	Anionic Conc., M	Percentage acetone in water			
		10	20	40	60
Cl^-	0.100	21.1	21.5	24.3	30.3
	0.050	37.5	38.8	47.8	65.1
	0.033	52.5	56.3	69.9	101.5
	0.025	70.4	75.6	93.5	133.6
	0.020	80.5	88.3	104.5	155.9
Br^-	0.100	32.5	33.3	33.9	37.7
	0.050	65.7	67.9	72.6	84.4
	0.033	98.2	100.9	110.8	131.9
	0.025	130.4	134.4	144.2	173.6
	0.020	160.5	162.6	179.6	219.3
I^-	0.100	53.7	54.4	50.2	44.9
	0.050	145.0	136.2	116.3	96.8
	0.033	249.2	229.0	199.9	159.2
	0.025	340.6	317.6	270.5	221.7
	0.020	505.6	426.2	350.0	272.6
CNS^-	0.100	59.0	54.3	42.7	34.6
	0.050	156.9	126.6	85.7	64.8
	0.033	280.0	190.5	129.2	92.5
	0.025	353.2	259.4	157.6	123.1
	0.020	351.6	279.2	198.2	131.03

The K_D data also gave the affinity sequence for these ions. It was as expected in solutions of 0.1 M concentration upto 20% (v/v) aqueous acetone containing solvents, *i.e.*,



But it changed to $\text{Cl}^- < \text{Br}^- < \text{CNS}^- < \text{I}^-$ for 40% (v/v) aqueous acetone and $\text{Cl}^- < \text{CNS}^- < \text{Br}^- < \text{I}^-$ for 60% (v/v) aqueous acetone solutions.

It was $\text{Cl}^- < \text{Br}^- < \text{I}^- < \text{CNS}^-$ for 0.02 M ionic concentration even up to 40% (v/v) aqueous acetone solution, while at 60% (v/v) aqueous acetone solution the sequence of affinity was $\text{CNS}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$. Thus it can be said that these ions change their positions with increasing acetone percentage⁴. It change with ionic loading also^{5,6}. As always aqueous solutions were used in earlier studies of halogens (not thiocyanate) the sequence of the hydrated ions were always same *i.e.* in the increasing order of their atomic numbers.

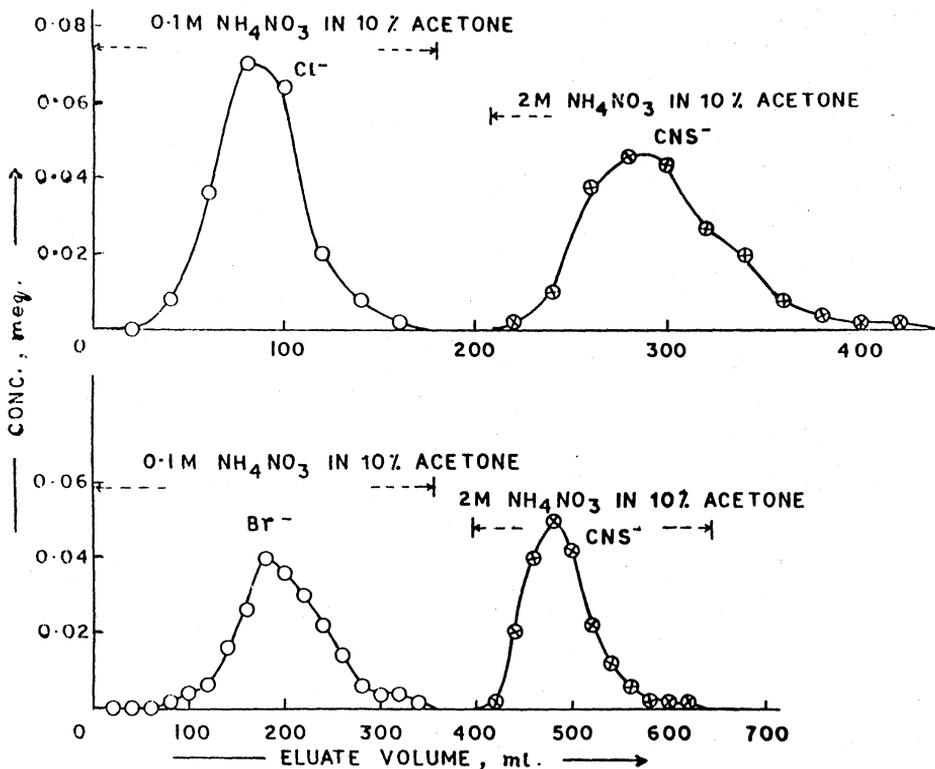


Fig. 2

TABLE 2
ERROR LIMITS IN THE SEPARATION CARRIED OUT

Sl. No.	Pairs of ions		Ratio v/v 0.02 M soln., ml	Theo. meq.	Recov. meq.	Error %	Total effluent Volume
	Ist Comp.	2nd Comp.					
Ist Component							
1.	Cl ⁻	I ⁻	10 : 10	0.200	0.206	+3	160
2.	Cl ⁻	CNS ⁻	10 : 10	0.200	0.208	+4	160
3.	Br ⁻	CNS ⁻	10 : 10	0.200	0.212	+6	340
4.	Br ⁻	I ⁻	10 : 10	0.200	0.204	+2	340
2nd Component							
5.	Cl ⁻	I ⁻	10 : 10	0.200	0.194	-3	180
6.	Cl ⁻	CNS ⁻	10 : 10	0.200	0.204	+2	220
7.	Br ⁻	CNS ⁻	10 : 10	0.200	0.200	0.0	220
8.	Br ⁻	I ⁻	10 : 10	0.200	0.196	-2	180

The separations of ions in binary pairs was possible as 0.1 M ammonium nitrate in 10% (v/v) aq. acetone was able to elute the chloride or bromide ions, while 2.0 M ammonium nitrate in 10% (v/v) aq. acetone was able to elute iodide or thiocyanate ions. Chloride needed only 12 fractions of 20 ml each, while bromide required 21 ml fractions of 20 ml each. Iodide and thiocyanate ions were eluted by 2.0 M ammonium nitrate in 10% (v/v) aq. acetone in 10 and 13 fraction of 20 ml each respectively. The last two ions eluted with 0.025, 0.1, 0.5 M eluents in a much greater number of fractions. They did not come at all with 0.1 M eluent. All binary separations were quantitative by differential elution technique. Table 2 gives the error limit for the pairs separated.

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