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Conductometric Study of the Solution Mixtures of Urinary Stone Forming Anions, Urine and Citric Acid

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Measurement of electrical conductance of the mixtures of solutions of urinary stone forming anions, *viz.*, oxalate or phosphate and stone inhibitor, *viz.*, citric acid have been carried out in different proportions in the presence and absence of urine as mixture component. Diagnosis and inhibition of urolithiasis has been discussed in the light of conductance data.

INTRODUCTION

Disposition to urolithiasis disease is a function of a number of risk factors[1]. Important among these are level of insoluble salt forming anions in urine, level of inhibitors of calculeogenesis in urine and urinary pH. These factors combinedly effect the physical properties of urine. Important physical properties like viscosity, surface tension, specific gravity and electrical conductivity of urine might throw light on the possibility of predisposition to urolithiasis[2] and thus can serve as important diagnostic tool at an early stage of the disease. Modification of these properties by the inhibitors of calculogenesis would throw light on the mechanism of their inhibitory action. With these views in mind we have presently studied the electrical conductance of the mixtures of solutions of urinary stone forming anions, *viz.*, oxalate or phosphate and citric acid in different proportions in the presence and absence of urine as mixture component.

EXPERIMENTAL

All solutions were prepared in conductivity water. Urine sample of a healthy 35 year old male was collected in sterilised plastic container. A 24 h urine output was collected and a bit of camphor was added as a preservative. It was used out in minimum possible time after collection. Citric acid treated urine was prepared by adding 50 mL of 0.01 M citric acid solution to 450 mL of urine.

Mixtures of solutions of varying propertions of the components were prepared in following combinations keeping the total volume of the mixture to 100 mL in each case.

1. Sodium oxalate (0.01 M) and citric acid (0.02 M)
2. Sodium phosphate (0.01 M) and citric acid (0.02 M)
3. Sodium phosphate (0.01 M), sodium oxalate (0.01 M) and citric acid (0.02 M)

4. Urine and oxalic acid (0.01 M)
5. Urine and phosphoric acid (0.01 M)
6. Urine and citric acid (0.01 M)
7. Citric acid treated urine and oxalic acid (0.01 M)
8. Citric acid treated urine and phosphoric acid (0.01 M)

Every mixture was stirred well after mixing to become uniform. Specific conductivities of the mixtures were recorded on a direct reading conductivity meter (Systronics type 303). The instrument was calibrated with a 0.1 M KCl solution. All experiments were carried out at 25 ± 0.1°C.

RESULTS AND DISCUSSION

Specific conductivity data of mixtures of solutions in different proportions, *viz.*, sodium oxalate and citric acid, sodium phosphate and citric acid, sodium phosphate and sodium oxalate and citric acid, urine and oxalic acid, urine and phosphoric acid, urine and citric acid, citric acid treated urine and oxalic acid, and citric acid treated urine and phosphoric acid are recorded in Tables 1–8 respectively. Inflection points on the plots (not shown) evidencing interactions between the components in solution are recorded in Table-9.

TABLE-1
CONDUCTIVITY DATA OF MIXTURES OF SOLUTIONS OF SODIUM OXALATE AND CITRIC ACID

Vol. of sodium oxalate solution (0.01 M) (mL)	Vol. of citric acid solution (0.02 M) (mL)	Sp. conductivity of mixture (m-mho cm^{-1})
100	0	3.30
90	10	3.00
80	20	2.85
70	30	2.40
60	40	2.40
50	50	2.40
40	60	2.37
30	70	2.37
20	80	2.37
10	90	2.37
0	100	2.40

The solution equillibria in the urinary tract including bladder would be complicated because a number of compounds simultaneously exist in solution. Different associative interactions among the components are likely. Single or mixed ligand complex equilibria involving chelation might also exist. The primary factor for urinary stone formation is the supersaturation of stone forming minerals in the urine. These minerals with very low solubility precipitate out from urine and accumulate over some suitable nidus in the tract and grow up into stone over the years. Stone formation in fact is a function of level of calculogenetic crystalloids and the level of inhibitors of calculogenesis in urine[3–5]. Citric acid is a natural inhibitor of urolithiasis. Study of the solution interactions between stone forming and inhibiting compounds and effect of such interactions on the physical properties of urine would be applicable in early diagnosis of the disease by simple techniques. Effect of oxalic acid on the physical properties of urine has been studied[6].

TABLE-2
CONDUCTIVITY DATA OF MIXTURES OF SOLUTIONS OF SODIUM PHOSPHATE AND CITRIC ACID

Vol. of sodium phosphate solution (0.01 M) (mL)	Vol. of citric acid solution (0.02 M) (mL)	Sp. conductivity of mixture (m-mho cm^{-1})
100	0	2.70
90	10	2.70
80	20	2.55
70	30	2.40
60	40	2.25
50	50	2.10
40	60	2.10
30	70	2.25
20	80	2.25
10	90	2.33
0	100	2.40

TABLE-3
CONDUCTIVITY DATA OF MIXTURES OF SOLUTIONS OF SODIUM OXALATE, SODIUM PHOSPHATE AND CITRIC ACID

Vol. of sodium oxalate solution (0.01 M) (mL)	Vol. of sodium phosphate solution (0.01 M) (mL)	Vol. of citric acid solution (0.02 M) (mL)	Sp. conductivity of mixture (m-mho cm^{-1})
50	50	0	3.00
45	45	10	2.70
40	40	20	2.70
35	35	30	2.40
30	30	40	2.30
25	25	50	2.40
20	20	60	2.32
15	15	70	2.32
10	10	80	2.40
5	5	90	2.40
0	0	100	2.40

TABLE-4
CONDUCTIVITY DATA OF MIXTURES OF URINE AND OXALIC ACID SOLUTION

Vol. of urine (mL)	Vol. of oxalic acid solution (0.01 M) (mL)	Specific conductivity of mixture (m-mho cm^{-1})
100	0	22.0
90	10	20.5
80	20	19.5
70	30	17.9
60	40	16.0
50	50	15.0
40	60	13.5
30	70	12.5
20	80	11.0
10	90	11.2
0	100	11.0

TABLE-5
CONDUCTIVITY DATA OF MIXTURES OF URINE AND CITRIC ACID SOLUTION

Vol. of urine (mL)	Vol. of citric acid solution (0.01 M) (mL)	Sp. conductivity of mixture (m-mho cm^{-1})
100	0	22.0
90	10	18.7
80	20	17.9
70	30	16.1
60	40	14.6
50	50	12.9
40	60	11.9
30	70	10.0
20	80	8.2
10	90	7.0
0	100	7.0

In the present study, variation of specific conductance with changing composition of sodium oxalate and citric acid mixtures (Table-1) shows a minima (inflection point) corresponding to 1 : 1 mole ratio between sodium oxalate and citric acid indicating some complexation between the two compounds in solution. Conductance of sodium phosphate and citric acid mixtures (Table-2) shows a minima corresponding to 1 : 2 mole ratio between sodium phosphate and citric acid suggesting a higher order (1 : 2) complexation between the two compounds. In case of a mixture of sodium oxalate, phosphate and citric acid too, the plot is similar to plot of sodium oxalate and citric acid. However, the break point corresponds to a 1 : 1 : 2 mole ratio among oxalate, phosphate and citric acid. The point seems to suggest some combined interaction of the mixture components in solution. Plots in case of urine-oxalic acid and urine-citric acid too show break points indicating interactions. The break point conductance in case of citric acid is much lower than that for oxalic acid. This suggests a superior complexing ability of citric acid towards urinary compounds with low dissociation of the complex in solution. Higher conductivities of urine-phosphoric acid mixtures might be due to a lower pK of phosphoric acid as well as weak complexing ability of the latter with the urinary cations.

TABLE-6

CONDUCTIVITY DATA OF MIXTURES OF URINE AND PHOSPHORIC ACID SOLUTION

Vol. of urine (mL)	Vol. of phosphoric acid solution. (0.01 M) (mL)	Sp. conductivity of mixture (m-mho cm^{-1})
100	0	22.0
90	10	20.4
80	20	17.5
70	30	17.4
60	40	17.4
50	50	17.7
40	60	17.5
30	70	17.5
20	80	17.4
10	90	17.4
0	100	18.1

TABLE-7

CONDUCTIVITY DATA OF MIXTURES OF CITRIC ACID TREATED URINE AND OXALIC ACID SOLUTION

Vol. of citric acid treated urine (mL)	Vol. of oxalic acid solution (0.01 M) (mL)	Sp. conductivity of mixture (m-mho cm^{-1})
100	0	18.5
90	10	16.5
80	20	15.0
70	30	15.0
60	40	13.0
50	50	12.0
40	60	11.0
30	70	9.2
20	80	8.2
10	90	7.0
0	100	11.0

TABLE-8
CONDUCTIVITY DATA OF MIXTURES OF CITRIC ACID TREATED URINE AND PHOSPHORIC ACID SOLUTION

Vol. of citric acid treated urine (mL)	Vol. of phosphoric acid solution (0.01 M) (mL)	Sp. conductivity of mixture (m-mho cm^{-1})
100	0	18.5
90	10	16.5
80	20	15.0
70	30	14.5
60	40	15.0
50	50	16.0
40	60	16.5
30	70	16.4
20	80	17.4
10	90	17.8
0	100	18.1

TABLE-9
INFLECTION POINT DATA OF CONDUCTIVITIES OF MIXTURES OF URINARY STONE FORMING ANIONS AND CITRIC ACID

Mixture	Inflection point (mL of citric acid) Found (Calcd.)	Mole ratio at inflection point (sodium oxalate/phosphate : citric acid)
Sodium oxalate and citric acid	32.0 (33.5)	1 : 1
Sodium phosphate and citric acid	52.5 (50.0)	1 : 2
Sodium oxalate, sodium phosphate and citric acid	30.0 (33.5)	1 : 1 : 2

Treatment of urine with citric acid lowers the conductivity of the former. The urine and oxalic acid mixtures show a minima with much lower conductance as compared to corresponding untreated urine-oxalic acid mixtures. This shows that the chelating/complexing ability of citric acid towards urinary cations is not affected by oxalic acid. The citric acid treated urine-phosphoric acid mixtures have also lower conductivities as compared to untreated urine-phosphoric acid mixtures indicating superior complexing ability of citric acid as compared to phosphoric acid.

Thus our present studies indicate that the urine of a normocitraturic person will have low conductance because of the presence of citrate-chelated cations of low mobility. As the person starts suffering from hypocitraturia the urine conductivity should increase due to the presence of more of unchelated cations with higher mobility. However, as the urinary stone formation starts the urine conductivity should once again decrease because of decrease of ionic load in urine as more and more stone forming cations and anions precipitate out to deposit as stone. Electrical conductivity of urine can thus be of some diagnostic importance in urolithiasis.

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