

NOTE

Solution Studies of Some Low-Valent Metal Complexes

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Low-valent metal complexes in solution phase of alkali and alkaline earth metals with unsaturated groups and/or binding site having high electron density formed in non-aqueous solvent have been studied with a view to study the cancerous diseases. The study is based and concluded mainly on pH measurements.

The name of disease cancer is attributed to Hippocrates who observed it as far back as the fourth century before our era. The disease is called cancer because it seized an organ like a crab grasps its prey. It is a formidable disease that is killing increasing number of people in virtually all the countries of the world¹. It has been established² that a wide variety of chemicals can induce cancer. Chemical carcinogens can be divided into certain groups in which nitrogen-containing unsaturated groups like (—N=N—) play a vital role.

Actually a number of differences have been observed between cancer and normal cells. Compared with normal cells, cancer cells have: (i) lower pH³ (ii) lower calcium ion and higher potassium ion concentrations⁴. The aim of our present work is to lower the potassium ion concentrations and/or to increase the Ca^{2+} ion concentration. Hence *o*-carboxyl benzene azo-2-naphthol and 1-benzene azo-2-naphthylamine having high selectivity value for these ions are taken and allowed to interact with potassium and calcium salts of 1-nitroso-2-naphthol and *o*-nitrophenol in absolute ethanolic medium.

The compounds *o*-carboxyl benzene azo-2-naphthol and 1-benzene azo-2-naphthylamine were prepared by standard method^{5,6} the potassium and calcium salts of 1-nitroso-2-naphthol and *o*-nitrophenol used were prepared in 95% ethanol.

We measured the pH of the solution of *o*-carboxyl benzene azo-2-naphthol in excess of absolute ethanol. Now, 500 mg of K-salt was added to it. The whole mixture was refluxed over a bath for about 30 min with stirring at frequent intervals. The solution was cooled at room temperature and its pH was determined. After adding 500 mg of salts we measured the pH of the reaction mixture. The process was continued till the addition of 2.5 g of the salt.

The same process was adopted for 1-benzene azo-2-naphthylamine with

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calcium salt; we started with 100 mg and the process of measuring pH in solution phase was continued till the addition of 1.0 g of the salt by adopting the same procedure as above.

It has been proposed that the carcinogenic process involves enzymatic epoxidation and subsequent reaction with nucleic acid and active electropositive ions⁷.

We have observed that pH of *o*-carboxyl benzene azo-2-naphthol and 1-benzene-azo-2-naphthylamine in excess absolute ethanol is 9.4 and 11.1 respectively. As we go on adding the K-salt and Ca-salt in it causing complexation in solution phase, the pH goes on decreasing till 2.5 g of K-salt (pH = 8.1 and pH = 8.4 respectively) and 1.0 g of ca-salt (pH = 7.1). After that further addition of salts either increases the pH or shows no change in pH.

Table-1 mentions the melting points of compounds and the pH of the mixture.

TABLE-1

Compounds in excess of absolute ethanol	Salt K1N2N added in milligrams	pH	Salt Ca1N2N added in milligrams	pH
	1N2N = 1-nitroso-2-naphthol.		1N2N = 1-nitroso-2-naphthol	
<i>o</i> -Carboxylbenzene azo-2-naphthol (m.p. 274°C)	–	9.4	–	9.4
	500	9.1	100	9.2
	1000	8.8	200	8.9
	1500	8.6	400	8.5
	2000	8.2	600	8.2
	2500	8.1	800	7.5
			1000	7.3
			1200	7.1
1-Benzene-azo-2-naphthylamine (m.p. 192°C)	–	11.1	–	11.1
	500	10.2	100	10.4
	1000	9.4	200	9.3
	1500	8.9	400	8.3
	2000	8.6	600	7.9
	2500	8.4	800	7.4
			1000	7.1
			1200	7.2

The present work is to study the role of azo-compounds in cancerous diseases. The high electron density on nitrogen plays an important role in this study. Further, we have *o,o'*-substituents as OH and NH₂ which have electron releasing nature making electron density on nitrogen very high. Thus apart from being β -naphthylamine as carcinogenic, the compound formed from it is interestingly highly carcinogenic.

Wherever we require lower concentration of K⁺, we use this process or even

if we require higher Ca^{2+} ion concentration, the calcium complexes may be decomposed for the purpose. Hence this work throws bright light on the chemical aspects of some of the developments in chemotherapy for cancerous diseases.

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(Received: 24 August 2001; Accepted: 23 November 2001)

AJC-2540

25th International Symposium on Capillary Chromatography

RIVA DEL GARDA, ITALY

13-17 MAY 2002

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