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Investigations of Solvent Effects on Paper Chromatography

Agnes PAUL and Pandarinath B. JANARDHAN[*1]

Analytical and Inorganic Chemistry, University of Madras, Madras, India

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The mechanism of paper chromatography consists of three stages: i) adsorption; ii) desorption; iii) migration due to solvation. Solvation depends on the physical properties of the solvent. The present paper will attempt to correlate the R_f values of metal ions with such physical properties of the solvent as (a) surface tension, (b) viscosity, (c) solubilisation, and (d) the dielectric constant. Experiments have been conducted with pure and mixed solvents of the aliphatic alcohol series. As a result, it may be reported that the R_f values of cations (silver, copper, nickel and ferric ions) bear almost a linear relationship to the dielectric constant/viscosity quotient.

Paper chromatography has come to be widely used because it is an analytical technique of unlimited scope. In spite of the enormous volume of work done[1-4] and the reports published on this technique, however, it has to be admitted that there has been until now something of a haziness regarding the actual mechanism of chromatographic migration on paper.[5-14] If only a few reports are scanned[15-20] it will be realized that the solvent is usually chosen more or less by rule of thumb. In our work with inorganic ions like silver, copper, nickel and iron, however, it has become clear that the mechanism of paper chromatography consists of: i) adsorption of the ions by the cellulose molecules[21-23] (Fig. 1), followed

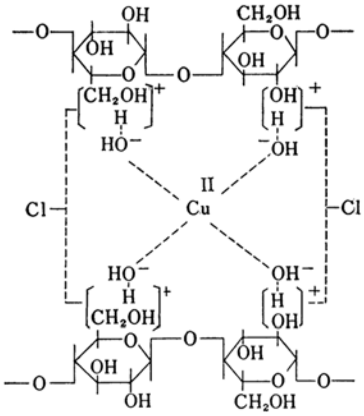

Fig. 1. The mode of adsorption of Cu^{2+} aquo-complex on cellulose.

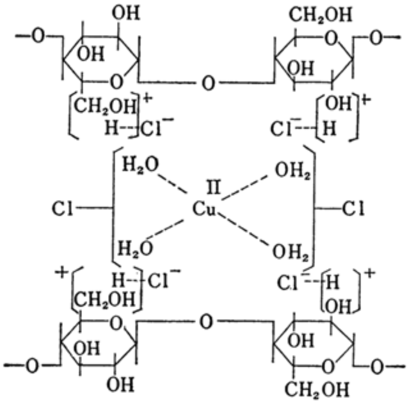

Fig. 2. The mode of desorption of Cu^{2+} ion in the presence of H^+ ion.

[*1] Laboratory of Analytical and Inorganic Chemistry, Madras University, A. C. College Campus, Madras-25, India.

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11) H. R. Bentley and J. K. Whitehead, *Biochem. J.*, **46**, 361 (1950).
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21) T. J. Beckmann and M. Lederer, *ibid.*, **3**, 498 (1960).
22) M. Lederer *et al.*, *ibid.*, **6**, 437; 518 (1961).
23) K. A. Kraus *et al.*, *J. Am. Chem. Soc.*, **81**, 3204 (1959).

by: ii) desorption of the ions adsorbed as a result of the formation of the oxonium ions by the interaction of cellulose with the hydrogen ions of an acid[22,24,25] (*vide* Fig. 2), and iii) solvation of the desorbed ions by a solvent[26] and the washing-away of the solvo-complex by the solvent stream.

This paper will be concerned with the last of the three factors, namely, solvation and migration. The possible physical parameter of the solvent that can affect solvation (the solubilization of the ions) is the dielectric constant of the solvent, which is more or less an index of its polarity. The effective number of carbon atoms in a solvent or solvent mixture may also be used as an approximate index of its polarity (*vide* Table 4). The other properties of the solvent that can affect the migration are surface tension and viscosity.

An attempt has been made in this work to correlate the R_f of the metal ions with i) the surface tension, ii) the viscosity, iii) the solubility, and iv) the dielectric constant.

Experimental

Preparation of Solution. 0.1 M solutions of analar silver(I), copper(II), nickel(II), and iron(III), all containing 5% of free nitric acid, were prepared. These metals were chosen to represent valencies ranging from 1 to 3.

Preparation of Solvents. *Simple Solvents.* The pure solvents used were: I) methanol (99—100% pure); II) ethanol (96%); III) *n*-propanol (99—100%); IV) *n*-butanol (99—100%); V) *n*-amyl alcohol (99—100%).

Each of these was mixed with 4 M HNO_3 in the ratio of 100 : 15 by volume.

Mixed Solvents. The mixed solvents were prepared by mixing equal volumes of two members of the homologous series extending from methanol to *n*-amyl alcohol.

As there is definite reason to believe that hydrogen ions are essential for chromatography,[22,24,25] each of the solvents was shaken with 4 M nitric acid in the solvent-to-acid ratio of 100 : 15 by volume.

Radial chromatograms were run as usual by the Rutter technique[26] by spotting the centre of a 12-cm circular filter paper with a drop of the solution and then irrigating it by means of a thread wick with the respective solvents.

Results and Discussion

Surface Tension. When the relationship between the R_f value and the surface tension is

TABLE 1. SURFACE TENSION OF SOLVENT *vs.* R_f OF IONS

	(a)					(b)		
Mixed solvents	A/M	B/E	A/E	B/P	A/B	E/M	P/M	P/E
Effective No. of carbon atoms (Index of polarity)	6	6	7	7	9	3	4	5
Surface tension dyn/cm at 30°C	25.83	25.87	26.22	26.45	27.35	26.79	26.08	25.79
Silver R_f	0.37	0.36	0.26	0.38	0.28	0.52	0.48	0.42
Copper R_f	0.42	0.46	0.34	0.39	0.23	0.85	0.71	0.63
Nickel R_f	0.37	0.36	0.24	0.37	0.23	0.85	0.70	0.57
Iron(III) R_f	0.43	0.42	0.30	0.35	0.12	0.88	0.83	0.69

A=*n*-Amyl alcohol, B=*n*-Butanol, P=*n*-Propanol, E=Ethanol, M=Methanol

TABLE 2. R_f OF IONS IN SIMPLE SOLVENTS

Simple solvents	Methanol	Ethanol	*n*-Propanol	*n*-Butanol	*n*-Amyl alcohol
No. of carbon atoms (Index of polarity)	1	2	3	4	5
*Dielectric constant at 25°C	32.63	24.3	20.1	17.1	13.9
Surface tension (dyn/cm at 30°C)	21.69	21.48	22.89	23.75	24.72
Viscosity ($10^2\eta$ at 30°C)	0.51	0.997	1.722	2.271	2.987
Dielectric constant/viscosity	63.97	24.52	11.68	7.53	4.65
Silver R_f	0.49	0.48	0.34	0.30	0.25
Copper R_f	0.93	0.75	0.45	0.29	0.20
Nickel R_f	0.94	0.74	0.37	0.20	0.10
Iron(III) R_f	1.00	0.80	0.47	0.27	0.18

* Values taken from handbooks and literatures. The effect of nitric acid on the dielectric constant of the solvent system is taken as a constant and has not been included in the value.

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24) Ossicini and M. Lederer, *J. Chromatog.*, **17**, 387 (1965).

25) H. M. Irving, *Quart. Rev.*, **5**, 200 (1951).

26) W. C. Brown, *Nature*, **143**, 377 (1939).

considered, the solvents fall into two groups: i) those whose surface tension increases with an increase in the effective number of carbon atoms (Table 1(a) and Table 2), and ii) those whose surface tension decreases with an increase in the effective number of carbon atoms (Table 1(b)).

In the former group, the R_f-*vs.*-surface tension

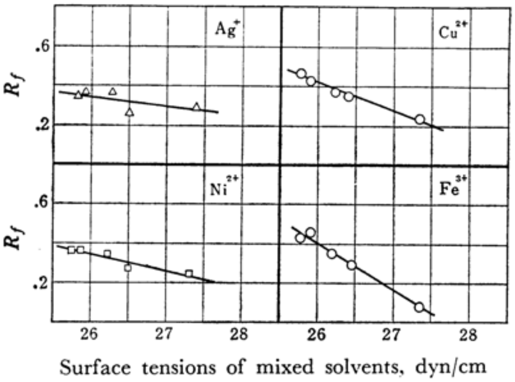


Fig. 3

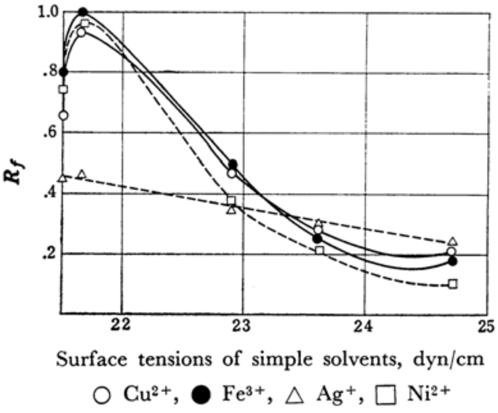


Fig. 4

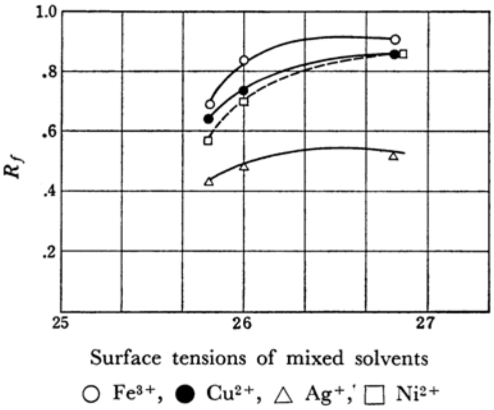
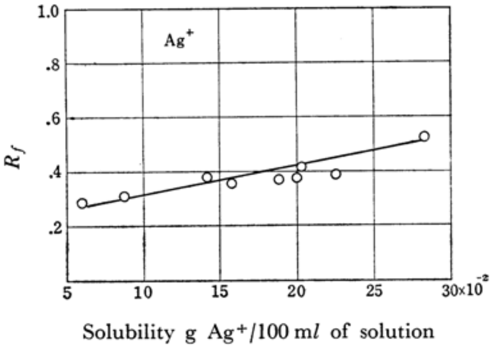


Fig. 5

Figs. 3–5. The relationship of R_f of metal ions with the surface tension of the solvents.



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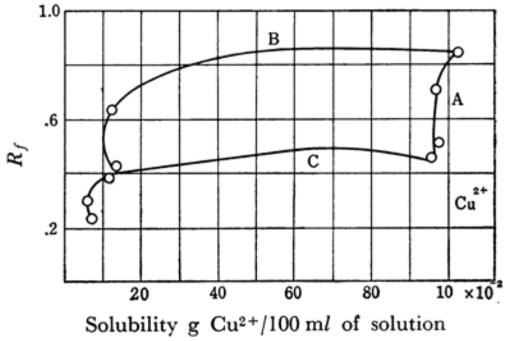

Fig. 7

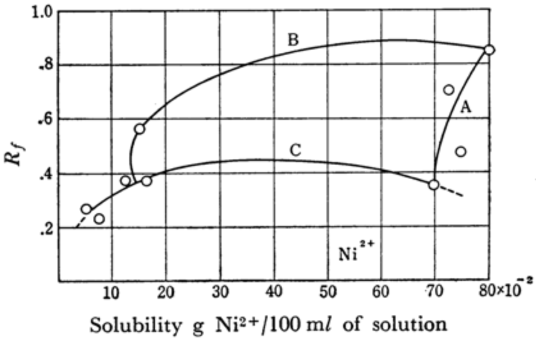

Fig. 8

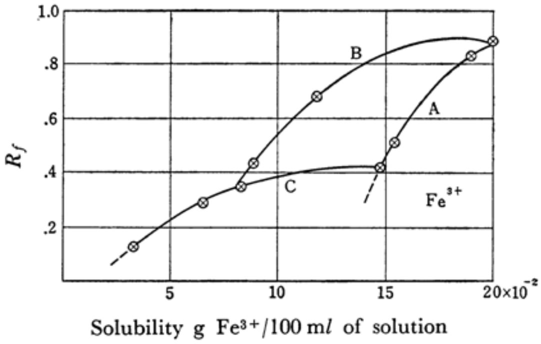

Fig. 6—9. The relationship of R_f of metal ions with their respective solubilities in binary solvents.

TABLE 3. R_f AND SOLUBILITY IN MIXED SOLVENTS

	Mixed solvents	A/B	A/P	A/E	A/M	B/E	B/M	P/E	P/M	E/M
Ag(I)	*Solubility:	0.5750	0.8530	1.4030	1.5230	1.8640	1.9840	2.0970	2.2170	2.8120
	R_f	0.28	0.32	0.38	0.36	0.37	0.37	0.42	0.48	0.52
Cu(II)	Solubility:	0.0778	0.0685	0.1180	0.9615	0·1427	0.9862	0.1334	0.9769	1.0265
	R_f	0.23	0.29	0.39	0.46	0.42	0.52	0.63	0.71	0.85
Ni(II)	Solubility:	0.0813	0.0591	0.1306	0.7026	0.1741	0.7487	0.1549	0.7270	0.7980
	R_f	0.23	0.26	0.37	0.36	0.37	0.48	0.57	0.70	0.85
Fe(III)	Solubility:	0.0355	0.0655	0.0831	0.1487	0.0885	0.1540	0.1185	0.1840	0.2017
	R_f	0.12	0.28	0.35	0.42	0.43	0.51	0.69	0.83	0.88

A=*n*-Amyl alcohol, B=*n*-Butanol, P=*n*-Propanol, E=Ethanol, M=Methanol
* The solubilities are given in g metal ion/100 m*l* solution.

TABLE 4. R_f *vs.* QUOTIENT OF DIELECTRIC CONSTANT BY VISCOSITY IN MIXED SOLVENTS

Mixed Solvent	A/B	A/P	A/E	B/P	A/M	B/E	P/M	E/M
Effective No. of carbon atoms (Index of polarity)	(9)	(8)	(7)	(7)	(6)	(6)	(4)	(3)
*Dielectric constant/viscosity	5.636	6.415	9.454	8.692	9.777	11.13	21.98	25.65
Silver R_f	0.28	0.32	0.38	—	0.36	0.38	0.48	0.58
Copper R_f	0.23	0.29	0.39	0.34	—	0.42	0.17	0.85
Nickel R_f	0.23	0.25	0.37	—	0.36	0.37	0.70	0.85
Iron(III) R_f	—	0.28	0.35	—	0.42	0.43	0.83	0.83

A=*n*-Amyl alcohol, B=*n*-Butanol, P=*n*-Propanol, E=Ethanol, M=Methanol
* Values of dielectric constant for this purpose were taken from literature.

curve (Figs. 3 and 4) slopes downwards, whereas in the latter group the curve slopes upwards (Fig. 5). The simple solvents, with the exception of methanol, and mixtures of amyl alcohol with methyl, ethyl and butyl alcohols, and butanol with ethyl and propyl alcohols belong to the former group, while mixtures of methanol with ethanol and propanol, and of propanol with ethanol belong to the latter. It may generally be seen that the first category of solvents contains a good proportion of water-immiscible alcohols, whereas in the second category there is a greater proportion of water-miscible alcohols.

Solubility. The solubilities of metal ions in alcohols generally decrease from methanol to *n*-amyl alcohol. From the solubility values, therefore, it may be inferred that a binary mixture containing any member of the C_1-to-C_5 series with methanol as the other constituent will evince a higher solubility for metal ions than any other binary mixture which does not contain methanol. Similarly, binary mixtures containing *n*-amyl alcohol as one of the constituents will show a lower solubility for metal ions than any other mixture which does not contain *n*-amyl alcohol. Other mixtures will evince solubilities whose values lie between the limiting values of the above two series.

Accordingly, the binary solvents in the present work may be classified into three series: A) the first series, containing methanol mixed with other members of the homologous series; B) the second series, containing ethanol mixed with other members of the homologous series, and C) the third series, containing *n*-amyl alcohol mixed with other lower members of the series. Although the R_f-*vs.*-solubility relationship is not quite linear, R_f values are found generally to increase with an increase in the solubility of the metal ion in the solvent (except in the two instances of copper and nickel in a *n*-propanol and *n*-amyl alcohol mixture).

Each series will have its own R_f-*vs.*-solubility curves, the forms of which will resemble the curves given in Fig. 5. When the R_f-*vs.*-solubility curves of all the three series mentioned above are combined, peculiar forms of curves are obtained, as in the case of nickel, copper and iron. Univalent silver gives more or less a linear relationship. This anomaly might be due to the photochemical side reactions, which gradually precipitate silver, thereby inhibiting the migration of the ions.

Dielectric Constant and Viscosity. It has been reported by Ghe and Placucci27) that the R_f values increase linearly with the dielectric constant for such metal ions as Mn^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+} in mixed solvents containing methanol or ethanol with other members of the homologous series. The results obtained in this laboratory show that the R_f-*vs.*-dielectric constant curve

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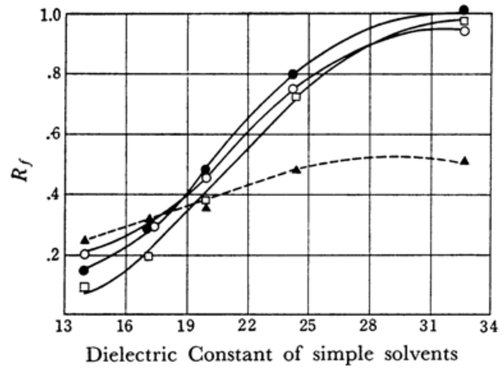
27) A. M. Ghe and A. Placucci, *Ann. Chim. (Rome)*, **49**, 1769 (1959).



○ Cu^{2+}, ● Fe^{3+}, ▲ Ag^{+}, □ Ni^{2+}

Fig. 10. The relationship of the R_f of metal ions with the dielectric constants of simple solvents.

is not quite linear in the case of simple solvents (Fig. 10, Table 2), while as for mixtures of solvents, there is not much of a linear relationship. Qureshi and Khan[28] have also attempted to correlate the R_f values with the dielectric constants of the solvent systems (alcohol series), using formic acid in the system. Except in the case of low concentrations of formic acid, these authors also report only a non-linear relationship in most of their chromatograms. It is quite possible therefore, that the R_f values of the metal ions depend on other physical properties of the solvent system besides its dielectric constant.

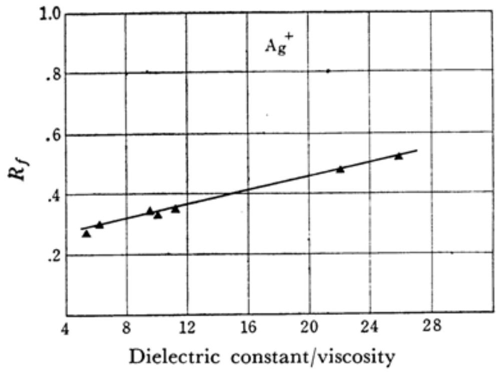


Fig. 11

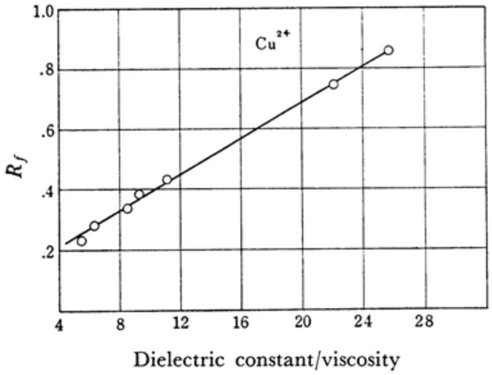


Fig. 12

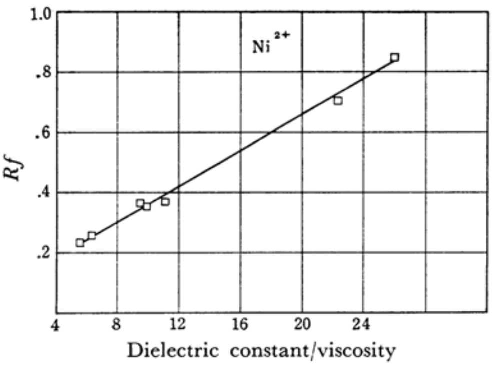


Fig. 13

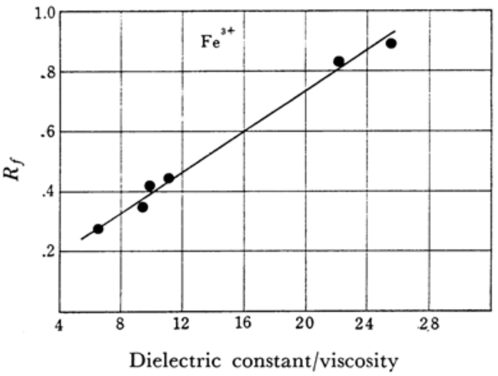
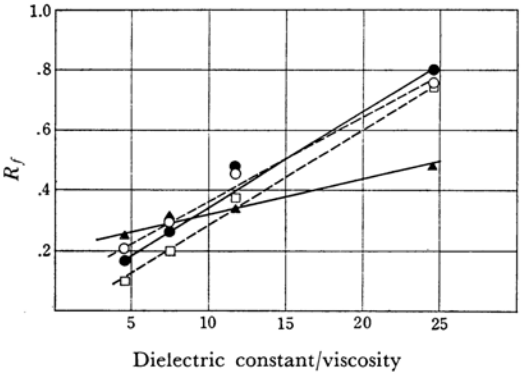


Fig. 14



▲ Ag^{+}, ○ Cu^{2+}, ● Fe^{3+}, □ Ni^{2+}

Fig. 15

Figs. 11—15. The relationship of R_f of metal ions with the quotient of D.E.C/Viscosity of the solvents.

We have observed that the viscosity of a solvent also has an important influence on the R_f value of the metal ions. The migration of the metal

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[28] M. Qureshi and M. A. Khan, *Talanta*, **13**, 117 (1966).

ion takes place through its solvation by the solvent system and is, therefore, governed by the rate of migration of the solvent itself through the capillaries of the cellulose substrate, which in its turn is governed by the viscosity of the mobile phase. In fact, a plot of R_f *vs.* the dielectric constant/viscosity quotient was found to be linear (see Figs. 11—14 (Table 4) and Fig. 15 (Table 2). It must, therefore, be inferred that the viscosity of the solvent exercises its effect on the R_f of the metal ions simultaneously with the dielectric constant.

Summary

The influence of solvents on the R_f of cations has been studied. The solvent parameters investigated were solubility, surface tension, viscosity, and the dielectric constant. While there is no linear relationship between R_f and the surface tension, the viscosity, or the dielectric constant considered individually, it was found R_f *vs.* the dielectric constant/viscosity quotient gave a straight line graph.