these ligands towards alkali metals; but these changes in the donor properties are not related in any simple way to the donor group, ring size of the ligand, electro-negativity or polarisability of the metals. They are most likely to be the resultant of some or all of the factors mentioned above.

The present work furnishes a comparative and interesting study of such ligands with those of the ligands of the previous work[1], which formed stabler adducts.

Infrared spectra of ML.NO_2-BAN and ML.Cl-BAN: The ir spectra was recorded in a Perkin-Elmer 521 spectrophotometer with expanded scale. In the adducts, OH stretching frequencies appeared at ~3100 cm^{-1}, which suggests[4] association of the OH group. The NO_2 assymetric frequency of the ligand at 1575 cm^{-1}, have been found to be shifted down due to the association[5] by 5-15 cm^{-1} in the adducts. The N=N band of the nitro- and chloro-ligands at 1555 and 1570 cm^{-1}, shifted down by 5-20 cm^{-1} in the adducts, suggesting again the weak[6] association of N=N group in the adducts. Selected ir frequencies are given in Table 2.

TABLE 2—SELECTED IR BANDS

Compd.	ν_{as} (NO_2) cm^{-1}	$\nu_{N=N}$ cm^{-1}
NO_2-BAN (=L)	1575	1555
Na1N2N.L	1570	1550
K1N2N.L	1565	1545
Li8HQ.L	1570	1550
Na8HQ.L	1565	1550
K8HQ.L	1560	1540
Na2H3NA.L	1570	1540
K2H3NA.L	1570	1550
NaSalA.L	1565	1540
NaSalH.L	1570	1550
Cl-BAN (=L′)		1570
Li1N2N.L′		1540
Na1N2N.L′		1555
K1N2N.L′		1540
Li8HQ.L′		1560
Na8HQ.L′		1560

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Solvent Extraction Behaviour of Iron(III) with Versatic 911 and its Application to Indian Minerals

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DURING the last decade considerable progress has been made in the application of solvent extraction to the separation of metals. In this respect high molecular weight carboxylic acids have found considerable interest as extractant in industry, atomic energy programme and in hydrometallurgical processing of ores because of low cost, ease of availability and high metal loading capacity[1,2]. The synthetic carboxylic acids Versatic 9, Versatic 911 and Versatic 10 have been extensively used in our Laboratory for the extraction of cerium(IV), thorium(IV) and uranium(VI)[3-5]. A survey of literature revealed that little work has been done on the extraction of iron(III) with versatic acids[5,6]. No work has yet been made on the extractive separation of iron from various binary mixtures, moreover, extraction studies has not yet been applied in hydrometallurgy. The present work describes the selective extraction of iron(III) from various metal ions using Versatic 911 as extractant. The study includes the hydrometallurgical separation of iron(III) from a number of available iron mineral.

Experimental

Versatic 911 (Shell Chemical Co., London) is a mixture of tertiary C_9-C_{11} monocarboxylic acid and its purity is 99% and strength is 5.83 *M*. Ferric chloride solution (5 mg ml^{-1}) was prepared from ferric chloride (A.R.) and standardised by complexometric titration with EDTA (disodium salt) using sulphosalicylic acid as indicator[7].

General extraction procedure: The procedure of the experiment was based on the solvent extraction technique. Test solution (10 mg of iron) was taken in a 250 ml separatory funnel and equilibrated with 10 ml Versatic 911 solution (10 ml; Versatic 911-butanol = 1 : 5) by manual shaking. The total volume of the aqueous phase was made up to 20 ml, *i.e.* the ultimate concentration of iron(III) in the aqueous phase was 8.9×10^{-3} *M*. The acetate ion concentration was kept at 0.1 *M* during extraction. The optimum contact time of 5 min was maintained during extraction. After equilibration both the phases were settled for 5 min and the aqueous phase was separated. To remove any trace of organic solvent entrained in the separated aqueous phase, the aqueous phase was washed with butanol (5 ml). The resulting butanol extract was mixed with the separated organic phase. The amount of iron(III) present in the aqueous phase was estimated by complexometric titration. The organic phase was stripped with 1 *M* HNO_3 (20 ml) and the acid extract, after adjusting the proper *p*H, was estimated.

Results and Discussion

Effect of variables on extraction : The extraction behaviour of Fe(III) with Versatic 911 in butanol medium at various *p*H was performed using buffer solutions of different *p*H. The extraction of Fe^{III} increases with increased *p*H and becomes quantitative at *p*H 2.6-3.8. So, *p*H of the aqueous phase was maintained at 2.8 for quantitative extraction throughout the experiments. The experiments were performed at constant acetate concentration (0.1 *M*) and constant metal ion concentration.

Various diluents : Iron(III) was extracted with Versatic 911 using various diluents, such as n-hexane, carbon tetrachloride, xylene, toluene, diisopropyl ether, chloroform, butanol and nitrobenzene. Quantitative extraction was achieved only in butanol and nitrobenzene systems having high dielectric constants whereas in case of other diluents extraction decreased. It was observed further that in case of nitrobenzene, emulsion forming tendency of the solvent increased during extraction requiring more settling time than that of butanol. To avoid this difficulty butanol was chosen as the suitable diluent for this extraction system. The distribution coefficient(D) reached a constant value within 0.5 min of shaking and back extraction was completed within 8 min. So, contact time and stripping was fixed to 5 min and 10 min, respectively in all the experiments.

Extractive separation : Iron(III) was separated from several binary and ternary mixtures using the recommended extraction procedure. The aqueous phase containing $8.9\times10^{-3}M$ iron(III) and appropriate quantity of foreign ions were equilibrated with $5.43\times10^{-1}M$ Versatic 911 (10 ml) in butanol for 5 min at *p*H 2.8. The organic phase after equilibration was stripped with 1 *M* HNO_3 (20 ml) for 10 min and iron(III) was estimated by complexometric titration with EDTA (disodium salt) using sulphosalicylic acid as indicator. Iron(III) was separated from Ca, Mg, Sr, Ba, Mn, Co, Ni, Cu, Zn, Cd, Hg, Pb and Al. Iron(III) was also separated from Pr, Nd, Sm, Gd, Tb and U. The extractive separation procedure is very simple and rapid and requires only *p*H control in all cases. The effect of foreign ions on extraction of iron(III) were given in Table 1. In order to assess the possible analytical application of the proposed method, the process was applied to extract iron(III) from several synthetic mixtures prepared by mixing 5 mg of each foreign ions and 10.9 mg of iron(III). The total volume of the aqueous phase was kept 20 ml and that of organic phase 10 ml. Extraction was carried out with $5.43\times10^{-1}M$ Versatic 911 at *p*H 2.8. In most of the cases, quantitative recovery of iron(III) was achieved. The results are given in Table 2.

Extraction of iron from ore solution : Extraction of iron from ore solution was performed with Versatic 911 according to the general extraction procedure as described earlier. The optimum *p*H for extraction was 2.8, and the contact time and stripping was kept 5 and 10 min, respectively in each case. The ratio of organic phase and aqueous phase was maintained 1 : 2. The concentrations of iron in the aqueous phase during extraction were 1.83×10^{-2} and $1.38\times10^{-2}M$, respectively. The results show that iron(III) has been selectively

TABLE 1—EFFECT OF DIVERSE IONS ON EXTRACTION OF IRON(III)

Versatic 911 = 5.4×10^{-1} *M*, $Fe^{III}=8.9\times10^{-3}$ *M*, *p*H = 2.8

Diverse ions	Amount added mg	Source	Fe^{III} extracted %
Ca^{II}	200	$CaCl_2.6H_2O$	99.3
Mg^{II}	200	$MgSO_4.7H_2O$	100
Ba^{II}	190	$BaCl_2.6H_2O$	100
Sr^{II}	170	$SrCl_2.6H_2O$	98.5
Mn^{II}	220	$MnCl_2.4H_2O$	100
Ni^{II}	200	$NiSO_4.7H_2O$	100
Co^{II}	180	$CoSO_4.4H_2O$	100
Pb^{II}	180	$Pb(CH_3COO)_2.3H_2O$	100
Hg^{II}	200	$HgCl_2$	99.3
Al^{III}	200	$Al(NO_3)_3$	100
Zn^{II}	100	$ZnSO_4.7H_2O$	100
Cu^{II}	200	$CuSO_4.5H_2O$	100
Cd^{II}	225	$CdSO_4.4H_2O$	100
Pr^{III}	50	$Pr(NO_3)_3.6H_2O$	100
Nd^{III}	50	$Nd(NO_3)_3.6H_2O$	100
Sm^{III}	50	$Sm(NO_3)_3.6H_2O$	100
Gd^{III}	50	$Gd(NO_3)_3.6H_2O$	100
Tb^{III}	50	$Tb(NO_3)_3.6H_2O$	100
U^{VI}	50	$UO_2(NO_3)_2.6H_2O$	100

TABLE 2—QUANTITATIVE RECOVERY OF IRON(III) FROM SYNTHETIC MIXTURE

Versatic 911 = 5.4×10^{-1} *M*, *p*H = 2.8

Sample no.	Synthetic mixture	Iron(III) Taken	Iron(III) Found	Error %
1	$Fe^{III}+Cu^{II}+Co^{II}$	10.93	10.93	0
2	$Fe^{III}+Cu^{II}+Zn^{II}$	10.93	10.93	0
3	$Fe^{III}+Pb^{II}+Cd^{II}$	10.93	10.82	1
4	$Fe^{III}+Co^{II}+Ni^{II}$	10.93	10.82	1
5	$Fe^{III}+Co^{II}+Mn^{II}$	10.93	10.93	0
6	$Fe^{III}+Cu^{II}+Ni^{II}$	10.93	10.82	1
7	$Fe^{III}+Pb^{II}+U^{VI}$	10.93	10.71	2
8	$Fe^{III}+Ni^{II}+Mn^{II}$	10.93	10.82	1
9	$Fe^{III}+Pb^{II}+Al^{III}$	10.93	10.82	1
10	$Fe^{III}+Mn^{II}+Co^{II}+Ni^{II}$	10.93	10.82	1
11	$Fe^{III}+Cu^{II}+Co^{II}+Ni^{II}$	10.93	10.93	0
12	$Fe^{III}+Cu^{II}+Mn^{II}+Co^{II}$	10.93	10.93	0
13	$Fe^{III}+Al^{III}+Cu^{II}+Ni^{II}$	10.93	10.93	0

recovered from its ore solution by the proposed solvent extraction technique.

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Electrochromatographic Analysis of d-Block Cations

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CHROMATOGRAPHIC analysis of cations complexed with a variety of organic ligands$^{1-3}$ including ketoanils$^{4-8}$ are well documented. Electrochromatographic analysis of mixtures of II, III and IV group transition basic radicals and their mixtures with Au^{III}, complexed with *p*-diethylaminoanil of thiopheneglyoxal (DEATG) unknown as yet, has been described in the present note.

Experimental

p-Diethylaminoanil of thiopheneglyoxal and its complexes were prepared and isolated by the reported method^8. In the synthetic work B.D.H. laboratory grade chemicals were used.

One or two drops of test solutions of moderate concentrations were applied in the middle of the 3×35 cm Whatman No. 1 filter paper strips with the help of fine capillaries and paper strips were dried in air. Loaded strips were carefully hanged in vertical type of apparatus having electrolytic solvent in its electrode chambers. When the paper strips were saturated with the solvent a constant voltage was applied for 1.5 to 3.0 h and chromatograms were dried in air. Direction and distance of spots from the point of application were noted.

Results and Discussion

All the complexes have shown unidirectional motion towards cathode. Migration rates of complexes spotted individually and in mixtures (Table 1) have not differed appreciably. Perusal of Table 1 shows that the method of electrophoresis could be successfully used to achieve qualitative separations of transitional basic radicals of II, III and IV groups and various mixtures of Au^{III} with Cr^{III}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II} and Hg^{II}, in diverse developing solvents. Chromatogram fragments were identified by their own colours, which being highly stable retained for a long time.

Table 1—Qualitative Analysis of Complex Mixtures

Complex mixture	Developing solvent	Spot colour	Distance travelled
$Hg(DEATG)Cl_2, H_2O$	AcOMe-AcOH (1 : 1, v/v)	Pink gray	2.2
$Cd(DEATG)_2Cl_2$		Yellow gray	0.8
$Cr(DEATG)Cl_2\ 4H_2O$	MeOH-H_2O (4 : 1, v/v)	Brown	1.5
$Fe(DEATG)_2Cl_3$		Brown	2.5
$Mn(DEATG)_2Cl_2.2H_2O$	AcOMe-AcOH (1 : 1, v/v)	Gray	0.2
$Co(DEATG)Cl_2$		Gray	0.7
$Ni(DEATG)_2Cl_2$		Pink	2.4
$Zn(DEATG)Cl_2.2H_2O$		Yellow	1.3
$Au(DEATG)Cl_3.H_2O$	AcOH	Orange	0.6
$Ni(DEATG)_2Cl_2$		Pink	0.0
$Fe(DEATG)_2Cl_3$		Brown	1.1
$Au(DEATG)Cl_3.H_2O$	AcOMe-AcOH (1 : 1, v/v)	Orange	0.0
$Cd(DEATG)_2Cl_2$		Yellow gray	0.8
$Zn(DEATG)Cl_2.2H_2O$		Yellow	1.3
$Hg(DEATG)Cl_2.H_2O$ (or $Ni(DEATG)_2Cl_2$)		Pink gray/Pink	2.2 (or 2.4)
$Au(DEATG)Cl_3.H_2O$	Iso-BuOH satd. with 0.1 *N* HCl	Orange	0.0
$Co(DEATG)Cl_2$		Gray	0.8
$Ni(DEATG)_2Cl_2$		Pink	1 4
$Au(DEATG)Cl_3.H_2O$	MeOH-H_2O (4 : 1, v/v)	Orange	0.0
$Ni(DEATG)_2Cl_2$		Pink	0.8
$Cr(DEATG)Cl_3.4H_2O$		Brown	1.5
$Fe(DEATG)_2Cl_3$		Brown	2.5