ANION EXCHANGE STUDIES ON HYDROUS ZIRCONIUM OXIDE IN PARTIALLY NON-AQUEOUS SOLVENT SYSTEM

Javed Iqbal, M. Latif Mirza and Shaheena Ghafoor

Chemistry Department, Islamia University, Bahawalpur, Pakistan

The anion exchange behaviour of the transition elements, chromium, manganese, iron and cobalt was studied over hydrous zirconium oxide (HZO) dried at 35°C using ethanol/methanol-water mixture containing hydrochloric acid as solvent system. The distribution coefficient (K_d) in ethanol-hydrochloric acid system is found to be higher than that observed in methanol-hydrochloric acid system. The selectivity order in both systems is Cr(III)>Fe(II)≥Co(II)>Mn(II). Successful column separation of metal ions has been carried out using such mixtures of suitable composition.

Key words: Anion exchange, Transition elements, Non-aqueous solvent system.

Introduction

The separation of metal ions as chloro complexes from aqueous hydrochloric acid solutions using ion exchange columns is well established and valuable analytical procedure [1-3]. It is reported that the metal ions are adsorbed strongly in lower hydrochloric acid concentration, if a water-miscible organic solvent is added to the aqueous hydrochloric acid [4]. Katzin and Gebert [5] studied adsorption of some metal ion salts on anion exchange resins from acetone solutions and suggested uptake of salt as complex anions. On the other hand Davies and Owen [6] have, however, suggested adsorption of metal ions through a solvent extraction process. Whereas Tuck and Welch [7] described that the uptake of plutonium (IV) by an anion exchange resin from a nitric acid-diethylene glycol dibutyl ether solution. The present studies describe adsorption and ion-exchange behaviour of transition metals from chromium to cobalt as chlorocomplexes on hydrous zirconium oxide (HZO) in partially non-aqueous media in various combinations of hydrochloric acid-water-methanol/ethanol alcohol and these results are compared with those observed earlier [8].

Experimental

The ion exchange resin HZO was prepared as described earlier [9]. Before use, the resin was washed several times by decantation to remove very fine particles, then washed with 1-2 M HCl to remove metallic impurities. In the end, the resin was washed with water and allowed it to air dry at 35°c. The water content was 17.6% which were determined by the formation of ZrO_2 at 600°c and the molar ratio of ZrO_2 to water was calculated to be 1:1.46. The metal salt solutions ranging from 1-10 ppm were prepared by appropriate dilution of the stock solutions (1000 ppm). Special precautions were made in preparing the test solutions of Mn (II), which were pretreated with a small amount of sodium hexanedioate (sodium adipate) for reduction of oxidized managnese. Solvent mixtures were prepared so that the amount of organic solvent and water was expressed as percentage by volume and hydrochloric acid concentration as molarity. For example one litre of 0.5 M hydrochloric acid in 15% methanol is prepared as follows: 150 ml of methanol was mixed with 42.3 ml concentrated hydrochloric acid and 807.7 ml distilled water. All solutions were stored in plastic vessels. The concentration of metal ions, manganese, cobalt, iron and chromium were determined using standard spectrophotometric methods [10, 11]. The k_d values were determined by batch equilibrium technique described earlier [12]. The amount of metal ions adsorbed was determined from the difference between the initial and the final solution concentration in the clear supernatant solutions. The column operation were carried out as described elsewhere [13].

Results and Discussion

Distribution Coefficients of Mn(II), Fe(II), Co(II) and Cr(III) on HZO. Based on measurements of distribution coefficients of chromium, manganese, iron and cobalt from various mixtures of methanol/ethanol and hydrochloric acid, the most suitable eluting conditions for column separation were selected. The K_d values and the separation factor 'α' of transition metals are listed in Table 1. From earlier reports [1,3] it can be seen that the K_d values of the divalent transition metal ions depend upon the concentration of hydrochloric acid. At high concentration of HCl, the k_d values are increased with the HCl concentration, whereas reverse is true for comparatively lower range of HCl concentration (10^{-5} - 0.1M). This behaviour is attributed to the formation of MCl_3^- and MCl^+ complexes respectively. In the present studies, the K_d values were calculated using alcoholic content affect the K_d

values to varying degree. Typical results are shown in Fig. 1. However, there is a little increase in k_d values with small increase in the HCl concentration. It is, therefore, suggested that fairly low concentration of HCl(upto 0.5 M) is sufficient to form a metal chloro complex MCl_3^- which is strongly held on to the anion exchanger. The effect of alcohol concentration is much stronger under similar experimental conditions. For example, in case of ethanol-hydrochloric acid system (Fig. 2), the K_d values are significantly higher than those observed in methanol hydrochloric acid system (Fig.3). This may be due to polarity of the solvents, since methanol is more polar than ethanol and probably formation of MCl_3^- is favoured in ethanol. The selectivity order in both of the solvents is Cr(III)>Fe(II)≥Co(II)>Mn (II), which is almost in accordance with the affinity sequence observed on hydrous chromium oxide without using organic solvent [8]. However, in the present case, the use of alcohol not only increases the K_d values of the metal ions, but also increases the separation factor 'x' (Table 1), with the result the separation of the metal ions from their mixture is more effective in the presence of the alcoholic solvent. When the solvent contains very high percentage (~90%) of alcohol the K_d value decreases till it tends to zero. This may be attributed due to formation of an uncharged solvated ion pair, $H^+MCl_3^-$(M=Co,Fe,Mn) or $H^+CrCl_4^-$.

TABLE 1. LOG K_d (ML G^{-1}) AND SEPARATION FACTOR (α) FOR CHROMIUM, IRON MANGANESE AND COBALT ON HZO.

| Solvent system	Parameters	Ions			
		Mn(II)	Co(II)	Fe(II)	Cr(III)
15% CH₃OH	log kd	0.63	0.80	1.10	1.41
0.5 M HCl	α	1.40	1.37	1.28	
15% C₂H₅OH	log kd	1.00	2.00	1.78	2.12
0.5 M HCL	α	2.00	1.12	1.19	
30% CH₃OH	log kd	0.63	0.90	1.30	1.49
0.5 M HCl	α	1.60	1.44	1.18	
30% C₂H₅OH	log kd	1.05	2.30	2.23	2.75
0.5 M HCl	α	2.42	1.03	1.23	
45% CH₃OH	log kd	0.70	1.23	1.42	1.58
0.5 m HCL	α	1.76	1.15	1.11	
45% C₂H₅OH	log kd	1.00	2.6	2.75	3.50
0.5 M HCl	α	2.60	1.06	1.27	
60% CH₃OH	log kd	0.89	1.26	1.46	1.65
0.5 M HCl	α	1.42	1.16	1.13	
60% C₂H₅OH	log kd	1.40	3.31	3.48	1.96
0.5 M HCl	α	2.36	1.05	1.78	
75% CH₃OH	log kd	1.12	1.33	0.84	1.68
0.5 M HCl	α	1.19	1.58	2.00	
75% C₂H₅OH	log kd	1.00	1.88	1.61	1.67
0.5 M HCl	α	1.88	1.17	1.04	
90% CH₃ OH	log kd	0.00	0.39	0.00	1.12
0.5 M HCl	α	–	–	–	
90% C₂H₅OH	log kd	0.30	1.66	1.39	1.31
0.5 M HCl	α	5.53	1.19	1.06	
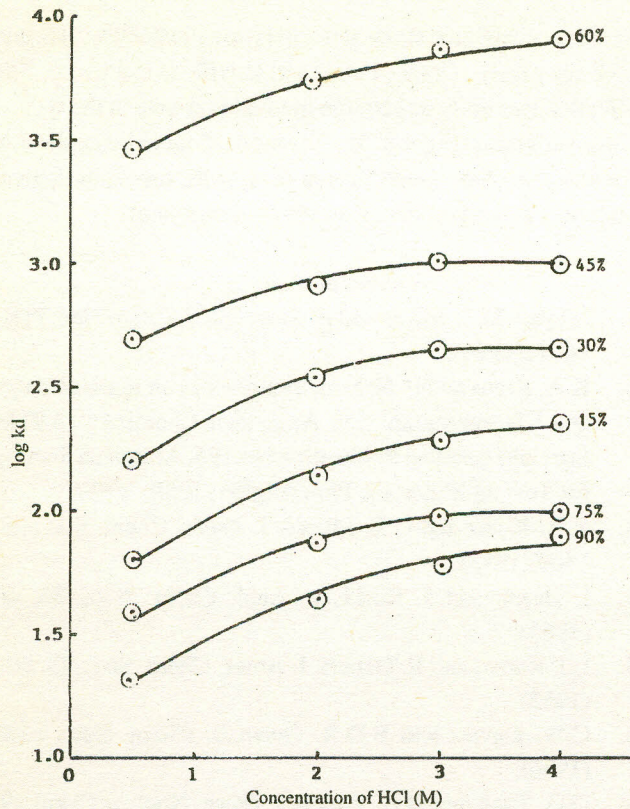
Fig. 1. Distribution coefficient (kd) of Fe(II) chloride in various concentrations of ethyl alcohol vs hydrochloric acid concentrations.

Column chromatographic separation of Mn(II), Fe(II), Co(II) and Cr (III). Batch distribution coefficient is used in selecting conditions for column separation. To separate the metal ions on an ion exchange column the alcohol composition in aqueous HCl is chosen in such a manner that one metal is rapidly eluted from the column while the others are co-adsorbed. Due to considerable differences in K_d values and high separation factor α', it can be expected that the metal separation on an anion exchange column of moderate length should be possible. Based on Fig. 2, and values obtained by Fig. 4, following elution scheme seems to be most promising for separation of the metal ions from each other:
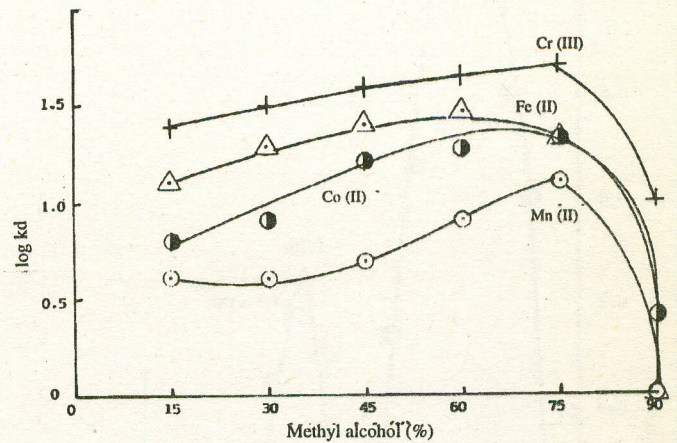

Fig. 3. Distribution coefficient of metal ions against percentage of ethyl alcohol in 0.5 M HCl.
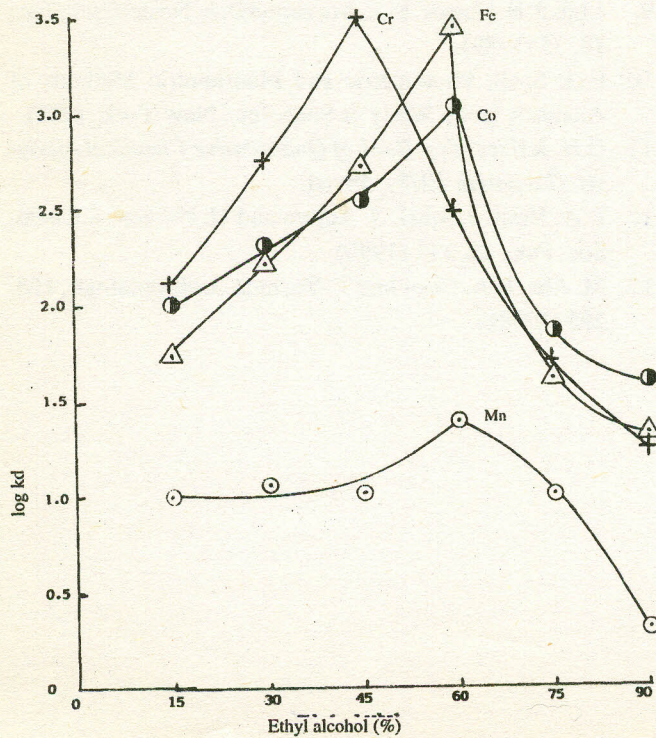

Fig. 2. Distribution coefficient of metal ions against percentage of ethyl alcohol in 0.5 M HCl.
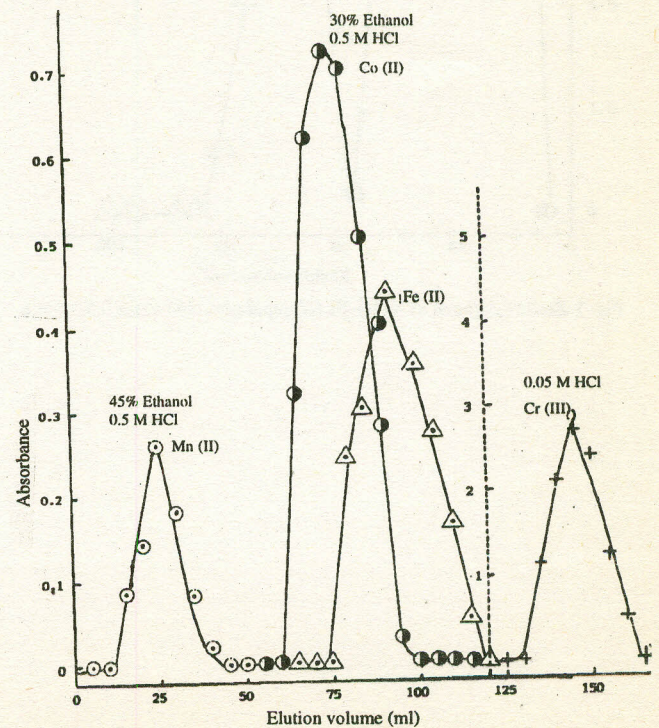

Fig. 4. Elution of transition metal ions. Flow rate 0.5 ml/min, concentration of metal ions 0.1 mg each.

Mn(II) is eluted with 45% ethanol-0.5M HCl, Co (II) and Fe(II) are eluted with 30% ethanol - 0.5 M HCl, and Cr(III) is eluted with 0.05M aqueous HCl. Similarly Co (II) and Fe(II) can be separated from each other using 30% methanol-0.5 M HCl and 90% methanol - 0.5 M HCl, respectively (Fig.2). Separation experiments showed that selected elements were effectively separated at a flow rate of 0.1 ml/min. The quanti-

tative determination showed recories up to 94%,90%,91% and 89% for Mn(II), Co(II), Fe(II) and Cr(III), respectively. The effectiveness of the separation method is shown in the typical chromatograms (Fig.4 & 5). This method could be applicable for analysis of the metal ions in ores, soils, ashes, biological materials and other natural synthetic substances.

References

1. J. Iqbal, M.L. Mirza and N. Sareecha, J. Chem. Soc. Pak., **16**, 22(1994).

2. K.A. Kraus and F. Nelson, Symposium on Ion-Exchange and Chromatography in Analytical Chemistry (ASTM Special Technical Publication No.195, American Society for Testing Materials, Philadelphia, 1958), pp27.

3. K.A. Kraus and G.E. Moore, J. Amer. Chem. Soc., **75**, 1460 (1953).

4. I. Hazan and J. Korkisch, Anal. Chem. Acta, **32**, 46 (1965).

5. L.I. Katzin and E. Gebert, J. Amer. Chem. Soc., **75**, 801 (1953).

6. C.W. Davies and B.D.R. Owen, J. Chem. Soc., 1676 (1956).

7. D.G. Tuck and G.A. Welch, J. Inorg. Nuclear Chem., **9**, 302 (1959).

8. J.Iqbal, H. Nawaz, M.L. Mirza and B.A. Nasir, J. Sci. Res., **18**, 35 (1989).

9. J.Iqbal, H. Nawaz, M.L. Mirza and B.A. Nasir, J. sci. Res., **18**, 35 (1989).

10. F.D. Snell, Photometric and Flourimetric Methods of Analysis, (John Wiely & Sons, Inc., New York, 1978).

11. G.H. Jeffery, *Text Book of Quantitative Chemical Analysis, (Longman 1978)*, 4th ed.

12. B.A. Nasir, J. Iqbal, S. Anjum and U. Noreen, J. Chem. Soc. Pak., **12**, 111 (1990).

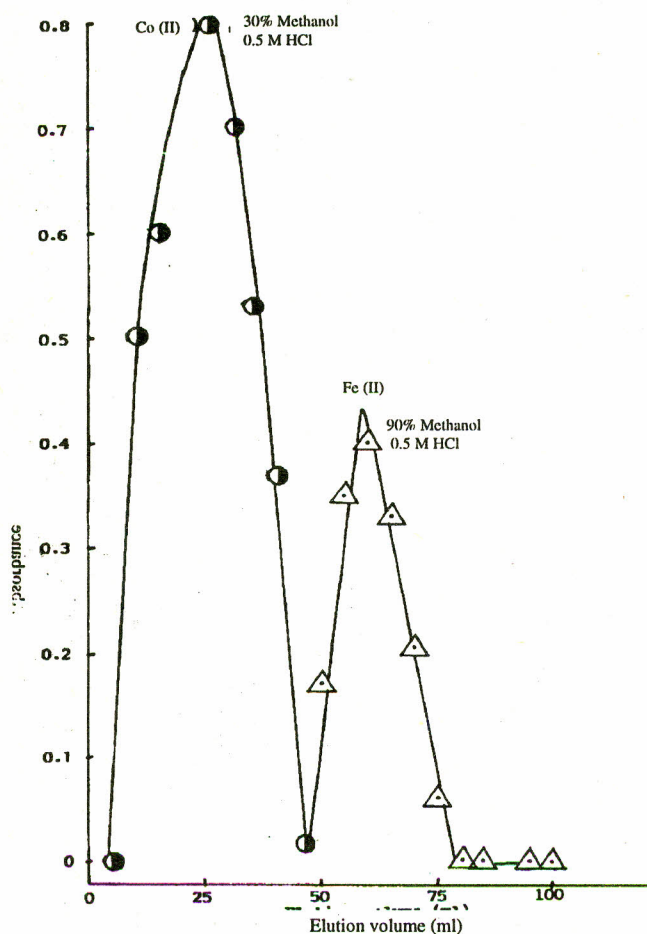13. M. Abe, B.A. Nasir and T. Yoshida, J. chromatogr., **153**, 295 (1978).

Fig. 5. Elution curve of a Co (II)–Fe (II) separation. Flow rate 0.5 ml/min.