## Note

___

## Chromatographic studies of metal complexes

## V. Thin-layer chromatography of some octahedral cobalt(III) and nickel(II) complexes

R. K. RAY*

*Department of Chemistry, Rama Krishna Mission Vivekananda Centenary College, Rahara-743186, 24-Parganas (North), West Bengal (India)*

MADHAB K. BANDYOPADHYAY

*Department of Physics, Rama Krishna Mission Vivekananda Centenary College, Rahara-743186, 24-Parganas (North), West Bengal (India)*

and

GEORGE B. KAUFFMAN

*Department of Chemistry, California State University, Fresno, CA 93740 (U.S.A.)*

(First received March 14th, 1988; revised manuscript received January 21st, 1989)

A number of studies have been made of the adsorption of complex cations on silica gel[1], and considerable evidence has accumulated that silica gel behaves as a weak cation-exchange resin[2]. The surface of silica gel consists of silanol (Si–OH) sites on which hydrogen atoms may be exchanged for cations in a resonably predictable manner[3]. Dugger *et al.*[4] have tabulated entropy, enthalpy and free-energy change values for the exchange reaction between the metal ions and the hydrogen atoms of the silanol group of the silica gel. The mechanism of the separation of different metal cations on silica gel may therefore be considered to occur according to the following steps:

(1) adsorption of metal cations on Si–OH groups;
(2) desorption of metal cations by acids or by salts[5–8];
(3) migration of metal cations due to solvation[9]:

$$n(\text{Si–OH}) + M^{n+} \rightarrow (\text{Si–O}^-)_n M + nH^+$$
$$(\text{Si–O}^-)_n M + nH^+ \rightarrow n(\text{Si–OH}) + [M(\text{solvent})_x]^{n+}$$
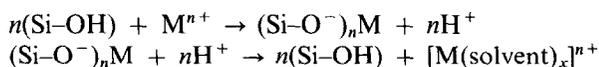
Strong binding is thus observed between the metal cation ($M^{n+}$) and the silanol anion (Si–O$^-$) of the silica gel, which resists the movement of the metal cation through the silica gel. Therefore, any explanation for the movement of a given cation should be sought in the electrical and other properties (*e.g.*, surface tension[10], viscosity[10], and dielectric constant[10–12]) of the solvent used to cause the cationic species to migrate through the anionic silica gel. Other workers[10–12] have attempted to correlate the movement of cationic complexes in terms of $R_F$ values with surface tension, viscosity

or dielectric constant considered individually. Interestingly, a linear relationship exists between the $R_F$ values of cations and the dielectric constant/viscosity ratio for organic solvents.

In this paper we show that the movement of complex cations is dependent on the joint effect of the surface tension of the developer and the anionic conductance of the electrolytes present in different developers.

EXPERIMENTAL

*Materials*

The complex compounds were prepared according to published procedures[13–16]. Their purity was established by conventional chemical analysis and spectral measurements.

*Procedures*

Merck silica gel G was slurried with distilled water (2 parts of water to 1 part of adsorbent) and spread on 0.25-mm thick glass thin-layer chromatographic (TLC) plates. The plates were dried in air, heated at 105–110°C for 1 h and stored in a desiccator as recommended by Stahl[17]. As $R_F$ values depend on the thickness of the adsorbent, we tried to maintain a thickness of 0.25 mm for the silica gel throughout this investigation. Chromatographic chambers were saturated with developer solvents for 2 days. Each complex was dissolved in water and the solution was spotted at a starting point 5 cm above the lower edge of the plate. The developer was allowed to travel 13–14 cm from the point of application. $R_F$ values were reproducible to within $\pm 0.02$ unit.

Aqueous solutions of NaCl, NaBr, NaI, $NaNO_2$, $NaNO_3$, $Na_2SO_4$ and $Na_2S_2O_3$ were used as developer solvents. Developer concentrations of 0.2 and 0.1 $M$ were used for the separation of cobalt(III) and nickel(II) complexes, respectively. Sodium sulphide solution was used as a spray reagent to detect the cobalt(III) complexes (the spots turned black) and an ethanolic solution of dithiooxamide (rubeanic acid) for the nickel(II) complexes (the spots turned blue).

RESULTS AND DISCUSSION

On the basis of electrophoresis, Mazzei and Lederer[18] measured the mobilities of $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(dip)_3]^{3+}$ and $[Co(o\text{-phen})_3]^{3+}$ ions (en = ethylenediamine; dip = dipyridyl; $o$-phen = $o$-phenanthroline) in several types of salt solutions and found a marked effect of ion association on the mobility of the complexes. They did not give a detailed discussion of the mechanism of association. In TLC studies, however, Lederer and Battilotti[19] employed the same cobalt(III) complexes used in the electrophoresis studies but different stationary phases (alumina, silica gel and cellulose–sulphonate) and various concentrations of electrolyte developers. They concluded that not only do the eluent anions form ion pairs with cobalt(III) complexes, but also ion-pair formation occurs between the stationary phase material (silica gel) and the developer electrolyte. Further, Lederer and Polcaro[20] studied the behaviour of inorganic anions on alumina and demonstrated that strong adsorption is due not to an ion-exchange process but to ion-pair formation, which favours the separation.

TLC and filter-paper chromatography have also shown that as the concentra-

TABLE I

VALUES OF ANIONIC CONDUCTANCE AND SURFACE TENSION FOR SODIUM SALT SOLUTIONS AT 25°C AND $R_F$ VALUES AT 25°C FOR [Ni(en)$_3$]$^{2+}$, [Co(NH$_3$)$_6$]$^{3+}$, [Co(bigH)$_3$]$^{3+}$ AND [Co(en)$_3$]$^{3+}$

Values of anionic conductance were calculated by subtracting the ionic conductance of Na$^+$ from the equivalent conductance of the corresponding sodium salts.

| Developer[a] | $\Lambda_i$ | $S-S_w$[b] | $\dfrac{S-S_w}{\Lambda_i}$ | $R_F$ | | | |
|---|---|---|---|---|---|---|---|
| | | | | $[Ni(en)_3]^{2+}$ | $[Co(NH_3)_6]^{3+}$ | $[Co(bigH)_3]^{3+}$ | $[Co(en)_3]^{3+}$ |
| I$^-$ | 67.9 | 0.1 | 0.0015 | 0.21 | | | |
| Br$^-$ | 68.0 | 0.14 | 0.0020 | 0.23 | | | |
| Cl$^-$ | 65.6 | 0.17 | 0.0025 | 0.30 | | | |
| NO$_3^-$ | 57.0 | 0.12 | 0.0021 | 0.24 | | | |
| NO$_2^-$ | 54.0 | 0.112 | 0.0021 | 0.24 | | | |
| S$_2$O$_3^{2-}$ | 121.0 | 0.40 | 0.0033 | 0.41 | | | |
| SO$_4^{2-}$ | 49.0 | 0.27 | 0.0055 | 0.62 | | | |
| I$^-$ | 66.45 | 0.20 | 0.0030 | | 0.30 | 0.30 | 0.26 |
| Br$^-$ | 65.55 | 0.26 | 0.0039 | | 0.38 | 0.33 | 0.31 |
| Cl$^-$ | 63.05 | 0.34 | 0.0054 | | 0.46 | 0.42 | 0.39 |
| NO$_3^-$ | 53.55 | 0.24 | 0.0045 | | 0.40 | 0.38 | 0.34 |
| NO$_2^-$ | 56.55 | 0.20 | 0.0035 | | 0.34 | 0.32 | 0.29 |
| S$_2$O$_3^-$ | 110 | 0.70 | 0.0064 | | 0.53 | 0.50 | 0.57 |
| SO$_4^{2-}$ | 43.05 | 0.54 | 0.0125 | | 0.85 | 0.80 | 0.78 |

[a] Developer concentrations were 0.1 and 0.2 $M$ for [Ni(en)$_3$]$^{2+}$ and cobalt(III) complexes, respectively.

[b] $S$ = Surface tension of the electrolyte solution; $S_w$ = surface tension of pure water. Values were obtained from International Critical Tables[28].

tion of the electrolyte in a given developer increases, the $R_F$ value of a particular complex cation also increases[21,22]. With an increase in concentration of a given developer electrolyte, the anionic conductance of the developer solution decreases. As TLC involves electrostatic processes, some relationship between the anionic conductance of electrolyte developers and the mobility of a given complex cation may exist[a]. In TLC and paper chromatography, the mobility of the complexes is shown by their $R_F$ values. In fact, a direct connection between $R_F$ values of the complex cation and the joint effect of the anionic conductance of the electrolyte and the surface tension of the developer solvent is observed (see Table I).

In order to minimize any further chemical reaction that might occur between the complex cation and the developer electrolyte[22,23] or between the complex cation and the stationary phase[3,5,23,24], we used only octahedral complexes. Any change in $R_F$ values may then be attributed to the differences in the equivalent conductance of the developer solution. However, the change in $R_F$ values in different electrolyte developers of the same concentration does not seem to bear any simple relationship to the anionic conductance. However, in most instances, the $R_F$ values decrease with an increase in conductance (see Table I).

The most striking exception is with Na$_2$S$_2$O$_3$ as developer. The equivalent

[a] Some workers prefer the direct use of salt activity as a measure of the interaction of the anions present in the developer solvent with the cations adsorbed on the chromatographic support. However, anionic conductance may be used at least as an indirect measure of such an interaction.

conductance of 0.1 $M$ $Na_2S_2O_3$ is almost double that of 0.1 $M$ NaI, so the $R_F$ value of a given complex should have been much less in the former developer. However, the experimental results reveal the reverse order. It may be pointed out that the surface tension of $Na_2S_2O_3$ solutions (expressed as the excess over the surface tension of pure water) is much greater than that of NaI solutions at the same concentrations.

Surface tension facilitates the migration of the complex cation. Hence the greater the surface tension of the developer, the higher will be the $R_F$ value. However, once again, no simple relationship exists between $R_F$ values and surface tension.

Although an increase in the surface tension of the developer solvent generally causes an increase in $R_F$ values, this is not strictly followed, as revealed by considering the $R_F$ values of a given complex in the $Na_2SO_3$ and $Na_2S_2O_3$ systems. The surface tension (expressed as the excess over that of pure water) of $Na_2S_2O_3$ solution is much higher than that of $Na_2SO_4$ solution of the same concentration, but every complex exhibited lower $R_F$ values in $Na_2S_2O_3$ than in $Na_2SO_4$ developer.

Therefore, the different $R_F$ values of a given complex cation in different electrolytes should be attributed to the joint effect of the surface tension ($S - S_w$, where $S$ is the surface tension of the electrolyte solution and $S_w$ is that of pure water) and the anionic conductance ($\Lambda_i$) of the developer ion. This hypothesis is supported by the fact that the $[Ni(en)_3]^{2+}$ ion shows the same $R_F$ value in $NaNO_2$ and $NaNO_3$ developers, which, incidentally, also have the same $(S - S_w)/\Lambda_i$ values as well. Therefore, the variation in $R_F$ values with $(S - S_w)/\Lambda_i$ is linear, at least for the $[Co(en)_3]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Co(bigH)_3]^{3+}$ and $[Ni(en)_3]^{2+}$ systems (bigH = biguanide) (see Figs. 1–4).

$R_F$ values of the same octahedral complexes were also measured with several potassium salts (KCl, KBr, KI, $KNO_3$, $KNO_2$, and $K_2SO_4$) as eluents in order to observe whether changing the cation of the developer electrolyte affects this linear relationship. We found that the $R_F$ values change only slightly (Table II) from the values obtained with the corresponding sodium salts as eluents (Table I). At any rate,
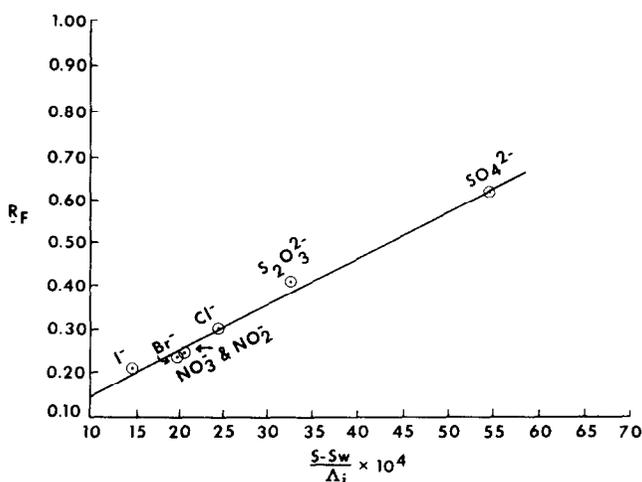


Fig. 1. Variation of $R_F$ for $[Ni(en)_3]^{2+}$ with $(S - S_w)/\Lambda_i$ values for different electrolyte solutions.
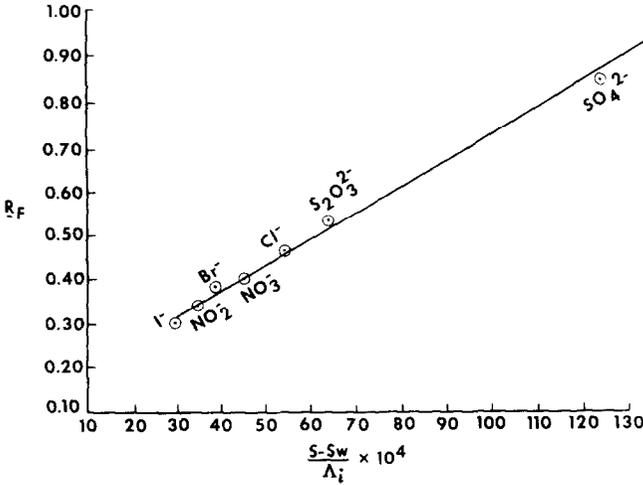
Fig. 2. Variation of $R_F$ for $[Co(NH_3)_6]^{3+}$ with $(S-S_w)/\Lambda_i$ values for different electrolyte solutions.

the linear relationship between $R_F$ and $(S-S_w)/\Lambda_i$ was also found with potassium salts as eluents.

Jenkins and Monk[25] and later De and Dutta[26] reported that the ion-associated constants of some cationic cobalt(III) complexes with halides and sulphate ions decrease with increase in the equivalent conductance of the complex salts. They also evaluated the ion-association constants of $[Co(en)_3]^{3+}$ and $[Co(bigH)_3]^{3+}$ with halides and sulphate ions and observed the order[25-27] $I^- < Br^- < Cl^- < SO_4^{2-}$. The movement of a cationic complex on a silica gel bed may be attributed to ion-pair formation between the complex cation and the anion of the electrolyte present in the developer, so that the overall effective charge of the complex cation is considerably reduced[19,21,24].
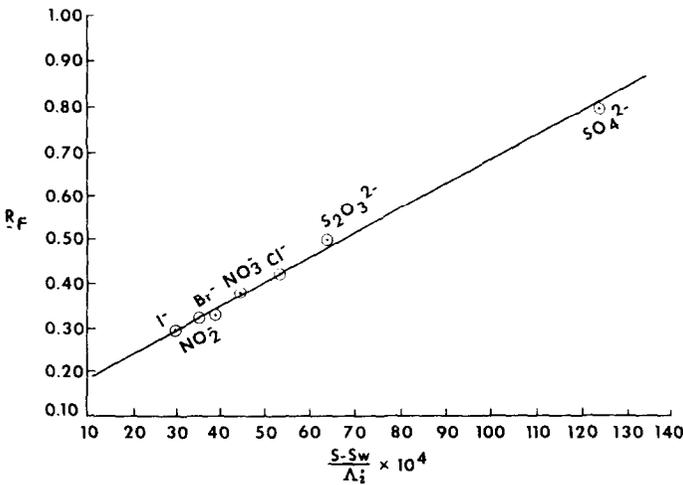
Fig. 3. Variation of $R_F$ for $[Co(bigH)_3]^{3+}$ with $(S-S_w)/\Lambda_i$ values for different electrolyte solutions.
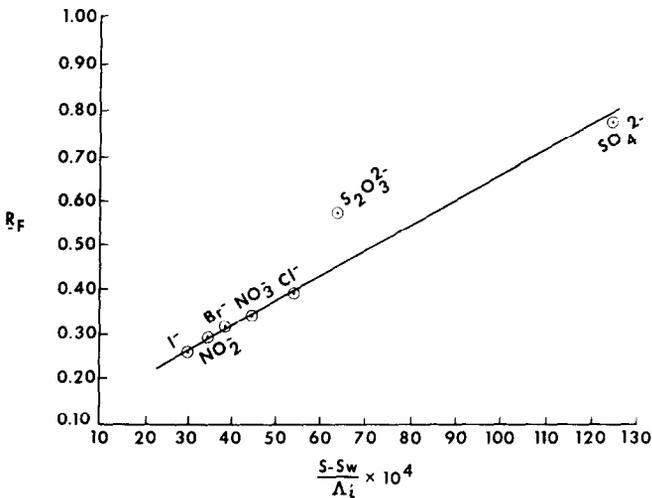
Fig. 4. Variation of $R_F$ for $[Co(en)_3]^{3+}$ with $(S - S_w)/\Lambda_i$ values for different electrolyte solutions.

$$[Co(bigH)_3]^{3+} + X^- \rightleftharpoons \{[Co(bigH)_3]^{3+}, X^-\}^{2+}$$
$$(X^- = Cl^-, Br^-, I^-);$$
$$[Co(bigH)_3]^{3+} + SO_4^{2-} \rightleftharpoons \{[Co(bigH)_3]^{3+}, SO_4^{2-}\}^+$$
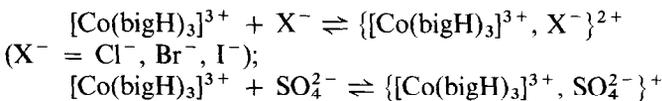
As the increase in equivalent conductance of the developer solution reduces the ion-pair formation between the complex cation and the anion[25–27], $R_F$ values should decrease with increase in equivalent conductance. This investigation supports this view if proper account is taken of the effect of surface tension.

TABLE II

VALUES OF ANIONIC CONDUCTANCE AND SURFACE TENSION FOR POTASSIUM SALT SOLUTIONS AT 25°C AND $R_F$ VALUES AT 25°C FOR $[Ni(en)_3]^{2+}$, $[Co(NH_3)_6]^{3+}$, $[Co(bigH)_3]^{3+}$ AND $[Co(en)_3]^{3+}$

Values of anionic conductance calculated by subtracting the ionic conductance of $K^+$ from the equivalent conductance of the corresponding potassium salts.

| Developer[a] | $\Lambda_i$ | $S - S_w$[b] | $\dfrac{S - S_w}{\Lambda_i}$ | $R_F$ | | | |
|---|---|---|---|---|---|---|---|
| | | | | $[Ni(en)_3]^{2+}$ | $[Co(NH_3)_6]^{3+}$ | $[Co(bigH)_3]^{3+}$ | $[Co(en)_3]^{3+}$ |
| $I^-$ | 63.3 | 0.168 | 0.0026 | 0.26 | 0.34 | 0.33 | 0.31 |
| $Br^-$ | 64 | 0.270 | 0.0042 | 0.30 | 0.42 | 0.39 | 0.36 |
| $Cl^-$ | 60.9 | 0.301 | 0.0049 | 0.36 | 0.47 | 0.44 | 0.43 |
| $NO_3^-$ | 50.2 | 0.22 | 0.0044 | 0.34 | 0.44 | 0.41 | 0.38 |
| $NO_2^-$ | 53.0 | 0.21 | 0.0040 | 0.31 | 0.40 | 0.39 | 0.37 |
| $SO_4^{2-}$ | 48.2 | 0.51 | 0.0106 | 0.67 | 0.81 | 0.79 | 0.80 |

[a] Developer concentrations were 0.2 $M$ for all complexes.
[b] $S$ = Surface tension of the electrolyte solution; $S_w$ = surface tension of pure water. Values were obtained from International Critical Tables[28].

REFERENCES

1  L. H. Reyerson and R. E. Clark, *J. Phys. Chem.*, 40 (1936) 1055.
2  F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, 1962.
3  R. L. Burwell, Jr., R. G. Pearson, G. L. Haller, P. B. Tjok and S. P. Chock, *Inorg. Chem.*, 4 (1965) 1123.
4  D. L. Dugger, J. H. Stanton, B. N. Irby, B. L. McConnell, W. W. Cummings and P. W. Maatman, *J. Phys. Chem.*, 68 (1964) 757.
5  R. L. Dutta, R. K. Ray and G. B. Kauffman, *Coord. Chem. Rev.*, 28 (1979) 23.
6  M. Lederer, *J. Chromatogr.*, 6 (1961) 437, 518.
7  L. Ossicini and M. Lederer, *J. Chromatogr.*, 17 (1965) 387.
8  H. M. Irving, *Q. Rev. Chem. Soc.*, 5 (1951) 200.
9  W. C. Brown, *Nature (London)*, 143 (1939) 377.
10  A. Paul and P. B. Janardhan, *Bull. Chem. Soc. Jpn.*, 40 (1967) 1131.
11  A. M. Ghe and A. Placucci, *Ann. Chim. (Rome)*, 49 (1959) 1769.
12  M. Qureshi and M. A. Khan, *Talanta*, 13 (1966) 117.
13  P. Rây, *Chem. Rev.*, 61 (1961) 313.
14  W. G. Palmer, *Experimental Inorganic Chemistry*, Cambridge University Press, Cambridge, 1959, p. 530.
15  J. B. Work, *Inorg. Synth.*, 2 (1946) 221.
16  H. M. State, *Inorg. Synth.*, 6 (1960) 200.
17  E. Stahl, *Thin Layer Chromatography: A Laboratory Handbook*, George Allen and Unwin, London, 2nd ed., 1969.
18  M. Mazzei and M. Lederer, *J. Chromatogr.*, 31 (1967) 196.
19  M. Lederer and M. Battilotti, *J. Chromatogr.*, 89 (1974) 380.
20  M. Lederer and C. Polcaro, *J. Chromatogr.*, 84 (1973) 379.
21  R. K. Ray and G. B. Kauffman, *J. Chromatogr.*, 442 (1988) 381.
22  R. L. Dutta and R. K. Ray, *J. Indian Chem. Soc.*, 51 (1974) 187.
23  R. K. Ray, *Analyst (London)*, submitted for publication.
24  T. Baba and H. Yoneda, *Bull. Chem. Soc. Jpn.*, 43 (1970) 2478.
25  I. L. Jenkins and C. B. Monk, *J. Chem. Soc.*, (1951) 68.
26  M. K. De and R. L. Dutta, *J. Indian Chem. Soc.*, 52 (1975) 67.
27  F. Basolo and R. G. Pearson, *Mechanisms of Inorganic Reactions*, Wiley, New York, 2nd ed., 1967, p. 37.
28  E. W. Washburn (Editor), *International Critical Tables of Numerical Data: Physics, Chemistry and Technology*, Vols. III–VII, McGraw-Hill, New York, London, 1928, 1929, 1930.