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Extraction of 3d Transition Metals from Molten Cesium-Sodium-Potassium/Acetate Eutectic Into Dodecane Using Organophosphorous Ligands

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ABSTRACT

Measurements have been made of the transfer of the transition metal cations Cr^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+} from molten cesium acetate-sodium acetate-potassium acetate eutectic (50-25-25 mol%, mp ~90°C) into dodecane solutions containing selected acidic and neutral organophosphorous extracting ligands. The ordering of the transition metals according to their relative extents of extraction into the dodecane phase when the ligand bis(2-ethylhexyl)-phosphinic acid, H[DEPH], is employed (and the conditions of extraction are the same for each cation) is $Co^{2+} > Fe^{2+} > Cr^{3+} > Ni^{2+}$. Comparisons of results obtained using the acidic ligand H[DEPH] and the neutral ligand tri-*n*-octylphosphine oxide, TOPO, indicate that the extractible TM complex does not contain acetate as a charge neutralizing ligand, but rather requires complete displacement of inner sphere acetate ions by protonated and/or deprotonated alkylphosphinate groups. The mechanism controlling the transfer kinetics has not been elucidated, but the rates of extraction from the acetate eutectic appear to be somewhat slower than has been observed for the extraction of transition metals from molten alkali metal thiocyanate and nitrate media at comparable temperatures, i.e., 140→180°C.

INTRODUCTION

There have been numerous studies of the rate and extent of extraction of metal cations from aqueous solutions into organic solvents using

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organophosphorous ligands. The purpose of this paper is to communicate some recent results of transition metal extraction experiments wherein an anhydrous molten alkali metal carboxylate is employed as the host (or feed) solvent and a dodecane solution containing an organophosphorous ligand serves as the extracting medium. Although detailed kinetics studies have not as yet been performed, these initial results do present an opportunity to examine the extraction of transition metal (TM) cations from a ligand field environment that differs in many respects from H_2O. Because the carboxylate ligands are charged instead of neutral (e.g., as in the case of H_2O), the complexation energies tend to be larger than with neutral ligands and, as a result, the rates of intermedium transfer of the TM cations (from molten carboxylate to dodecane solution) could turn out to be slower than those obtained when water is the host solvent. In addition, some molten carboxylates exhibit high viscosity and surface tension at temperatures well above their melting points, which would also tend to slow down intermedium transfer. While slower kinetics is generally not desirable in most practical applications, molten carboxylates may present some new opportunities for the development of extraction schemes having greater selectivity. For example, molten carboxylates might find application in connection with advanced metal winning concepts that employ biological agents to leach TMs from minerals and waste materials.

This particular study reports information on the extents and, in a very qualitative way, the rates of extraction of the 3d TM cations Cr^{3+}, Fe^{2+}, Co^{2+}, and Ni^{2+} from a low-melting alkali metal carboxylate eutectic--the cesium-sodium-potassium/acetate eutectic--using selected neutral and acidic organophosphorous ligands in an organic solvent. The results are compared with related published data for the extraction of 3d TM cations from aqueous solution (1-6), from molten KSCN-NaSCN eutectic (7), and from molten $LiNO_3$-KNO_3 eutectic (8), also employing organophosphorous ligands.

EXPERIMENTAL

The alkali metal acetate (Ac) eutectic used in this work--the cesium acetate-sodium acetate-potassium acetate eutectic (50-25-25 mol%)--has a melting point of ~90°C and will hereafter be designated as Ac-02. This eutectic was prepared from the constituent acetate salts using commercially available reagent-grade chemicals. The reagent salts were dried in a vacuum oven overnight at ~110°C and stored in capped jars in a helium atmosphere glove box ($<$ 1 volume ppm moisture) prior to use. (All subsequent handling of these salts and the eutectics prepared from them was done in the glove box, unless otherwise noted.) The preparation of the eutectic consisted of weighing out and mixing the constituent salts, placing them in a Pyrex filter tube with a sealed bottom, and capping off the filter tube with a stopcock joint. The loaded filter tube was then removed from the glove box, placed in a 25-mm-bore Marshall furnace, and connected to a glass vacuum line. The salt mixture was fused under vacuum and maintained in this condition for at least 24 hours to remove any remaining moisture. Following this, the salt was forced through the Pyrex filter (10→20 μm pore size) by pressurization to ~10^5 Pa with dry helium. The filter tube was then removed from the furnace, allowed to cool, and returned to the glove box, where the filtered eutectic was broken free from the portion of the tube below the filterand stored in a capped bottle. Solutions of Cr^{3+}, Fe^{2+}, Co^{2+}, and Ni^{2+} in Ac-02 were prepared by mixing weighed quantities of the TM acetates (commercial reagent-grade chemicals) and Ac-02 and again fusing under vacuum and filtering as described above.

The three organophosphorous ligands used in the extraction experiments--bis(2-ethylhexyl)phosphinic acid (designated herein as H[DEPH]), bis-(2-ethylhexyl)phosphoric acid (designated as HDEPH), and tri-*n*-octylphosphine oxide (designated as TOPO)--were obtained from other workers. The H[DEPH] was prepared by the method described in Ref. (9) for a related phosphinic acid derivative but was purified using the procedure of Partridge and Jensen (10). The source and purification of the HDEPH is described in Ref. (2). The TOPO, purchased from Eastman Kodak (99% pure product), was used as-supplied without further purification. The dodecane was obtained from Phillips 66 (Pure Grade, 99% minimum) and was stored over #4A molecular sieve to minimize moisture contamination.

Standardized solutions of the organophosphorous ligands in dodecane were made up by adding appropriate weights of each ligand to the dodecane and bringing the solution to the required volume. In the case of H[DEPH] and HDEPH, 1.0M solutions were prepared, and aliquots of these were further diluted to obtain 0.1M solutions. For the TOPO, only 0.1M solutions were prepared, as the solubility of TOPO in dodecane at room temperature was observed to be not much greater than 0.1M. A standardized solution of Co^{2+} in 1.0M H[DEPH]/dodecane was prepared by extractively transferring all of the cobalt from a measured aliquot of a standardized aqueous solution of Co^{2+} to a slightly lesser volume of the 1.0M H[DEPH]/dodecane solution. The H[DEPH]/dodecane extract was then separated from the aqueous phase and brought up to a volume equal to that of the aliquot of the standard aqueous Co^{2+} solution. The organophosphorous ligand/dodecane solutions were stored over #4A molecular sieve in capped bottles but were kept outside the glove box. Additions of these solutions to tubes or cells containing the TM/Ac-02 samples were made through a stopcock joint having a side arm that terminated with a septum cap. Measured aliquots were introduced hypodermically through the septum with calibrated syringes.

Equilibration experiments were performed in Pyrex tubes that were 10 mm in diameter. Tubes, with sealed-off bottoms (~200 mm in length), were loaded with weighed quantities of the solidified TM/Ac-02 solutions and measured volumes of the standardized organophosphorous ligand/dodecane solutions, capped, and transferred to the vacuum line, where they were sealed off under slightly reduced pressure, using a glass-blowing torch. The overall length of the sealed tubes was nominally 100 mm, ~80 mm of which was taken up by the sample. The equilibrations were carried out in the 25-mm-bore Marshall furnace. After several of the extraction experiments employing H[DEPH], chemical analyses were made to determine the concentrations of the TMs and the alkali metals in the dodecane phase. These analyses were performed by back-extracting the TMs and alkali metals into concentrated aqueous HCl and analyzing the extract by inductively coupled plasma/atomic emission spectroscopy. The completeness of the back-extraction was checked by conducting an energy dispersive X-ray fluorescence analysis of the stripped dodecane.

Electronic absorption spectra were recorded using a Cary 17H Absorption Spectrophotometer coupled with a specially designed furnace for elevated-temperature spectrophotometric measurements. Experiments with single-phase samples of Ac-02 or dodecane solutions (involving only the recording of a spectrum) were performed by placing the sample in a capped optical cell. These cells consisted of a 15-mm diameter quartz tube, 200 mm in length, with a 10-mm-path-length, UV-grade quartz cuvette (12.5 mm wide and 45 mm high, from J&S Scientific) fused to one end and a ground glass joint fused to the other end. After loading an Ac-02 sample in the glove box, the cell was capped off with a stopcock joint, returned to the Marshall furnace, connected to the glass vacuum line, evacuated, and heated to ~150° C. When the sample was completely melted, the cell was backfilled with dry helium and then rapidly transferred to the preheated spectrophotometer furance before the sample had a chance to solidify. For dodecane solutions, the loaded, capped optical cell was placed in the beam of the spectrophotometer and the spectra were recorded at room temperature.

In spectrophotometric experiments with two liquid phases, where attempts were made to quantify extraction rates, a sealed cell was employed. The procedure with these cells differed from the one used with the capped cells in that solidified TM/Ac-02 solution and dodecane solution were introduced to the same cell, the cell was attached to the vacuum line, and the neck of the cell was sealed off under slightly reduced internal pressure. The overall length of the sealed cell (~90 mm) was such that it fit entirely within the isothermal zone of the spectrophotometer furnace. With this configuration and with proper adjustment of the amounts of the two phases, it was possible to view the bottom phase (i.e., Ac-02) during the elevated-temperature extraction without any evaporative loss of the dodecane.

RESULTS

In the first series of experiments performed as part of this research, 0.1M solutions of Cr^{3+}, Fe^{2+}, Co^{2+}, and Ni^{2+} in Ac-02 were equilibrated with neat dodecane (referred to as blanks) and with 0.1M solutions of each of the three organophosphorous ligands (H[DEPH], HDEPH, and TOPO) in dodecane. Where organophosphorous ligands (OPLs) were present, an excess of the dodecane solution was used, such that the ratio of OPL to TM was ~10:1 in each case, and the equilibrations were carried out at temperatures in the range 140→180°C. Samples containing mixtures of pure Ac-02 with each of the OPL/dodecane solutions were equilibrated to verify that these constituents were chemically stable in a TM-free environment. All of these equilibrations were carried out in sealed glass tubes as described in the Experimental section.

Typically, the equilibrations were carried out for a period of 10 to 14 days. Their progress was assisted by periodic shaking and was monitored by visual observation of the liquid phases present in the sealed tubes. The interface between the Ac-02 and the dodecane phases was always readily discernable. Furthermore, because of the distinct color that each TM has in Ac-02 (11) and in OPL/dodecane solutions (discussed further on), the extent of transfer of the TMs from Ac-02 to the dodecane phase could be gauged during the course of the periodic visual observations. Table 1 contains a summary of test results for a set of equilibrations carried out at 145±5°C.

The combined results of the above equilibration tests are best described as follows: (i) In the absence of an OPL, there is no extraction of TM into the dodecane phase. (ii) On the time scale of the equilibrations, none of the TM cations is extracted into the dodecane phase by the neutral TOPO ligand. (iii) With the HDEPH/dodecane solution, a third liquid phase develops between the Ac-02 and the dodecane, and this new phase appears to contain an appreciable quantity of the transition metal in all cases. The new phase is observed to be a solid at room temperature, but has otherwise not been characterized. (iv) The most interesting results were obtained with the H[DEPH]/dodecane solution. Within a period of a week, most of the Co^{2+} was extracted into the dodecane phase, and after 10 to 14 days, evidence for partial extraction of Fe^{2+} and Cr^{3+} was apparent as well. At the end of the equilibration period, there was still no sign of Ni^{2+} extraction. However, the appearance of a grayish color in the Ni^{2+}/Ac-02 phase after several of the

TABLE 1.

Equilibration Test Results for the Extraction of Cr^{3+}, Fe^{2+}, Co^{2+}, and Ni^{2+} from Ac-02 Using Solutions of Selected Organophosphorous Ligands in Dodecane (at 145±5°C)

Transition Metal Cation	Approximate Equilibration Time (h)	Organophosphorous Ligand in Dodecane[a]			
		Blank[b]	H[DEPH][c]	HDEPH[c]	TOPO[c]
Cr^{3+}	20	No Ext.	No Ext.	No Ext.	No Ext.
	125	No Ext.	No Ext.	3rd Phase	No Ext.
	250	No Ext.	Part. Ext.	3rd Phase	No Ext.
Fe^{2+}	20	No Ext.	No Ext.	No Ext.	No Ext.
	125	No Ext.	Bgn. Ext.	3rd Phase	No Ext.
	250	No Ext.	Part. Ext.	3rd Phase	No Ext.
Co^{2+}	20	No Ext.	Bgn. Ext.	No Ext.	No Ext.
	125	No Ext.	Part. Ext.	3rd Phase	No Ext.
	250	No Ext.	Cmpl. Ext.	3rd Phase	No Ext.
Ni^{2+}	20	No Ext.	No Ext.	No Ext.	No Ext.
	125	No Ext.	No Ext.	3rd Phase	No Ext.
	250	No Ext.	No Ext.	3rd Phase	No Ext.

[a] No Ext.=no extraction observed, Bgn. Ext.=evidence of slight extraction, Part. Ext.=obvious partial extraction, Cmpl. Ext.= complete extraction, and 3rd Phase=evidence for formation of a third liquid phase.

[b] Blank sample of TM/Ac-02/dodecane containing no ligand.

[c] Ligand concentration=0.1M.

tests suggests that a partial decomposition of the sample can not be ruled out in all cases. From a strictly qualitative assessment, based on the visual observations, the ordering of the TMs according to their relative extents of extraction was judged to be $Co^{2+} > Fe^{2+} > Cr^{3+} > Ni^{2+}$.

Following these qualitative extraction tests, two controlled equilibrations were conducted wherein equivalent amounts of the four 0.1M TM/Ac-02 solutions were mixed together and sealed in tubes that contained 0.1M and 1.0M H[DEPH] in dodecane, respectively. The amounts of the two phases were adjusted so that the mole ratio of H[DEPH] to total TM was 10:1. The purpose of this experiment was to obtain some quantitative information on the extent of extraction of each TM under identical conditions and to determine the sensitivity of the extraction kinetics to OPL concentration at constant OPL/TM ratio. The two samples were equilibrated at 175±5°C for ~95 hours, with periodic shaking, then removed from the furnace and allowed to cool. After cooling, the tubes were broken open at the top and the dodecane phase was poured into a volumetric flask, diluted to a measured volume with dodecane rinsings of the equilibration tube, and submitted for chemical analysis.

The results of the chemical analyses are given in Table 2. It should be noted in viewing these results that the values for Cr^{3+} and Fe^{2+} in the experiment employing 1.0M H[DEPH] are suspect, owing to evidence of incomplete stripping of these cations during the back-extraction step of the analytical procedure (for details see the Experimental section). Also, an analysis for cesium was not made on the two samples, but one should suspect that the the cesium level (in terms of molar equivalents) is comparable to the reported concentrations of sodium and potassium. Nonetheless, the data in Table 2 support the observations from the initial equilibration tests (viz. Table 1) that the ordering of the extents of extraction with H[DEPH]/dodecane is $Co^{2+} > Fe^{2+} > Cr^{3+} > Ni^{2+}$.

One additional experiment was conducted, in which measured quantities of 0.1M Co^{2+}/Ac-02 and 1.0M H[DEPH]/dodecane (H[DEPH]/Co^{2+}=

TABLE 2.

Results of Chemical Analyses of the H[DEPH]/Dodecane Phase From Extraction Experiments on $Cr^{3+}/Fe^{2+}/Co^{2+}/Ni^{2+}$/Ac-02 Carried Out at 175±5°C for a Period of 95 h

	Percent of TM Extracted From Ac-02 Phase				Concentration in Dodecane (mg/L)	
Concentration	Cr	Fe	Co	Ni	Na	K
0.1M H[DEPH]	19	77	~100	<2	135	160
1.0M H[DEPH]	(10)[a]	(61)[a]	~100	14	1270	1700

[a] Incomplete back extraction in this case. Correct value should be greater than the value in parenthesis.

10:1) were sealed in a spectrophotometer cell (as described in the Experimental section), placed in the spectrophotometer furnace at 150±5°C, and allowed to equilibrate for a period of ~200 hours. During this period, the following procedure was repeated once every 24 hours: (i) a spectrum was recorded of the bottom (Ac-02) phase; (ii) the sample cell was removed from the furnace, shaken vigorously for a few seconds, returned to the furnace, and allowed to stand for 2→3 hours (to ensure complete separation of the two phases); and then (iii) another spectrum was taken of the bottom (Ac-02) phase. Four of the spectra recorded during the equilibration period are shown in Fig. 1. The curves at 3h, 71h, and 97h (h=hours) were recorded after shaking and separation; the curve at 95h was recorded just prior to the shaking and separation that preceeded the curve at 97h. From a comparison of the absorbance values just before and just after shaking, it is quite apparent that much more of the transfer of Co^{2+} from the Ac-02 phase to the dodecane phase occurs during shaking than during the stagnant periods. After ~150h there was no remaining evidence of Co^{2+} in the Ac-02 phase.

Upon completion of the equilibration, the cell was removed from the furnace and immediately inverted so that the Ac-02 phase would flow to the end of the cell opposite the optical zone (cuvette). After the Ac-02 had solidified, the cell was returned to the spectrophotometer, and the spectrum of the dodecane phase was recorded at room temperature. (Because the Ac-02 was frozen in the top end of the cell, the dodecane phase could now occupy the optical zone.) The spectrum obtained for the dodecane phase is shown in Fig. 2. From the known molar absorptivities of Co^{2+} in Ac-02 (11) and in 1.0M H[DEPH]/dodecane (see the Experimental section) it was possible to conclude that the final distribution ratio, ($[Co^{2+}]$ in dodecane phase)/($[Co^{2+}]$ in Ac-02), was greater than 100.

DISCUSSION

The results of the experiments described in the previous section, although largely qualitative in nature, provide some useful insights concerning the chemical behavior of molten carboxylates as host media in solvent extrac-

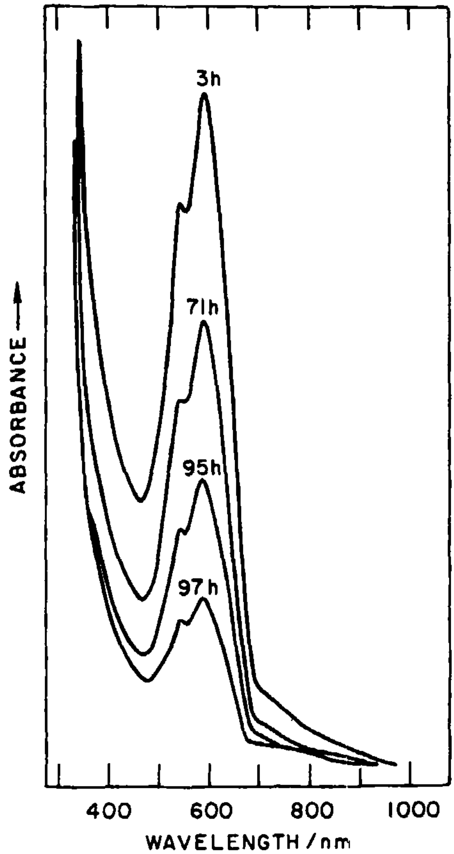

FIGURE 1. Absorption spectra of Ac-02 phase at various times during extraction of Co^{2+} from molten Ac-02 using H[DEPH] in dodecane.

tion processes. The "blank" equilibrations (some of which are summarized in Table 1) showed that the TM/Ac-02/dodecane systems (TM=Cr^{3+}, Fe^{2+}, Co^{2+}, and Ni^{2+}) are quite stable chemically at temperatures as high as 180°C. With the possible exception of the Ni^{2+}/Ac-02/OPL/dodecane combination, the introduction of H[DEPH], HDEPH, and TOPO does not appear to alter this stability. The appearance of a third liquid phase when HDEPH was used complicates the elucidation of the extraction chemistry, but does suggest some interesting possibilities for future, more extensive research.

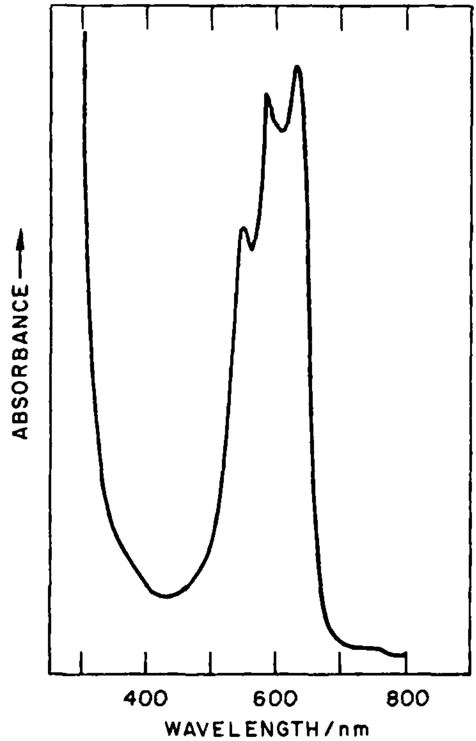

FIGURE 2. Absorption spectrum of the dodecane phase after extraction of Co^{2+} from Ac-02 using H[DEPH].

For the purposes of this study, however, nothing more will be said of experiments involving HDEPH. Instead, the remainder of the discussion will focus on the results obtained with OPL=H[DEPH] and TOPO, starting with a few thoughts concerning the extraction mechanism(s), followed by some considerations of the kinetics.

Previous work from this laboratory (11) has shown that the 3d TM cations Cr^{3+}, Fe^{2+}, Co^{2+}, and Ni^{2+} exist in either octahedral or dodecahedral crystal fields in Ac-02 melts, where complexes of the type $[ML_6]^{q-6}$, $[ML'_4]^{q-4}$, $[ML_2L'_2]^{q-4}$, and $[ML'_3]^{q-3}$ (L=monodentate Ac^-, L'=bidentate Ac^-, and q=the charge on the cation) are possible. Simple electrostatic calculations supported the likelihood of such complexes and further suggested that the preferred coordination arrangement was one which left the overall complex with a net negative charge in all cases. It follows, therefore, that in Ac-02 media the TM cation is presented to the extraction medium in the form of a negatively charged complex, whereas with aqueous media this is not the case, unless strongly complexing anions are present in the aqueous phase.

With regard to the organic phase, it is clear from the data in Fig. 2 that the extracted cobalt complex is structurally and electronically the same as is normally found when Co^{2+} is extracted from aqueous media using alkylphosphinic acids (4). Specifically, the spectrum in Fig. 2 is characteristic of Co^{2+} in a tetrahedral crystal field (12). From a mechanistic viewpoint then, the extraction of Co^{2+} from molten Ac-02 into dodecane (a solvent of very low dielectric strength) must involve a ligand exchange process that leads to a neutralized tetrahedral Co^{2+} complex. Without writing down all the intermediate steps, the overall process might involve reactions of one of the following types:

$$[CoAc_4]^{2-} + 2\,OPL \rightarrow CoAc_2(OPL)_2 + 2\,Ac^- \qquad (1)$$

$$[CoAc_4]^{2-} + 4\,OPL \rightarrow Co(OPL')_2(OPL)_2 + 2\,HAc + 2\,Ac^- \qquad (2)$$

$$[CoAc_4]^{2-} + 4\,OPL + 2\,A^+ \rightarrow A_2Co(OPL')_4 + 4\,HAc \qquad (3)$$

where A^+ is an alkali metal cation and OPL′ is the deprotonated form of OPL, i.e., $OPL \rightleftharpoons (OPL')^- + H^+$. The observation was earlier made that TOPO, which cannot undergo deprotonation, is seemingly ineffective in transferring Co^{2+} from Ac-02 to the dodecane phase, but H[DEPH], which can be deprotonated, is an effective extractant. This observation lends strong support to the adoption of Eq. 2 or Eq. 3 as the more likely reaction.

The results in Table 2 show that increasing the concentration of the OPL increases the amount of Ni^{2+} extracted. It is not possible to determine the effect of increasing OPL concentration on Cr^{3+}, Fe^{2+}, and Co^{2+} extraction from these results because ~100% of the Co^{2+} is extracted at each H[DEPH] concentration studied and the results for Cr^{3+} and Fe^{2+} are obscured by difficulties encountered in back-extracting these cations from the 1.0M H[DEPH]/dodecane solution. Also of note from Table 2 is the sensitivity of the sodium and potassium levels in the dodecane phase to H[DEPH] concentration. It may be that appreciable quantities of alkali metal alkylphosphinates are forming due to reaction of the Ac-02 with excess H[DEPH]. If it is assumed that four to six equivalents of H[DEPH] are required to transfer one equivalent of TM cation and that one equivalent of H[DEPH] is required to transfer one equivalent of alkali metal cation, then it is possible to account for well over half of the H[DEPH] present at each H[DEPH] concentration in Table 2, based solely on the elements listed in the table. Taken collectively, the results in Tables 1 and 2 suggest that optimum conditions for separating Co^{2+} from Ni^{2+} (and perhaps from Cr^{3+} and Fe^{2+} as well) would call for the use of dilute OPL solutions and an extraction time that is just long enough to allow transfer of the bulk of the Co^{2+}. Identification of the proper ranges for these conditions will, of course, require more detailed studies than are presented here.

The order found in this study for the relative extents of transfer of the individual TMs, i.e., $Co^{2+} > Fe^{2+} > Cr^{3+} > Ni^{2+}$, is generally consistent with previous investigations of the transfer of TM cations from aqueous and nonaqueous media to OPL/organic solvent media. De Haas et al. (7), in their studies of the transfer of selected TM cations from KSCN-NaSCN eutectic to TBP/diphenyl (over the temperature range 140→180°C), found in the case of cobalt and nickel that the extents of extraction were $Co^{2+} >> Ni^{2+}$. Isaac et al. (8) reported the same trend in experiments where molten alkali metal nitrates were the host medium. Results obtained when aqueous media are used as the host solvent, as typified, for example, by the work of Preston (4), also normally show $Co^{2+} > Ni^{2+}$ when all conditions of the extraction are identical.

Due to the nature of the procedures employed in this study, relatively little can be said regarding the kinetics of extraction of TMs from Ac-02 using OPL/dodecane solutions. From a very qualitative viewpoint, the rates do seem to be slower than those reported in other media, which would not be surprising considering the high viscosity and surface tension generally exhibited by molten carboxylates (11,13). Clearly, in stagnant systems, the rate of interfacial mass transfer accross the Ac-02/dodecane interface is extremely slow; and there is little doubt that in properly agitated systems, the time required to achieve equilibrium distributions of the TMs would be considerably shorter than the hundreds-of-hours time scale reported herein. The combined set of data for the experiment represented in Fig. 1 does in fact show that most (but not all) of the extraction of Co^{2+} from the Ac-02 phase occurred during the brief shaking steps that were conducted several times a day. Elucidation of the kinetics of extraction of TM cations from Ac-02 and related melts in a manner that allows comparison with results for other host media must await a more systematic series of investigations than those presented here.

CONCLUSIONS

The relative extents of extraction of Cr^{3+}, Fe^{2+}, Co^{2+}, and Ni^{2+} from the cesium acetate-sodium acetate-potassium acetate eutectic (Ac-02) into H[DEPH]/dodecane under equivalent conditions appear to be in the order $Co^{2+} > Fe^{2+} > Cr^{3+} > Ni^{2+}$. The combined results of investigations employing the acidic ligand H[DEPH] and the neutral ligand TOPO give evidence that the extractible TM complex does not contain acetate as a charge neutralizing ligand, but rather is charge balanced by deprotonated alkylphosphinate groups. The mechanism of the actual kinetic process has not been elucidated, but transfer from Ac-02 to the OPL/dodecane phase may be slower than has been reported in studies involving other molten salts over the same temperature range (i.e., 140→180°C). In future efforts to pursue the study of the transfer kinetics involved in extractions of metal cations from molten salts by state-of-the-art measuring techniques, the molten carboxylates, as typified by Ac-02, would appear to provide an interesting test of theories and methods.

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