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Unusual Selectivities of Stannic Arsenate Layers in DMSO–HCl Systems: Separation of Zirconium from Numerous Metal Ions

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Abstract

The adsorption behavior of 52 metal ions has been studied in DMSO–HCl systems using stannic arsenate layers. A remarkable feature of this study is a dramatic decrease in adsorption of many ions when compared to the corresponding water–HCl systems. This specific DMSO effect has been explained and used for important binary and ternary separations. In DMSO–5 *M* HCl (1:1), Zr^{4+} and Mo^{6+} have been separated from each other and from a mixture of Th^{4+}, Ca^{2+}, Y^{3+}, Nb^{5+}, Ta^{5+}, In^{3+}, Ti^{4+}, and the rare earths.

INTRODUCTION

The selectivity of the ion-exchange process depends upon the ion-exchange material being used in the process as well as on the medium of exchange. The conventional ion-exchange resins do not usually exhibit striking selectivities. Efforts have, therefore, been made to use organic solvents in conjunction with conventional resins to enhance their selectivity. Before 1968 the organic solvents used had low dielectric constants, e.g., acetone and butanol, which favored the formation of nondissociated metal complexes. In 1968 a solvent of high dielectric constant, i.e., dimethylsulfoxide (DMSO) was introduced in ion exchange simultaneously by Janauer, Birze, Fritz, and Phipps. Janauer (*1*) studied the ion exchange behavior of Mg^{2+}, Ca^{2+}, Sr^{2+}, Be^{2+}, Ga^{3+}, In^{3+}, Sn^{2+}, and Pb^{2+} in various DMSO–HCl mixtures using the Dowex 50 WX8 resin. He found that K_d values were quite different from the aqueous systems, particularly in 20 to 50 mole-% of DMSO. Birze et al. (*2*) studied cations, i.e., Bi^{3+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, Ag^{+}, Sn^{4+}, and Zn^{2+}, in DMSO–HCl systems using the same resin. They noticed a dramatic increase in the solubility of the chlorides of Bi^{3+}, Pb^{2+}, and Ag^{+}, which they used for some binary and ternary separations. Surprisingly, two studies were reported on anion exchangers in the same year by Fritz and Phipps. Fritz et al. (*3*) independently pointed out the unusually strong solvating effect of DMSO on metal chloride complexes and carried out the separation of Ag^{+} and Pb^{2+} chlorides on anion exchange columns. Phipps (*4*) studied the ion exchange behavior of some anions in DMSO systems and observed that the selectivity sequence was quite different from the one in aqueous media. Smits et al. (*5*) studied the behavior of Ca^{2+} and Mg^{2+} in DMSO–HCl systems and showed that the DMSO systems were no better than the aqueous systems for the Ca^{2+}–Mg^{2+} separation. Janauer et al. (*6*) examined the behavior of Be^{2+}, Co^{2+}, Ni^{2+}, Pd^{2+}, Al^{3+}, and Bi^{3+} in DMSO–HCl systems and developed methods for the separation of Pd^{2+} from Ni^{2+} and of In^{3+} from Ga^{3+} and Al^{3+}.

All these studies suffer from the following limitations: (a) only conventional ion-exchange resins have been used, and (b) numerous ions have not been systematically studied. We therefore introduced DMSO in chromatography on papers impregnated with stannic antimonate (*7*). In this article we wish to present some striking selectivities exhibited by the stannic arsenate layers when used in conjunction with DMSO–HCl systems.

EXPERIMENTAL

Apparatus

A thin-layer chromatography apparatus (Toshniwal, India) for the preparation of stannic arsenate thin layers on 20 × 3.5 cm glass plates was used. The chromatography was performed in 24 × 6 cm glass jars.

Reagents

Stannic chloride pentahydrate (Poland), sodium arsenate (Reidel, Germany), and dimethylsulfoxide (B.D.H., England) were used. All other chemicals were of AnalaR grade.

Test Solutions and Detectors

The test solutions were generally 0.1 *M* in the metal nitrate or chloride and were prepared as described earlier (*8*). Tantalum pentaoxide was dissolved in concentrated sulfuric acid and ammonium sulfate. Conventional spot test reagents were used for detection purposes.

Preparation of Thin-Layer Plates

Stannic arsenate was prepared by mixing 0.05 *M* solutions (*9*) of stannic chloride and sodium arsenate in the volume ratio of 3:2 and digesting the resulting precipitate at room temperature for 24 hr. After filtering and drying, the precipitate was cracked in demineralized water and then placed in 2 *M* HNO_3 to convert it to the H^+ form. The material was finally washed with demineralized water and dried at 40 °C. Ten grams of stannic arsenate granules thus obtained were mixed in about 5 ml of distilled water and the slurry was made by grinding the mixture vigorously in a glass mortar for a long time. This step proved to be very important for complete adhesion. The grinding of the granules must be complete and the slurry should be in the form of a fine paste without any solid particles being left. The slurry was then spread over the clean glass plates with the help of an applicator to give 0.10 mm thick layers. The plates were ready for use after drying at room temperature.

Procedure

Cation solutions were spotted on the plates which were developed in the chosen solvent system by the ascending technique. The ascent of the solvent was fixed at 10 cm in all cases. After development, the plates were dried and the cation spots were detected using the appropriate spraying reagent.

Solvent Systems

In all, 15 solvent systems were used: The R_F values in solvents S_1 to S_5 were plotted as a function of the mole fraction of DMSO while R_F values

TABLE 1

Compositions of the Solvents Studied

Solvent	Composition	Mole fraction of DMSO	Mole fraction of water	Mole fraction of HCl
S_1	DMSO + 2 *M* HCl (1:5)	.06	.90	.04
S_2	DMSO + 2 *M* HCl (2:4)	.13	.84	.04
S_3	DMSO + 2 *M* HCl (3:3)	.23	.74	.03
S_4	DMSO + 2 *M* HCl (4:2)	.37	.60	.03
S_5	DMSO + 2 *M* HCl (5:1)	.60	.38	.02
S_6	DMSO + 1 *M* HCl (1:1)	.22	.77	.02
S_7	DMSO + 2 *M* HCl (1:1)	.23	.74	.03
S_8	DMSO + 3 *M* HCl (1:1)	.25	.70	.05
S_9	DMSO + 4 *M* HCl (1:1)	.26	.66	.08
S_{10}	DMSO + 5 *M* HCl (1:1)	.29	.61	.10
S_{11}	DMSO + 6 *M* HCl (1:1)	.31	.56	.13
S_{12}	Water + 1 *M* HCl (1:1)	—	.98	.02
S_{13}	Water + 2 *M* HCl (1:1)	—	.96	.03
S_{14}	Water + 4 *M* HCl (1:1)	—	.93	.07
S_{15}	Water + 6 *M* HCl (1:1)	—	.90	.10

in solvents S_6 to S_{15} were plotted as a function of the mole fraction of HCl because in the former case the DMSO mole fraction shows a greater variation and in the latter case the same is true for the HCl mole fraction. The various solvents used in this study and their compositions are given in Table 1.

RESULTS

Plots of R_F values versus mole fraction of DMSO for solvents S_1 to S_5 are given in Figs. 1A and 1B while plots of R_F values versus mole fraction of HCl for systems S_6 to S_{15} are given in Figs. 2A and 2B. The separations predicted by the results given in Figs. 1A, 1B, 2A, and 2B and achieved experimentally are given in Table 2. In order to check the reproducibility of the R_F values, solvents S_6 to S_{11} were chosen and some ions were chromatographed. It was found that the variation does not exceed 10% of the average R_F value (Table 3).

DISCUSSION

A novel feature of this study is a significant difference in R_F values of chemically similar elements leading to fantastic separation possibilities

(Table 2). Thus Ag^+ can be separated from Pb^{2+}, $Hg_2{}^{2+}$, Cu^{2+}, and Au^{3+}; Mo^{6+} from W^{6+}; Zr^{4+} from Th^{4+}; and Se^{4+} from Te^{4+}. These interesting separation possibilities arise from three effects. (a) DMSO, being an aprotic dipolar solvent with hard oxygen and soft sulfur, is a strong solvating agent for cations. It also decreases the dielectric constant leading to the formation of nondissociated complexes. (b) The presence of HCl is responsible for the formation of chlorocomplexes. (c) Stannic arsenate layers selectively adsorb certain cations.

The two apparently contradicting tendencies, i.e. a lower dielectric constant than water and a higher solvating power, lead to a strange consequence. In almost all cases the R_F values in DMSO are greater than or equal to those in water (Figs. 2A and 2B). In a few cases the R_F values in water are greater than those in DMSO, but even in such cases the difference in R_F values is not significant. Thus DMSO first removes the water molecules from the coordination sphere of the cation and then solvates the cation itself. The DMSO solvated cation, being larger than the aquo cation, is excluded more by the exchanger and shows a higher R_F value. This result is in contrast to our earlier observations that the R_F increases linearly with the dielectric constant (*10*, *11*).

Another notable feature of this study is the low adsorption of Fe^{3+}, $UO_2{}^{2+}$, In^{3+}, and Au^{3+}. Mo^{6+} also shows a low adsorption at high HCl concentration. These ions were studied by Fritz et al. (*3*) who found that they have high adsorption in CH_3OH but low adsorption in CH_3OH–DMSO. It is striking that these ions should show a low adsorption in DMSO medium on an anion exchange resin and also on a cation exchanger like stannic arsenate. Fritz et al. (*3*) have explained the low adsorption in DMSO and high adsorption in CH_3OH by an interesting reasoning. According to them, "The solvation of the metal chloride complex by the solution outside the resin competes with the process by which the metal complex is taken into the resin phase. Ordinarily, uptake by the resin predominates but an unusually strong solvating effect may cause the metal complex to remain in the solution phase." We feel that the explanation for the exclusion of these ions from the anion exchange resin in the presence of DMSO also holds good for the cation exchanger stannic arsenate.

It is worthwhile to comment on the chromatographic behavior of Pb^{2+} and $Hg_2{}^{2+}$. As the chloride ion concentration increases, the R_F values of the two ions increase. The behavior of Pb^{2+} has been studied by Birze (2) and Fritz (*3*) in DMSO–HCl media. Birze noticed a striking increase in the solubility of the chlorides of Bi^{3+}, Pb^{2+}, and Ag^+. They explained

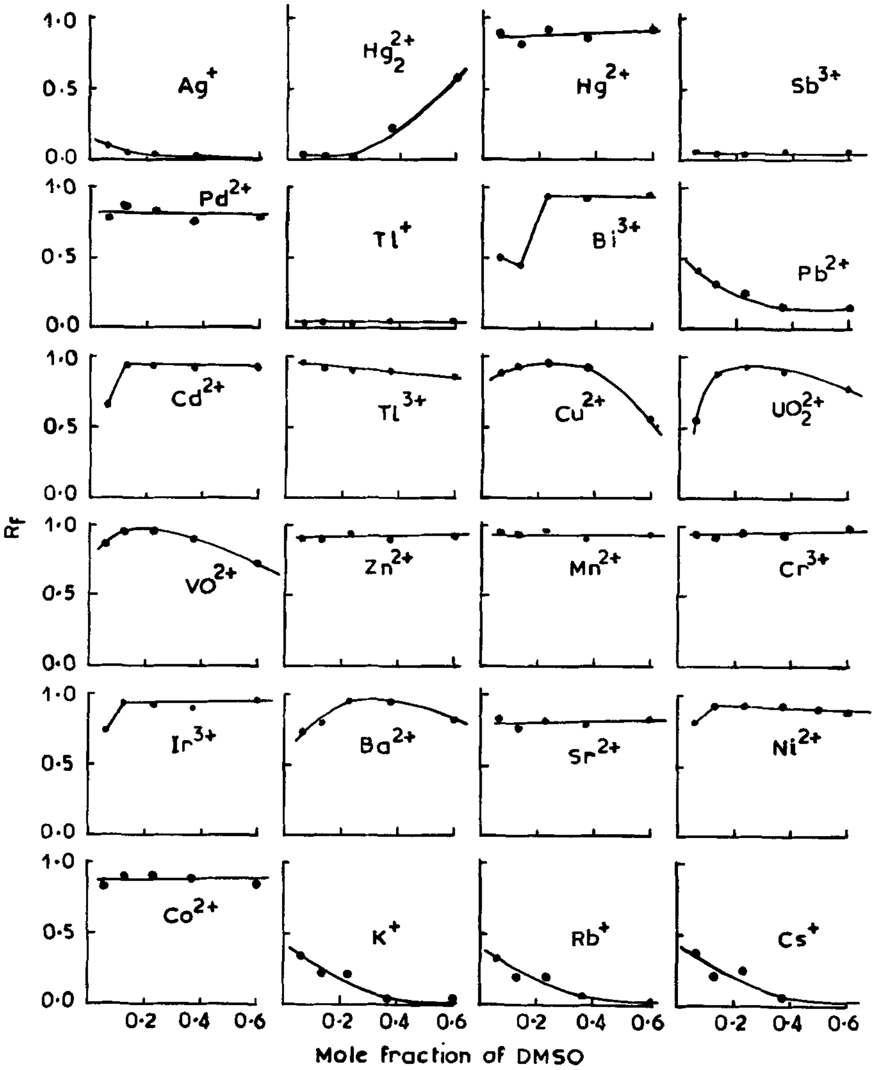

FIG. 1A. Plots of R_F vs mole fraction of DMSO (Solvents S_1 to S_5).

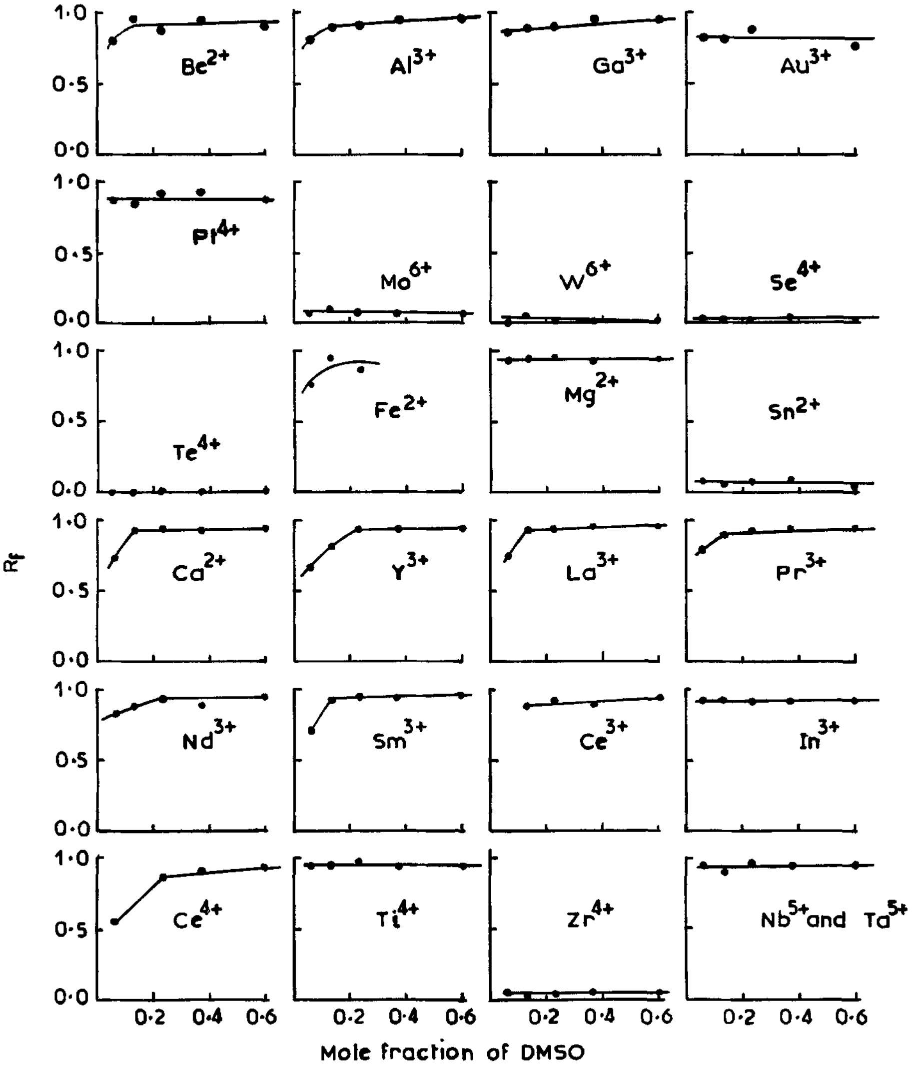

FIG. 1B. Plots of R_F vs mole fraction of DMSO (Solvents S_1 to S_5).

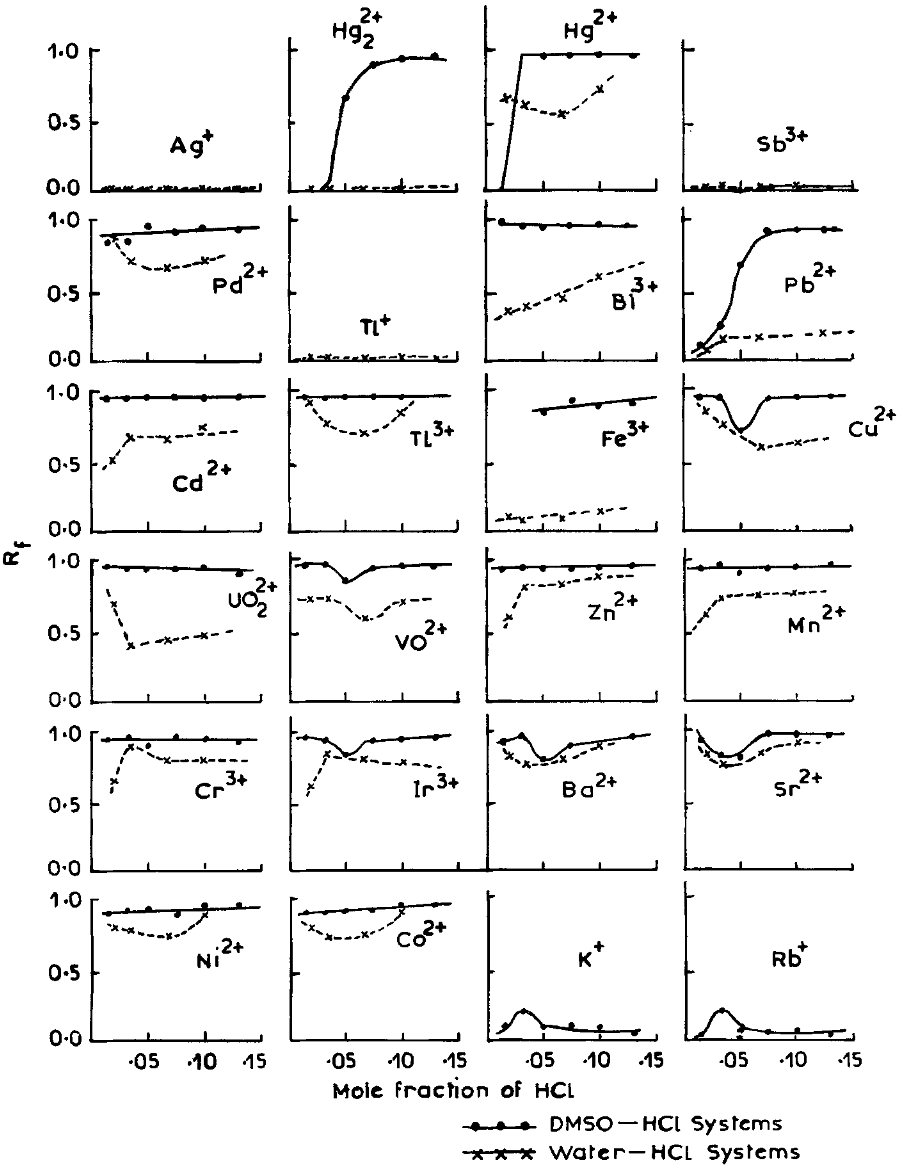

FIG. 2A. Plots of R_F vs mole fraction of HCl (Solvents S_6 to S_{15}).

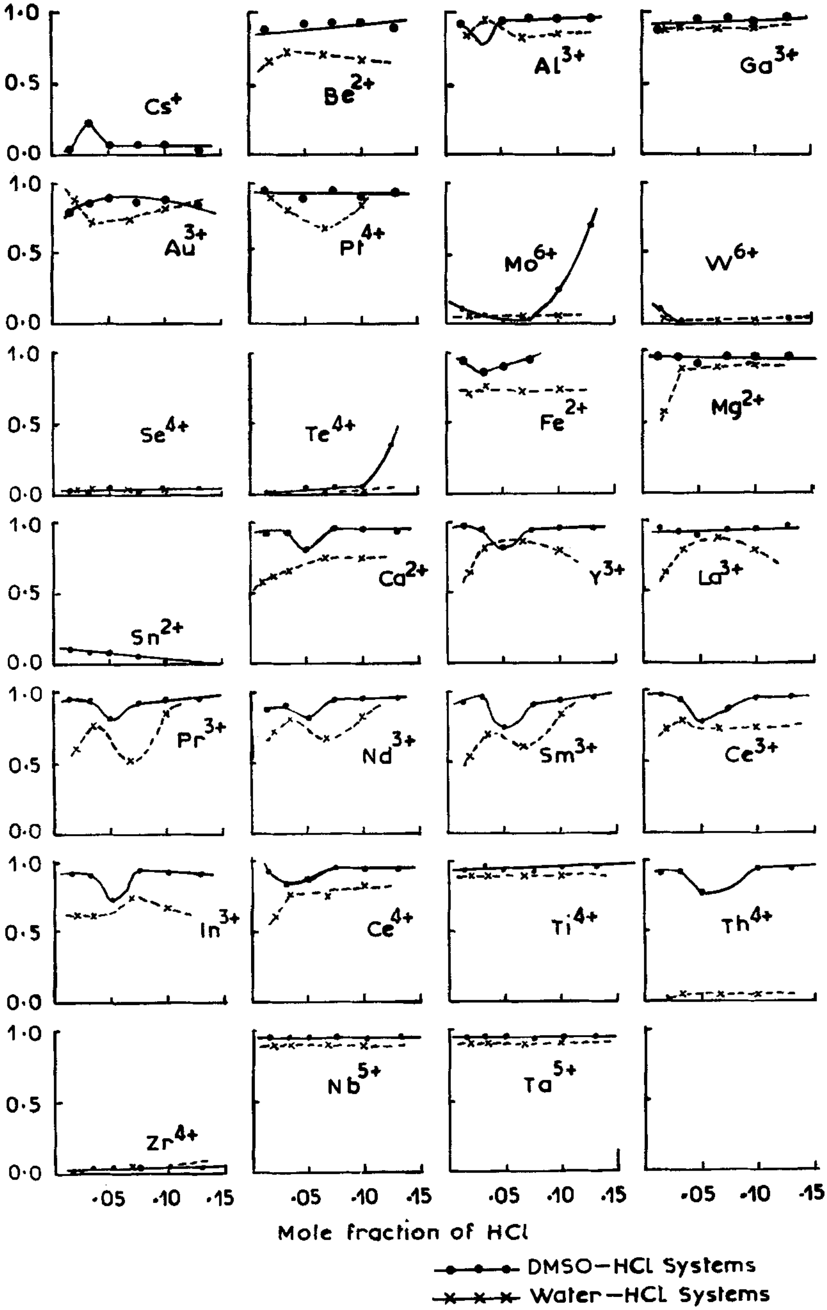

FIG. 2B. Plots of R_F vs mole fraction of HCl (Solvents S_6 to S_{15}).

TABLE 2

Separations Actually Achieved in DMSO–HCl Systems

Solvent	Separations achieved ($R_T - R_L$)
S_1	Tl^{+}(0.00–0.10)–Bi^{3+}(0.42–0.60)–Hg^{2+}(0.88–1.00)
	Tl^{+}(0.00–0.12)–Cu^{2+}(0.86–1.00)–Pb^{2+}(0.48–0.70)
	Ag^{+}(0.00–0.08)–Pb^{2+}(0.50–0.72)–Hg^{2+}(0.86–0.95)
	Te^{4+}(0.00–0.00)–Bi^{3+}(0.47–0.60)–Pd^{2+}(0.70–0.93)
	Mo^{6+}(0.00–0.10)–$UO_2{}^{2+}$(0.50–0.68)–VO^{2+}(0.82–1.00)
	Th^{4+}(0.00–0.30)–$UO_2{}^{2+}$(0.45–0.67)
	Th^{4+}(0.00–0.32)–VO^{2+}(0.84–0.96)
	Th^{4+}(0.00–0.27)–La^{3+}(0.65–0.90)
	Sb^{3+}(0.00–0.10)–Cd^{2+}(0.60–0.82)
	Fe^{3+}(0.00–0.37)–VO^{2+}(0.78–0.98)
	Ir^{3+}(0.55–0.69)–Pt^{4+}(0.78–1.00)
S_2	Ag^{+}(0.00–0.08)–Bi^{3+}(0.40–0.52)–Cu^{2+}(0.82–1.00)
	Fe^{2+}(0.91–1.00)–Fe^{3+}(0.00–0.32)
	Cd^{2+}(0.90–1.00)–Bi^{3+}(0.35–0.50)
	Fe^{3+}(0.00–0.40)–Al^{3+}(0.77–0.98)
	Fe^{3+}(0.00–0.35)–Zn^{2+}(0.78–1.00)
	Fe^{3+}(0.00–0.36)–Co^{2+}(0.79–1.00)
	Fe^{3+}(0.00–0.38)–Cr^{3+}(0.85–1.00)
S_3	K^{+}(0.18–0.32)–Ti^{4+}(0.93–1.00)
	$Hg_2{}^{2+}$(0.00–0.00)–Hg^{2+}(0.84–1.00)
	Te^{4+}(0.00–0.04)–Au^{3+}(0.76–1.00)
	Fe^{2+}(0.75–1.00)–Mo^{6+}(0.00–0.15)
	Rb^{+}(0.15–0.28)–Sr^{2+}(0.75–0.90)
	Tl^{+}(0.00–0.04)–Ni^{2+}(0.87–1.00)
	Mo^{6+}(0.00–0.15)–Cr^{3+}(0.92–1.00)
	Se^{4+}(0.00–0.03)–Au^{3+}(0.78–0.97)
S_4	Ag^{+}(0.00–0.05)–Pb^{2+}(0.55–0.73)–Cu^{2+}(0.98–1.00)
	Mo^{6+}(0.00–0.10)–Pb^{2+}(0.52–0.72)–$UO_2{}^{2+}$(0.85–1.00)
	Sn^{2+}(0.00–0.18)–Pb^{2+}(0.52–0.70)–$UO_2{}^{2+}$(0.83–0.98)
	Tl^{+}(0.00–0.10)–Ga^{3+}(0.87–1.00)

(*continued*)

TABLE 2 (continued)

Solvent	Separations achieved ($R_T - R_L$)
S_5	Ag^+(0.00–0.04)-Cu^{2+}(0.45–0.68)-Ni^{2+}(0.75–0.97)
	Cu^{2+}(0.50–0.75)-Sn^{2+}(0.00–0.10)
	Cu^{2+}(0.48–0.70)-Cd^{2+}(0.86–1.00)
S_6	Ag^+(0.00–0.03)-Cd^{2+}(0.85–1.00)
	Bi^{3+}(0.88–1.00)-Pb^{2+}(0.000–0.18)
	Bi^{3+}(0.84–0.98)-Sb^{3+}(0.00–0.04)
	Hg^{2+}(0.00–0.00)-Cd^{2+}(0.87–1.00)
	Tl^+(0.00–0.08)-Tl^{3+}(0.88–1.00)
	La^{3+}(0.90–1.00)-Se^{4+}(0.00–0.08)
	Te^{4+}(0.00–0.05)-Au^{3+}(0.70–0.95)
S_8	Tl^+(0.00–0.08)-Pb^{2+}(0.60–0.72)-Hg^{2+}(0.88–1.00)
	Ag^+(0.00–0.05)-$Hg_2{}^{2+}$(0.58–0.75)-Hg^{2+}(0.90–1.00)
	Se^{4+}(0.00–0.12)-Ni^{2+}(0.84–1.00)
	Tl^+(0.00–0.10)-Zn^{2+}(0.90–1.00)
	Ag^+(0.00–0.08)-Pd^{2+}(0.83–1.00)
	Fe^{3+}(0.65–0.95)-Mo^{6+}(0.00–0.10)
S_9	Te^{4+}(0.00–0.08)-Ni^{2+}(0.80–0.97)
	Te^{4+}(0.00–0.12)-Bi^{3+}(0.78–0.95)
	Te^{4+}(0.00–0.11)-Cd^{2+}(0.82–1.00)
	Sb^{3+}(0.00–0.04)-Bi^{3+}(0.84–1.00)
S_{10}	Zr^{4+}(0.00–0.03)-Mo^{6+}(0.26–0.41)-a mixture of Ca^{2+}, Y^{3+}, In^{3+}, Th^{4+}, Ti^{4+}, Nb^{5+}, Ta^{5+}, and rare earths (0.90–1.00)
	Y^{3+}(0.80–1.00)-Se^{4+}(0.00–0.10)
S_{11}	Mo^{6+}(0.55–0.77)-W^{6+}(0.00–0.00)
	Se^{4+}(0.00–0.08)-Te^{4+}(0.36–0.75)
	Zr^{4+}(0.00–0.10)-$UO_2{}^{2+}$ (0.88–1.00)

TABLE 3

Reproducibility of Results on

Solvent number	Cations	S_6			S_7		
		I	II	III	I	II	III
1	Ag^+	0.00	0.00	0.00	0.02	0.02	0.04
2	Pd^{2+}	0.84	0.78	0.80	0.82	0.80	0.84
3	Cd^{2+}	0.95	0.91	0.95	0.94	0.93	0.90
4	$UO_2{}^{2+}$	0.95	0.90	0.93	0.92	0.95	0.93
5	Zn^{2+}	0.92	0.88	0.90	0.95	0.91	0.93
6	Ba^{2+}	0.92	0.90	0.88	0.97	0.95	0.96
7	Be^{2+}	0.87	0.90	0.93	0.86	0.92	0.90
8	Mo^{6+}	0.10	0.07	0.06	0.07	0.05	0.05
9	La^{3+}	0.97	0.95	0.97	0.92	0.95	0.95
10	Zr^{4+}	0.00	0.00	0.03	0.04	0.04	0.02

the effect by postulating that DMSO promotes the formation of nondissociated chloro compounds and DMSO compounds by mass action and a decrease in the dielectric constant. Fritz et al. went a step further and postulated the probable solvation of the chlor anions of lead by a shift to the right of

$$PbCl_2(s) + xCl^- \rightleftarrows (PbCl_{x+2})^{x-}$$

We, however, suggest the following scheme:

$$(CH_3)_2SO + HCl \rightleftarrows (CH_3)_2SOH^+ + Cl^-$$

$$PbCl_2 + Cl^- \rightleftarrows PbCl_3{}^-$$

$$PbCl_3{}^- + (CH_3)_2SOH^+ \rightleftarrows [PbCl_3{}^-][(CH_3)_2SOH^+]$$

This explanation is supported by the following facts:

(a) DMSO has a high affinity for H^+ ions, making Cl^- ions strong nucleophiles.

(b) DMSO has a large solvation effect on cations and a small solvation effect on anions.

The increase in the R_F of $Hg_2{}^{2+}$ may be explained on similar lines. Contrary to Birze, we found that Ag^+ is strongly adsorbed on stannic arsenate and has almost zero R_F value. This may be explained as follows:

Stannic Arsenate Thin Layers

R_F values in solvent systems											
S_8			S_9			S_{10}			S_{11}		
I	II	III	I	II	III	I	II	III	I	II	III
0.03	0.00	0.02	0.00	0.00	0.02	0.00	0.00	0.03	0.03	0.02	0.02
0.95	0.90	0.89	0.90	0.89	0.93	0.95	0.96	0.91	0.94	0.90	0.95
0.92	0.90	0.88	0.93	0.90	0.90	0.95	0.96	0.95	0.95	0.93	0.92
0.92	0.90	0.94	0.93	0.91	0.94	0.94	0.90	0.88	0.89	0.90	0.92
0.92	0.90	0.87	0.93	0.91	0.95	0.95	0.90	0.90	0.95	0.92	0.93
0.79	0.86	0.87	0.90	0.92	0.90	0.91	0.90	0.93	0.95	0.93	0.95
0.93	0.89	0.91	0.93	0.89	0.90	0.93	0.94	0.90	0.90	0.93	0.93
0.00	0.00	0.02	0.00	0.02	0.02	0.00	0.00	0.00	0.02	0.00	0.02
0.90	0.92	0.94	0.94	0.97	0.93	0.95	0.97	0.97	0.97	0.95	0.95
0.05	0.03	0.03	0.05	0.05	0.04	0.05	0.05	0.04	0.05	0.05	0.06

(a) Stannic arsenate exerts a specific effect on Ag^+ ions. Thus we found that in butanol–HNO_3 systems there was a very small increase in the R_F value of Ag^+ on stannic arsenate papers as compared to Pb^{2+} (*8*).

(b) Birze found that the solubility of AgCl in DMSO–HCl mixture is very tricky. Unless a set order of addition of reagents, i.e., DMSO, $AgClO_4$, H_2O, and HCl, is used, AgCl does not dissolve while $PbCl_2$ does. In our case the order of the addition of reagents is different than the one suggested by Birze and hence AgCl should not dissolve significantly.

We now proceed to explain the low R_F values (strong adsorption) shown by Sb^{3+}, Tl^+, W^{6+}, Se^{4+}, Te^{4+}, Sn^{2+}, and Zr^{4+}. Tl^+ is probably precipitated as TlCl or thallous arsenate. Zr^{4+} and Sn^{2+} precipitate as arsenates. Sn^{4+} from the stannic arsenate precipitates Se^{4+}, Te^{4+}, Mo^{6+}, and W^{6+}. In DMSO + 5 *M* HCl (1: 1) and DMSO + 6 *M* HCl (1: 1), Mo^{6+} has a higher R_F value than W^{6+}. This may be explained by the fact that while both stannic molybdate and stannic tungstate are insoluble in dilute HCl, the solubility of stannic molybdate increases significantly at high HCl concentration while the solubility of stannic tungstate does not increase at all.

The behavior of the alkali metals is interesting. As the DMSO and HCl mole fractions increase, the R_F value first increases and then decreases, passing through a maximum. Alkali metals are not known to form complexes. It is therefore possible that as the DMSO and Cl^- concentrations increase, K^+, Rb^+, and Cs^+ are adsorbed as ion pairs.

A plot of R_F vs mole fraction of DMSO in solvents S_1 to S_5 is given in Figs. 1A and 1B. The following trends are noticeable:

(a) For most cations there is no change in R_F values. Hg^{2+}, Pd^{2+}, Tl^{3+}, Zn^{2+}, Mn^{2+}, Cr^{3+}, Ba^{2+}, Sr^{2+}, Ni^{2+}, Cd^{2+}, Co^{2+}, Be^{2+}, Al^{3+}, Ga^{3+}, Au^{3+}, Pt^{4+}, Mg^{2+}, Ca^{2+}, Y^{3+}, La^{3+}, Fe^{2+}, Ir^{3+}, Nd^{3+}, Pr^{3+}, Sm^{3+}, Ce^{3+}, In^{3+}, Ce^{4+}, Ti^{4+}, Nb^{5+}, and Ta^{5+} have very high and constant R_F values. Zr^{4+}, Sn^{2+}, Se^{4+}, Te^{4+}, Mo^{6+}, W^{6+}, Sb^{3+}, Tl^+, and Ag^+ have constant very low R_F values.

(b) The R_F values of K^+, Rb^+, Cs^+, and Pb^{2+} decrease as the DMSO mole fraction increases.

(c) The ions which appear to be most affected by DMSO mole fractions are Cu^{2+}, $UO_2{}^{2+}$, VO^{2+}, and Bi^{3+}.

(d) $Hg_2{}^{2+}$ is unique. Its R_F value increases with an increase in the mole fraction of DMSO.

The high but constant R_F values are due to the solvation of the cations or their chlorocomplexes. The low constant R_F values are due to the precipitation of the chlorides or arsenates as explained above. The R_F values of the alkali metal ions decrease with an increase in DMSO mole fraction because the KCl, RbCl, and CsCl are completely insoluble in DMSO. The behavior of Pb^{2+} may be explained on similar lines. The increase in the R_F value of $Hg_2{}^{2+}$ takes place partly due to a decrease in the Cl^- concentration and partly because of the solvation of the chlorocomplex of the mercurous ion. The Cu^{2+}, $UO_2{}^{2+}$, VO^{2+}, and Bi^{3+} are probably strongly solvated by DMSO and show a marked change in R_F value with DMSO concentration. The most remarkable conclusion from these spectra (Figs. 1A and 1B) is that at low Cl^- concentrations (mole fraction 0.016–0.04), even a sixfold increase in DMSO mole fraction (0.1–0.6) does not have much effect on R_F values.

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