arations (A) as well as in intact cells (B), decrease with an approximate half-time of 2–4 days (evaluated from semilog plots).
Again a significantly slower disappearance of β-adrenoceptor sites ($t_{1/2}$ approximately 8 days) is observed (C).
Discussion. From results presented previously, it has been concluded that, during the maturation process of the red blood cell from rats, the enzymatic activity of adenyl cyclase and the β-adrenoceptor are lost at the same rate: the fluoride activated enzyme activity and the isoprenaline (Ipn) stimulated enzyme activity decreased parallel with decreasing reticulocyte counts[2,3]. The results of ligand studies presented here reveal that this previous conclusion (drawn only from enzymatic experiments) was incorrect: cAMP synthesis and β-adrenoceptor density decrease at distinctly different rates[8,11]. These observations, however, are not in agreement with findings in growing rats[12] with decreasing reticulocyte counts; in this instance, a parallel decrease of adenyl cyclase activity and receptor density has been assumed. These results[12], however, were obtained in only 2 groups of animals of different age.
It must be taken into account, however, that the β-adrenoceptor unit is coupled to the enzymatic unit by a GTP-binding unit[13]. If this subunit of the receptor-effector system disappears more rapidly during the maturation process than the enzymatic unit, the whole system will be uncoupled. This would result in an apparently more pronounced decrease of adenyl cyclase activity. Furthermore, a relative lack of the activator of the coupling unit, i.e. GTP, could lead to such an uncoupling process. It is known that the GTP concentration in mature red cells is much lower than in immature cells[14].

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Studies on the metal-complex of acetyl salicylic acid (aspirin)

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Summary. The present communication deals with the isolation of acetyl salicylic acid (aspirin) complexes with Bi^{+3}, Zn^{+2} and UO_2^{+2}. The characterization of 1:2 complexes have been carried out with the help of conductometric, pH metric, elemental analysis and IR spectral studies. Spectrophotometric studies in case of UO_2^{+2} (the only colored complex) in range of 4.2 to 5.5 pH show absorption at 490 nm and complex obey Beers Law at the concentration range of 0.01 M to 0.1 M.

Very little work has been reported in the literature[1-5] on the complexes of metals and acetyl salicylic acid (aspirin) which is used for various pains of the human body. The complexes of metal ions like Pb^{+2}, Sn^{+2}, Al^{+3}, Cu^{+2}, In^{+3}, Ni^{+2} and Cd^{+2} have been reported. However, no work has been done on the complexes of Bi^{+3}, Zn^{+2} and UO_2^{+2}. The present communication deals with the isolation, characterization by elemental analyses and various studies in solutions with the help of spectrophotometer, conductometer, pH meter and IR spectral studies of the complexes. Spectrophotometric studies in the case of UO_2^{+2} (the only colored complex) in the range of 4.2 to 5.5 pH show absorption at 490 nm and complex obeys the Lambert and Beer Law at the concentration range of 0.01 M to 0.1 M. The pH metric, conductometric titration and Job's method of continuous variation observed 1:2 ratio (metal:ligand) in the complexes; this fact was confirmed by elemental analyses of the complexes.
Experimental. Acetyl salicylic acid has been isolated and crystallized as reported[6]. The nitrate of bismuth chloride of zinc and uranyl acetate used were of AnalaR grade. The standard solution of bismuth nitrate was prepared by dissolving it in HCl and making it upto mark with absolute alcohol in maintained pH up to 2. The solutions of zinc chloride and uranyl acetate were prepared by dissolving them in alcohol and conductivity water, respectively. All the conductometric titrations were performed by using Toshniwal conductivity bridge type CL01/02A and a dip type cell. pH metric studies were recorded with a Elico pH meter model L1-10 using hydrogen and calomel electrodes. Spectrophotometric studies were done on Bausch and Lomb's spectrophotometer model spectronic-20[7]. The IR-spectra of bismuth complex was taken in KBr while that of zinc and uranyl acetate complex were performed in nujol mull on a Perkins-Elmer model-621 spectrophotometer in the range of 4000 to 200 cm^{-1}.
The complexes of Bi^{+3} and Zn^{+2} were isolated as a crystals in alcoholic medium. The solutions of metal and ligand were mixed in the molar ratio of 1:2 (metal:ligand) stirred with magnetic stirrer. The solutions were then refluxed on a water bath; on cooling over night, defined pinkish crystals of Bi^{+3} and white crystals of Zn^{+2} complexes were separat-

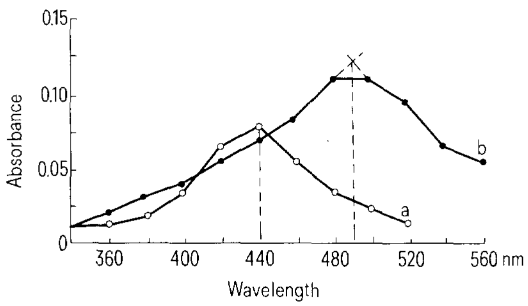

Fig. 1. a: Absorption curve of UO_2^{+2} ion ($\lambda_1 max = 440$ nm). b: Absorption curve of the complex ($\lambda_2 max = 490$ nm).

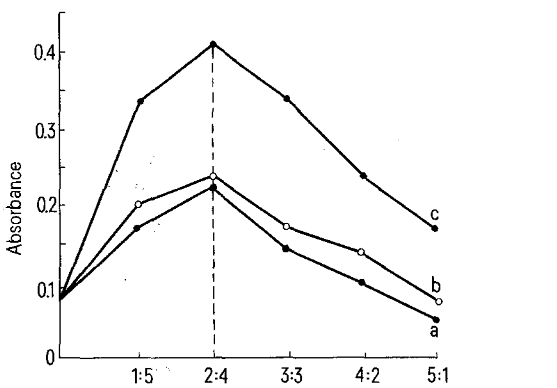

Fig. 2. Ratio of metal: ligand, total volume = 6 ml. a: At room temperature color changes yellow to orange. b: After 1 h color changes orange to brown. c: Heated up to 80 °C sharp change in color orange to dark-brown.

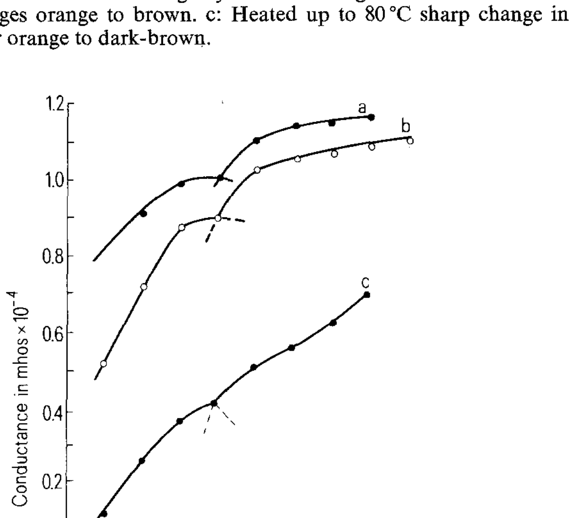

Fig. 3. Volume of metal ion added. a: 40 ml of 0.01 M aspirin vs 0.1 M UO_2^{+2} (pH 4.2–5.5). b: 40 ml of 0.01 M aspirin vs 0.1 M Bi^{+3} (pH 2–5.5). c: 40 ml of 0.01 M aspirin vs 0.1 M Zn^{+2} (pH 4–5.5).

ed out, washed several times with alcohol and dried over vacuo. Similarly the orange-brown crystals of uranyl complex were isolated in aqueous medium. The complexes were microanalyzed for carbon and hydrogen.

Results and discussion. Reverse conductometric[8] (figure 3), pH metric titration (figure 4) and Job's method of continued variation[9] using spectrophotometer (in case of UO_2^{+2} ion) gave the molar ratio 1:2 (metal: ligand) for Bi^{+3}, Zn^{+2} and UO_2^{+2} with acetyl salicylic acid. The pH of the solutions was kept constant in all cases for Bi^{+3}, pH 2.5–5.5,

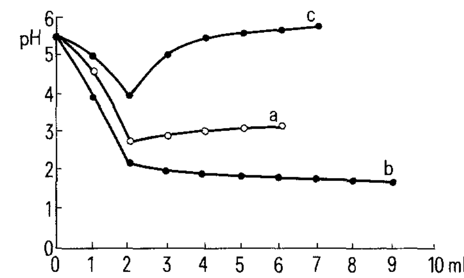

Fig. 4. Volume of 0.1 M metal ion added. a: 40 ml of 0.01 M aspirin vs UO_2^{+2} ion in water. b: 40 ml of 0.01 M aspirin vs Bi^{+3} ion in alcohol. c: 40 ml of 0.01 M aspirin vs Zn^{+2} ion in alcohol.

Zn^{+2}, pH 4–5.5, and for UO_2^{+2}, pH 4.2–5.5. The only colored complex with UO_2^{+2} ion was studied with the help of Job's method of continued variation in which the absorbance values were plotted against the ratio of concentrations of uranyl ion to total concentration of ligand (figure 2) at $\lambda_2$max 490 nm (figure 1). There was no change in wavelength in the range of 4.2 to 5.5 pH. The elemental analyses gave the composition of complex 1:2, this further confirms the ratio of complexes.

In the IR-spectra of acetyl salicylic acid about 40 bands can be seen, and it is unnecessary to give the specific assignment to all the bands present in the spectra. According to structure, 2 pertinent positions may be prone to coordinate in acetyl salicylic acid: they are carboxyl group and carbonyl of acetyl group[10].

In the spectra of salicylic acid, we assign the weak band at 2500–2600 cm^{-1} to COOH stretching vibration[11], 1750 cm^{-1} to –CO of dimer and monomer[11] and 1460 cm^{-1} may be assigned for methyl group[11]. The medium peak in the region of 1140 to 1120 cm^{-1} can be assigned to $-OCH_3CO$[12].

In a complex with metals like Bi^{+3}, Zn^{+2} and UO_2^{+2}, a change is expected in the spectra of acetyl salicylic acid. The shifting of 1750, 1680 and 1200 cm^{-1} band indicates that the coordination is taking place through both groups, i.e. carboxylic and acetyl group. The weakening of 1460 and 2500–2600 cm^{-1} peaks also confirms this fact. These changes are clear in the spectra of the complexes. The acetyl salicylic acid must therefore be acting as bidentate ligand.

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