TRACE METAL SPECIATION IN SALINE WATERS
AFFECTED BY GEOTHERMAL BRINES

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ABSTRACT

A description is given of the chemical equilibrium computer program GEOCHEM, which has been developed to calculate trace element speciation in soil, irrigation, drainage, or Salton Sea waters affected by geo-thermal brine. GEOCHEM is applied to irrigation water-brine mixtures and to Salton Sea water-brine mixtures in order to compute the chemical speciation of the elements Cd, Cu, Hg, Ni, Pb, and Zn, along with the oxyanions of As and B. The results suggest that the computer simulation can have an important effect on a program for managing brine spills.

This report describes the research carried out since July 1, 1976, on the project, "Trace Metal Speciation in Saline Waters Affected by Geothermal Brines". The objectives of the project are: (1) to develop a computer program for the accurate calculation of trace metal equilibria in saline waters and (2) to initiate application of the computer program to numerical studies of Cd, Cu, Mn, Pb, and Zn and other trace element solubilities in natural waters intruded by geothermal brine.

1. Development of the Chemical Equilibrium Program GEOCHEM

The chemical equilibrium program GEOCHEM has been developed from the computer program REDEQL2, which originated at Caltech (McDuff and Morel, 1974). The basic structure of this computer program has been described by Morel and Morgan (1972) and by Sposito and Mattigod (1977). A copy of the paper by Sposito and Mattigod (1977) appears in the Appendix to this report.

After the initial phase of development of GEOCHEM had been completed, a review of the available chemical, geochemical, and soil chemical literature was conducted in order to obtain thermodynamic stability constants for all the metal-inorganic ligand complexes deemed relevant to mixtures of saline soil, irrigation, drainage, or lake waters with geothermal brines. The data obtained were compiled and loaded into GEOCHEM. The literature search indicated that stability constants for complexes of Mn^{2+} , Fe^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} with inorganic ligands were rather sparse in the cases of CO_3^{2-} , HCO_3^- , HSO_4^- , PO_4^{3-} , HPO_4^{2-} , and $H_2PO_4^-$. This lack of data would seriously impair

the effectiveness of calculations using GEOCHEM. Therefore, it was determined to use estimated values of association constants for complexes for which experimental data do not exist. The methods employed to estimate the stability constants and a table of 100 of these constants for complexes of the above-named divalent trace metal cations with the ligands CO_3^{2-} , HCO_3^- , SO_4^{2-} , HSO_4^- , PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , Cl^- , and OH^- are given in Table 1, taken from Mattigod and Sposito (1977). A copy of this paper appears in the Appendix to this report.

In the computer program REDEQL2, the activity coefficients were computed from Davies' revised equation (see, e.g., Stumm and Morgan, 1970). Generally, this equation is used for the computation of activity coefficients of ions in aqueous solutions up to an ionic strength of 0.5 M. In the case of the present project, there is a need for computing ionic activity coefficients for trace metals in much more concentrated solutions, e.g., at ionic strengths up to 3 M.

For concentrated multicomponent electrolyte solutions, with sodium chloride as the dominant component, Helgeson (1969) has proposed an equation for calculating the true individual ion activity coefficients for Na^+ , Cl^- , and for other ions present in small concentrations. This equation is a modification of the Stokes-Robinson equation and is expressed as:

$$\log \gamma_i = \frac{-AZ_i^2 \sqrt{I}}{1+a_i B \sqrt{I}} + B^0 I$$

Table 1. Association constants ($\log K_{ML_n}$) for some trace metal-ligand complexes at 25°C and 1 atm.

Ligand	n	Cation				
		Mn ²⁺	Fe ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺
CO ₃ ²⁻	1	6.31	6.57	6.87	6.73	6.63
	2	8.99	9.51	10.11	9.83	9.63
HCO ₃ ⁻	1	1.95	2.05	2.14	2.10	2.07
SO ₄ ²⁻	1	2.26	2.20	2.33	2.35	2.38
	2	0.88	0.76	1.02	1.06	1.12
HSO ₄ ⁻	1	1.05	1.08	1.10	1.09	1.08
PO ₄ ³⁻	1	6.18	6.32	6.46	6.40	6.35
	2	8.72	9.00	9.28	9.16	9.06
HPO ₄ ²⁻	1	3.58	3.60	2.93	3.20	3.30
	2	3.52	3.56	2.22	2.76	2.96
H ₂ PO ₄ ⁻	1	1.50	2.70	1.61	1.59	1.60
	2	-0.64	1.76	0.42	-0.46	-0.44
Cl ⁻	1	-0.14	-0.07	-0.43	+0.21	-0.19
	2	-1.88	-0.59	0.96	-0.39	0.18
	3	-3.61	-1.89	0.18	-1.78	-1.40
	4	-4.67	-2.80	-0.55	-3.95	-1.52
OH ⁻	1	3.41	4.50	4.14	6.00	5.04
	2	5.80	7.40	9.00	10.70	11.10
	3	7.20	11.00	12.00	14.20	13.60
	4	7.70	10.00	12.00	16.40	14.80

where γ_i = Activity coefficient (individual) of the i^{th} ion.

Z_i = Charge on the i^{th} ion.

I = True ionic strength (M).

A and B = Debye-Huckel parameters

(A = 0.5116 liter $^{1/2}$ /mole $^{1/2}$ at 25°C)

(B = 0.3292 x 10⁸ liter $^{1/2}$ cm/mole $^{1/2}$ at 25°C).

a_i = "Distance of closest approach" of the i^{th} ion (in cms).

B^0 = "Deviation function" (0.041 liters/mole at 25°C).

According to Helgeson (1969), this equation can be used to compute the individual free ion activity coefficients for the ions indicated above in solutions (of sodium chloride) of true ionic strength up to 3.0 M.

The "distance of closest approach" parameters are usually listed separately for each ion and complex. However, this distance parameter for hundreds of complexes included in GEOCHEM is not available. This lack of data can be circumvented if the recommendations of Truesdell and Jones (1973) are followed. These authors indicate that the distance parameter can be assumed to be $4A^0$, $5A^0$ and $6A^0$ for monovalent, divalent and trivalent (and higher valences) ions, respectively.

In addition to the activity coefficient calculations for charged species in high ionic strength solutions, Helgeson (1969) has suggested an equation for the calculation of the activity coefficient of neutral species which deviate significantly from unity at high ionic strengths.

$$\log \gamma^0 = 0.1 I$$

where γ^0 = Activity coefficient of a neutral complex.

I = True ionic strength (M).

The subroutine IONCOR in the program GEOCHEM accordingly has been modified as follows: The Davies' equation has been removed from IONCOR. The modified Davies' equation (Stumm and Morgan, 1970) and Helgeson's equations have been included in a new subroutine called GAM(M). In this subroutine, the activity coefficient calculations are made by the Davies' or by Helgeson's equation, depending on the ionic strength of the solution. For all solutions with true ionic strength less than or equal to 0.5 M , Davies' equation is used. For other solutions (greater than 0.5 M ionic strength) Helgeson's equation is used. At present, no upper limit of ionic strength is imposed on Helgeson's equation. If this limit is needed, it can be added at a later date. In this subroutine, the activity coefficient for a neutral species is computed at all ionic strengths. However, at present there is no provision for modifying the activity of water at higher ionic strengths.

There still remains a need to incorporate a subroutine for cation exchange into GEOCHEM. In order to accomplish this part of our objective, it seems necessary to reformulate the thermodynamic theory of cation exchange so as to bring out its natural similarity to the theory of complex formation. Initial work on this reformulation has been summarized in a paper by Sullivan (1977), which appears in the Appendix to this report. Also, the soil chemistry literature on cation exchange has been reviewed thoroughly to obtain thermodynamic data that may be used to validate the theory to be developed.

2. Trace Element Speciation in Mixtures with Other Natural Waters

As a first step toward simulating the chemistry of geothermal brine intrusion into the natural waters of the Imperial Valley, GEOCHEM was employed to compute the chemical equilibrium of several mixtures of brine and irrigation water. The total concentrations of the elements in the highly saline brine obtained from the Sinclair 4 well and in an irrigation water obtained from the Vail 4 canal were taken directly from an IVEP report by Phelps and Anspaugh (1976). In all, 18 metals and 10 ligands were considered. These elements could form 355 soluble complexes and 79 possible solids, which were included in the calculations carried out using GEOCHEM. Only parts of the results of these calculations are shown in Tables 2-10.

Table 2 shows the chemical speciation of all of the elements in the geothermal brine under oxidizing conditions at 25°C and 1 atm. pressure. Under these conditions, only K, Li, Na, Rb, Cl, F, and NO_3^- are expected to exist as free ions in significant amounts. Most of the metal cations are complexed with Cl^- and NO_3^- . As, B, Fe, Si, and SO_4^{2-} are expected to precipitate as solids. The principal chemical features of the brine are its low pH, very low HCO_3^- content, and very high Cl content. These features play an important role in the interpretation of the data in Tables 3-10.

Table 2. Chemical Speciation in a Geothermal Brine under Oxidizing Conditions at 25 C and 1 atm. Pressure (pH = 5.3).

Element	Tot. Conc. (M)	% Free	% Complexed (Cl, NO ₃)	% Solid
Ba	7.9×10^{-3}	3.6	91.4	5.0 (sulfate)
Ca	6.8×10^{-1}	--	86.1	13.8 (borate)
Cd	4.5×10^{-8}	--	100.0	--
Co	1.0×10^{-8}	7.2	92.8	--
Cu	4.7×10^{-8}	0.9	99.0	--
Fe	2.4×10^{-2}	--	--	100.0 (hydroxide)
Hg	1.0×10^{-6}	--	100.0	--
K	3.8×10^{-1}	89.3	10.7	--
Li	5.0×10^{-2}	19.6	80.4	--
Mg	3.0×10^{-2}	--	99.9	--
Mn	2.7×10^{-2}	3.6	96.4	--
Na	2.5×10^0	89.7	10.2	--
Ni	6.8×10^{-5}	--	99.9	--
Pb	2.9×10^{-4}	--	100.0	--
Rb	1.0×10^{-8}	58.9	41.0	--
Sr	5.1×10^{-3}	0.6	99.4	--
Zn	9.1×10^{-3}	0.4	99.6	--
AsO ₄	1.3×10^{-4}	--	--	100.0 (Ba)
B(OH) ₄	9.3×10^{-2}	--	--	100.0 (Ca)
Cl	4.4×10^0	60.3	39.7	--
F	7.4×10^{-4}	29.6	5.4	65.0 (Ca)
NO ₃	2.5×10^{-2}	41.4	58.6	--
SiO ₃	1.4×10^{-2}	--	4.9	95.1 (Na)
SO ₄	2.0×10^{-4}	--	0.3	99.7 (Ba)

Table 3 shows the results for Cd. It is seen that, in the irrigation water (3rd column), most of the Cd is in the form of Cd^{2+} . However, in the presence of brine (4th and 5th columns), the equilibrium quickly shifts to chloride complexes of Cd. Moreover, these complexes tend to be neutral or negatively-charged species. Thus it may be expected that brine-affected irrigation water applied to soil will contain Cd in especially mobile forms that will not be adsorbed on the negatively-charged soil exchange complex.

Table 4 gives a description of the speciation of Cu. In the irrigation water, Cu is found primarily as borate and carbonate complexes. When brine intrudes, however, one-fifth to one-half of the Cu in solution precipitates as a carbonate and the Cu remaining in solution exists predominantly in free ionic form as Cu^{2+} . This is because the brine contains considerable Cu, enough to have the solubility product of malachite exceeded, while the irrigation water contains considerable HCO_3^- . In this case, a dilute mixture of brine in irrigation water is ideal for immobilizing Cu in a precipitate. The soil exchange complex may act to further immobilize the Cu present as Cu^{2+} .

Table 5 shows that Hg will behave similarly to Cd in that neutral and negatively-charged Cl complexes dominate when brine intrudes irrigation water.

Table 6 shows that brine intrusion provides for an increase in the percentage of free Ni as well as in the percentage of the neutral complex NiCl_2^0 . This pattern is a result of the relatively high affinity of Ni^{2+} for CO_3^{2-} and its relatively low affinity for Cl^- (see Table 1). Thus Ni may exhibit about the same mobility as Cu in soil, but for different reasons.

Table 3. Chemical Speciation of Cd (%) in Brine-Irrigation Water Mixtures.

Brine: Irr. Water		0:1*	1:10**	1:5***
Tot. Conc. (M)		10^{-8}	10^{-8}	10^{-8}
Free:	Cd^{2+}	61.6	1.7	--
	CdCO_3^0	1.4	--	--
	CdHCO_3^+	1.9	--	--
	CdCl^+	20.9	17.4	5.0
Complexes:	CdCl_2^0	--	26.3	19.4
	CdCl_3^-	--	1.5	1.3
	CdCl_4^{2-}	--	52.5	74.0
	CdSO_4^0	12.9	--	--

* pH = 8.2

** pH = 7.3

*** pH = 6.9

Note: Complexes which comprise less than 1% of the total concentration of Cd are omitted from this table.

Table 4. Chemical speciation of Cu (%) in Brine-Irrigation Water Mixtures.

Brine:Irg. Water		0:1*	1:10**	1:5***
Tot. Conc. (M)		3×10^{-8}	4.3×10^{-6}	7.9×10^{-6}
Free:	Cu^{2+}	1.6	20.5	45.8
	CuB(OH)_4^+	38.9	8.0	2.6
	$\text{Cu[B(OH)}_4]_2^0$	18.6	1.0	--
	CuCO_3^0	38.0	9.0	8.5
	CuCl^+	--	3.5	14.5
	Cu(Cl)_2^0	--	--	2.7
	CuOH^+	2.0	1.9	1.9
Complexes:				
Solid:	$\text{Cu}_2(\text{CO}_3)(\text{OH})_2$	--	55.0	21.9

Note: Complexes which comprise less than 1% of the total concentration of Cu are omitted from this table.

* pH = 8.2

** pH = 7.3

*** pH = 6.9

Table 5. Chemical Speciation of Hg (%) in Brine-Irrigation Water Mixtures.

Brine: Irr. Water		0:1*	1:10**	1:5***
Tot. Conc. (M)		10^{-8}	9.6×10^{-8}	1.7×10^{-7}
Free:	Hg^{2+}	--	--	--
	HgCl_2^0	1.3	11.0	6.4
	HgCl_3^-	--	20.0	14.5
Complexes:	HgCl_4^{2-}	--	69.0	79.1
	HgOH^+	--	--	--
	$\text{Hg}(\text{OH})_2^0$	98.7	--	--

* pH = 8.2

** pH = 7.3

*** pH = 6.9

Note: Complexes which comprise less than 1% of the total concentration of Hg are omitted from this table.

Table 6. Chemical Speciation of Ni (%) in Brine-Irrigation Water Mixtures.

Brine: Irg. Water		0:1*	1:10**	1:5***
Tot. Conc. (M)		8.5×10^{-8}	6.3×10^{-6}	1.1×10^{-5}
Free:	Ni ²⁺	2.5	46.8	34.9
	NiB(OH) ₄ ⁺	3.0	--	--
	NiCl ⁺	--	2.0	2.8
	NiCl ₂ ⁰	--	14.5	47.9
Complexes:	NiCl ₃ ⁻	--	--	2.2
	NiCO ₃ ⁰	91.2	33.1	10.2
	Ni(CO ₃) ²⁻	1.9	--	--
	NiSO ₄ ⁰	--	1.1	--

* pH = 8.2

** pH = 7.3

*** pH = 6.9

Note: Complexes which comprise less than 1% of the total concentration of Ni are omitted from this table.

Table 7 gives the results for Pb. In this case, Pb changes from a neutral carbonate complex in the irrigation water to a lead hydroxycarbonate solid in a 1:10 brine/irrigation water mixture. However, as more brine is mixed in, chloride complexes begin to dominate and the Pb becomes soluble (and possibly very mobile) again. The behavior here is similar to that of Cu, but with Pb being in a more mobile form, generally, than Cu.

The results for Zn are shown in Table 8. In this case the behavior is very similar to that of Cu. Finally, data for arsenate and borate are shown in Tables 9 and 10. It may be seen that As remains insoluble at all times, whereas B is made more soluble with the addition of fresh water to the brine. Accordingly, As should be relatively immobile and B relatively mobile in brine-intruded irrigation water.

These eight examples are preliminary in nature, but they do illustrate the power of GEOCHEM to make predictions that could have a strong impact on the management of brine intrusion problems.

Table 11 shows a part of similar calculations for brine mixtures with Salton Sea water. (Data on the total concentrations of the elements in the Salton Sea were taken from Phelps and Anspaugh (1976).) It may be seen that the trends are much like those observed in Tables 3-10.

Table 7. Chemical speciation of Pb (%) in Brine-Irrigated Water Mixtures.

Brine:Irg. Water		0:1*	1:10**	1:5***
Tot. Conc. (M)		1.9×10^{-8}	2.6×10^{-5}	4.8×10^{-5}
Free:	Pb ²⁺	1.2	2.4	4.8
	PbCO ₃ ⁰	91.2	3.4	2.8
Complexes:	Pb(CO ₃) ₂ ²⁻	2.6	--	--
	PbCl ⁺	--	9.8	35.5
	PbCl ₂ ⁰	--	4.7	41.7
	PbCl ₃ ⁻	--	--	9.1
	PbCl ₄ ²⁻	--	--	4.9
Solid:	Pb ₃ (CO ₃) ₂ (OH) ₂	--	77.5	--

Note: Complexes which comprise less than 1% of the total concentration of lead are omitted from this table.

* pH = 8.2

** pH = 7.3

*** pH = 6.9

Table 8. Chemical speciation of Zn (%) in Brine-Irrigated Water Mixtures.

Brine:Irg. Water		0:1*	1:10**	1:5***
Tot. Conc. (M)		1.5×10^{-7}	8.3×10^{-4}	1.5×10^{-3}
Free:	Zn^{2+}	4.8	25.8	61.8
Complexes:	$\text{ZnB}(\text{OH})_4^+$	2.3	--	--
	ZnCl^+	--	1.7	7.8
	ZnCl_2^0	--	1.3	14.5
	ZnOHCl^0	--	--	1.5
	ZnCO_3^0	89.1	9.1	9.1
	$\text{Zn}(\text{CO}_3)_2^{2-}$	1.2	--	--
	$\text{Zn}(\text{OH})_2^0$	1.1	--	--
	ZnSO_4^0	1.3	--	--
Solid:	ZnCO_3	--	59.8	3.0

* pH = 8.2

** pH = 7.3

*** pH = 6.9

Note: Complexes which comprise less than 1% of the total concentration of Zn are omitted from this table.

Table 9. Chemical speciation of As (%) in Brine-Irrigated Water Mixtures.

Brine:Irg. Water		0:1*	1:10**	1:5***
Tot. Conc. (M)		2.7×10^{-8}	1.2×10^{-5}	2.2×10^{-5}
Free:	AsO_4^{2-}	--	--	--
Solid:	BaAsO_4	99.9	100.0	100.0

* pH = 8.2

** pH = 7.3

*** pH = 6.9

Table 10. Chemical speciation of B (%) in Brine-Irrigated Water Mixtures.

Brine:Irg. Water		0:1*	1:10**	1:5***
Tot. Conc. (M)		3×10^{-5}	2.8×10^{-3}	5.1×10^{-3}
Free:	$\text{B}(\text{OH})_4^-$	10.9	--	--
Complex:	H_3BO_3	88.4	--	--
Solid:	CaB_2O_4	--	99.5	99.9

* pH = 8.2

** pH = 7.3

*** pH = 6.9

Table 11. Chemical speciation (%) following brine intrusion into
Salton Sea water

Metal	Brine:Sea Water Ratio		
	0:1	1:10	1:5
Cd			
C _T (M)	10 ⁻⁸	4.5x10 ⁻⁸	4.5x10 ⁻⁸
Free	7.6	1.6	.8
*Complexed	92.3 (Cl)	98.4 (Cl)	99.2 (Cl)
Solid	.0	.0	.0
Cu			
C _T (M)	7.9x10 ⁻⁸	4.4x10 ⁻⁶	7.9x10 ⁻⁶
Free	4.1	25.1	20.7
*Complexed	95.9 (B(OH) ₄)	74.9 (B(OH) ₄)	79.3 (B(OH) ₄)
Solid	.0	.0	.0
Hg			
C _T (M)	10 ⁻⁶	10 ⁻⁶	10 ⁻⁷
Free	.0	.0	.0
*Complexed	100.0 (Cl)	100.0 (Cl)	100.0 (Cl)
Solid	.0	.0	.0
Ni			
C _T (M)	5.1x10 ⁻⁸	6.2x10 ⁻⁶	1.1x10 ⁻⁵
Free	27.0	67.1	74.4
*Complexed	73.0 (CO ₃ , B(OH) ₄)	32.9 (CO ₃)	25.6 (CO ₃)
Solid	.0	.0	.0
Pb			
C _T (M)	10 ⁻⁸	2.6x10 ⁻⁵	4.8x10 ⁻⁵
Free	13.5	4.4	4.0
*Complexed	86.5 (CO ₃ , Cl)	10.7 (Cl, CO ₃)	8.9 (Cl, CO ₃)
Solid	.0	84.9 (CO ₃) ₃	87.1 (CO ₃) ₃
Zn			
C _T (M)	9.5x10 ⁻⁷	8.3x10 ⁻⁴	1.5x10 ⁻³
Free	43.3	44.6	31.7
*Complexed	56.7 (CO ₃ , B(OH) ₄)	11.1 (CO ₃ , B(OH) ₄)	5.3 (CO ₃ , B(OH) ₄)
Solid	.0	44.3 (CO ₃) ₃	63.0 (CO ₃) ₃
pH	7.7	7.5	7.6

* Includes the sum of concentrations of all species.

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APPENDIX

1. Flowchart for the computer program GEOCHEM.
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Organization of the Chemical
Equilibrium Program GEOCHEM

On the Chemical Foundation of the Sodium Adsorption Ratio¹

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ABSTRACT

The theoretical chemical basis of the sodium adsorption ratio (SAR) was examined in order to clarify two important issues that arise in connection with the problem of estimating potential sodium hazard: (i) the relation between SAR and the theory of cation exchange, and (ii) the implications of the universal practice of replacing SAR by what may be termed the practical SAR, which employs total concentrations of Na, Ca, and Mg instead of their free cationic concentrations. In regard to (i), it was confirmed that SAR can be given a chemical basis in terms of the Gapon cation exchange equilibrium constant which is provided in this paper with a rigorous derivation for the first time. The Gapon constant is shown to differ from the Vanselow exchange constant only because of the (arbitrary) convention adopted as to what entity is termed the ligand in the cation exchange reaction. In regard to (ii), it was shown through a direct calculation of SAR and the practical SAR for 161 different soil solutions or water extracts, utilizing a comprehensive chemical equilibrium computer program, that an exact functional relationship between the two parameters does not exist. Only a statistical correlation between SAR and practical SAR could be established because of the random variation in the composition of metal-complexing anions in the soil solutions or water extracts. These anions reduce the free cationic concentrations of Na, Ca, and Mg, but their amounts are not chemically related to the presence of the metals and, therefore, to the value of the practical SAR. It follows that the practical SAR has no exact chemical relation to the theory of cation exchange, although its use in strictly empirical studies of Na hazard may be justified, in a statistical sense, by its acknowledged practical value.

Additional Index words: cation exchange in soils, cation exchange theory, computer studies of soil solutions, exchangeable Na, Gapon equation, Na hazard.

IT HAS BEEN KNOWN for many years that the presence of sodium ions on the cation exchange sites in a soil can exert a profound deleterious influence on the chemical and physical properties of the soil (Richards, 1954; Rhoades, 1972). Extensive field experience with soils affected by exchangeable Na and many laboratory analyses of saturation extracts have led to the conclusion that the sodium adsorption ratio (SAR) is an effective measure of the potential Na hazard of a water that is in exchange equilibrium with a soil (Rhoades and Bernstein, 1971; Rhoades, 1972). In USDA Handbook 60 (Richards, 1954, p. 72), it is stated that SAR "is defined by the equation

$$SAR = \frac{Na^+}{([Ca^{2+} + Mg^{2+}]/2)^{1/2}} \quad [1a]$$

where Na^+ , Ca^{2+} , and Mg^{2+} represent the concentrations in milliequivalents per liter of the respective ions." If the concentrations of the ions are expressed in mmoles/liter instead of meq/liter, Eq. [1a] becomes

$$SAR = \frac{[Na^+]}{([Ca^{2+}] + [Mg^{2+}])^{1/2}} \quad [1b]$$

where [] refers to a concentration expressed in mmoles/liter. SAR is widely regarded as the primary factor to be con-

sidered in evaluating the possible Na hazard of an irrigation water applied to a soil. Other factors, related to the leaching fraction, the weathering of Ca- and Mg-containing soil minerals, and the precipitation of lime, then may be combined with SAR in order to estimate semiempirically the ultimate, equilibrium SAR of the soil water (Rhoades and Bernstein, 1971; R. S. Ayers and R. L. Branson, 1975³).

The practical use of SAR in predicting Na hazard has traditionally involved two important developments. First, the ionic concentrations that appear in Eq. [1a] and [1b] have been taken to be equal to the analytical concentrations of the metals. The quantity $(SAR)_p$, which here will be called the practical SAR, is thereby defined:

$$(SAR)_p = \frac{Na_T}{(Ca_T + Mg_T)^{1/2}} \quad [2]$$

where the subscript *T* refers to the total concentration of the metal, in mmoles/liter. Conventionally the right-hand side of Eq. [2] has been designated simply SAR, following the practice in Handbook 60 (Richards, 1954). In the present case, however, it will prove useful to maintain a careful distinction between the right-hand sides of Eq. [1b] and [2].

In the second, well-known development of the SAR concept, an empirical correlation equation has been found to relate $(SAR)_p$ to the proportion of exchangeable Na in a soil that is in exchange equilibrium with a water of a given $(SAR)_p$ (Richards, 1954; Rhoades and Bernstein, 1971, p. 199). The correlation equation then may be employed to estimate soil properties whose dependence on the degree of saturation of the cation exchange complex by Na ions has been determined experimentally. From these experimental relationships, empirical guidelines may be set up that provide for an evaluation of Na hazard directly in terms of the calculated value of $(SAR)_p$ (R. S. Ayers and R. L. Branson, 1975³).

Although the consensus of experience as summarized in the literature of soil chemistry gives a firm recognition of the practical utility of $(SAR)_p$ in the management of irrigated soils, there remains a need to establish clearly the relationship between this useful concept and the chemistry of the soil solution. It is evident that the basic chemical assumptions that validate the use of $(SAR)_p$ are that the particular mathematical combination of the concentration variables given in Eq. [1] determines the quantity of exchangeable Na, that Ca^{2+} and Mg^{2+} are chemically indistinguishable insofar as cation exchange is concerned, and that the formation of soluble complexes by Na^+ , Ca^{2+} , and Mg^{2+} is negligible. The mathematical form of SAR is based on the expression for the cation exchange selectivity coeffi-

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³R. S. Ayers and R. L. Branson, 1975. Water quality. Univ. of Calif. Coop. Ext., Davis and Riverside, Calif.

cient first derived by Gapon (Rhoades and Bernstein, 1971, p. 198; Gapon, 1933). In the case of Na-Ca exchange, the Gapon selectivity coefficient is written

$$K_G = \frac{[Na^+] E_{Ca(1/2)X}}{[Ca^{2+}]^{1/2} E_{NaX}} \text{ (mmole/liter)}^{1/2} \quad [3]$$

where X refers to the anionic portion of the soil cation exchanger and E is the equivalent fraction of an exchangeable cation. Given that the exchangeable cations in a soil are exclusively Na^+ and Ca^{2+} (with Mg^{2+} regarded as chemically identical to Ca^{2+}), Eq. [3] provides for a direct relationship between SAR and the relative proportion of the exchange sites that are occupied by Na ions. However, the chemical basis of Eq. [3] in the context of ion exchange theory has often been questioned (see, e.g., Babcock, 1963; Bolt, 1967) and there exists at present a considerable doubt as to the validity of the Gapon selectivity coefficient since no rigorous derivation of K_G has been published.

A similar criticism may be lodged against the replacement of SAR by $(SAR)_p$, although this conventional practice does not appear to have been questioned as extensively. Rao et al. (1968) have suggested on the basis of Na-Ca and Na-Mg exchange experiments in chloride and sulfate systems that $(SAR)_p$ should be replaced with an expression of the same form as Eq. [1] but containing ionic activities instead of concentrations. Van Beek and Bolt (1973) have confirmed this suggestion through a comparison of the values of exchange equilibrium constants with selectivity coefficients for Na-Ca exchange. These authors have emphasized the fundamental point, made earlier in papers by Longenecker (1960), Dutt and Doneen (1963), and Babcock and Schulz (1963), that ion-pair formation must be accounted for in order to describe properly exchange equilibria involving Na^+ , Ca^{2+} , and Mg^{2+} in soil solutions. Indeed, for those soil waters containing significant amounts of, for example, sulfate, bicarbonate, and carbonate ions, the extent of formation of soluble complexes by Ca^{2+} , Mg^{2+} , and possibly Na^+ , can be appreciable. In that case, the difference in magnitude between SAR and $(SAR)_p$ could be quite large and a direct relationship between $(SAR)_p$ and the proportion of exchangeable Na would become highly questionable on chemical grounds. Moreover, because soluble complex formation depends on both the cationic and anionic concentrations, and because the anionic composition of soil water is not expected to be a function of SAR, there may not be a causal relation between SAR and $(SAR)_p$ when complex-forming anions are abundant. The differences in numerical value between the two Na hazard indices thus would become a random function whose fluctuations could effectively obscure any detailed understanding of the chemistry of exchangeable Na.

The principal objective of this paper is to make a contribution toward establishing the degree to which $(SAR)_p$ has a theoretical chemical basis for being a determining factor in Na-Ca exchange in soils. In the sections that follow, the connection between K_G and the theory of cation exchange will be examined and clarified, and the relation between SAR and $(SAR)_p$ will be found through a detailed computer analysis of the chemical speciation of Na(I), K(I), Ca(II), and Mg(II) in a large number of soil solutions and saturation

extracts. The question of the chemical similarity of Ca^{2+} and Mg^{2+} in exchange processes will not be considered further by reason of its lesser significance in comparison with the other questions that arise concerning Eq. [2] and [3].

DATA AND METHODS

The Chemical Equilibrium Program GEOCHEM

The computation of SAR for soil water extracts and soil solutions of known elemental composition and pH, with no solid allowed to precipitate, was carried out with the help of the comprehensive chemical equilibrium program GEOCHEM. GEOCHEM is adapted from the computer program REDEQL2, which was developed at Caltech by Morel and Morgan and their coworkers (Morel and Morgan, 1972; Morel et al., 1973; R. E. McDuff and F. M. M. Morel, 1974. Description and use of the chemical equilibrium program REDEQL2. Tech. Rpt. EQ-73-02, W. M. Keck Laboratory, California Institute of Technology, Pasadena.) REDEQL2 is organized using a notation that differentiates metals from ligands and represents chemical compounds in a tableau form (Morel and Morgan, 1972). Free concentrations of the chemical components (e.g., Ca, Na, or CO_3) are employed in the program as the principal variables for solving the nonlinear mole balance equations dictated by chemical equilibrium. If solids are present, they are eliminated from the working equations by linear combination of the appropriate mole balance expressions followed by the definition of new secondary variables (Morel and Morgan, 1972). Values for the principal variables that are self-consistent under iteration to within 0.01% then are computed by applying the Newton-Raphson method to solve the mole balance equations. The program presently has the capability to describe numerically the chemical equilibrium of a solution containing up to 30 different metals and 30 different ligands that may combine to form as many as 700 complexes. Acid-base, coordination, solubility, redox, and adsorption phenomena may be described and corrections for ionic strength may be made. GEOCHEM differs from its predecessor, REDEQL2, in three major ways: (i) it includes formation constants for complexes, solids, and mixed solids that are relevant to soil chemical behavior, but are not contained in REDEQL2; (ii) it contains values of formation constants for solids that are considered to represent what occurs in soil (e.g., metastable, adsorbed, microcrystalline solid phases) as opposed to what occurs in a reaction vessel in the laboratory under conditions that promote the appearance of the pure, crystalline solid; and (iii) it will contain a subroutine for ion exchange that is not based on the Langmuir isotherm, as is the adsorption model utilized in REDEQL2.

Stability Constants

Table 1 lists the common logarithms of the stability constants incorporated into GEOCHEM for the present investigation. The formation constants describe the chemical reaction

where M, L, and H stand for metal, ligand, and hydrogen ion, respectively. If OH^- appears in the reaction instead of H^+ , the stoichiometric coefficient γ is set equal to minus the actual coefficient for OH in order to keep the notation simple. The stability constant appropriate to Eq. [4] is

$$K_{st} = \{M_\alpha H_\gamma L_\beta\} / \{M\}^\alpha \{H\}^\gamma \{L\}^\beta \quad [5]$$

where the curly brackets refer to the activity. It may be noted that Eq. [5] conforms to the usual way in which soluble complexes are described by equilibrium constants but is inverse to a common way of describing reactions involving precipitates.

The employment of values for stability constants in the numerical treatment of chemical equilibrium problems is a matter for critical evaluation and judgement. Not only must the methods by

Table 1—Stability constants for aqueous species at 25° C under 1 atm pressure.

Reaction	log K	Reference
1. $\text{CO}_2(\text{g}) + \text{H}_2\text{O} = \text{H}_2\text{CO}_3^0$	-1.46 ± 0.003	Harned and Davis (1943)
2. $\text{H}^+ + \text{HCO}_3^- = \text{H}_2\text{CO}_3^0$	6.36 ± 0.004	Harned and Scholes (1941), Nakayama (1970)
3. $\text{H}^+ + \text{CO}_3^{2-} = \text{HCO}_3^-$	10.33 ± 0.04	Harned and Scholes (1941), Nakayama (1970)
4. $\text{H}^+ + \text{SO}_4^{2-} = \text{HSO}_4^-$	1.99 ± 0.004	Dunsmore and Nancollas (1964)
5. $\text{H}^+ + \text{OH}^- = \text{H}_2\text{O}$	14.00 ± 0.001	Olofsson and Hepler (1975)
6. $\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3^0$	3.15 ± 0.08	Reardon and Langmuir (1974)
7. $\text{Ca}^{2+} + \text{HCO}_3^- = \text{CaHCO}_3^+$	1.02 ± 0.10	Jacobson and Langmuir (1974)
8. $\text{Ca}^{2+} + \text{SO}_4^{2-} = \text{CaSO}_4^0$	2.31 ± 0.04	Nakayama and Rasnick (1967)
9. $\text{Ca}^{2+} + \text{OH}^- = \text{CaOH}^+$	1.39 ± 0.04	Bell and George (1953)
10. $\text{Mg}^{2+} + \text{CO}_3^{2-} = \text{MgCO}_3^0$	2.88 ± 0.05	Reardon and Langmuir (1974)
11. $\text{Mg}^{2+} + \text{HCO}_3^- = \text{MgHCO}_3^+$	0.96	Reardon et al. (1973)
12. $\text{Mg}^{2+} + \text{SO}_4^{2-} = \text{MgSO}_4^0$	2.24 ± 0.02	Hanna et al. (1971)
13. $\text{Mg}^{2+} + \text{OH}^- = \text{MgOH}^+$	2.21 ± 0.05	McGee and Hostetler (1975)
14. $\text{Na}^+ + \text{CO}_3^{2-} = \text{NaCO}_3^-$	0.55	Nakayama (1970, 1971a)
15. $\text{Na}^+ + \text{HCO}_3^- = \text{NaHCO}_3^0$	0.16 ± 0.06	Nakayama (1970, 1971a)
16. $\text{Na}^+ + \text{SO}_4^{2-} = \text{NaSO}_4^-$	1.10 ± 0.08	Fisher and Fox (1975), Fisher (1975)
17. $\text{K}^+ + \text{SO}_4^{2-} = \text{KSO}_4^-$	0.85 ± 0.02	Truesdell and Hostetler (1968)
18. $\text{H}^+ + \text{H}_3\text{SiO}_4^- = \text{H}_4\text{SiO}_4^0$	9.86 ± 0.07	Mesmer and Baes (1974)
19. $2\text{H}^+ + \text{H}_2\text{SiO}_4^{2-} = \text{H}_4\text{SiO}_4^0$	22.92 ± 0.06	Mesmer and Baes (1974)

which the constants have been determined be examined for their degree of exactness and precision and for their dependence on the results of other, independent investigations, but the constants themselves must be considered in relation to the solid phases and aqueous species actually expected to occur in the chemical system under study. The list in Table 1 represents our present best judgement as to the available stability constants that are germane to the calculation of macroion speciation in the absence of solid phases and, in particular, SAR in a soil solution or water extract at 25°C under 1 atm pressure. The standard errors quoted indicate the extent to which the data may be imprecise. The basis for our selection of the data given in Table 1 is discussed in the Appendix.

Calculation of SAR

The relation between SAR and $(\text{SAR})_p$ is established most conveniently in terms of the three distribution functions

$$\alpha_{\text{Na}} = \frac{[\text{Na}^+]}{[\text{Na}^+]} \quad \alpha_{\text{Ca}} = \frac{[\text{Ca}^{2+}]}{[\text{Ca}^{2+}]} \quad \alpha_{\text{Mg}} = \frac{[\text{Mg}^{2+}]}{[\text{Mg}^{2+}]} \quad [6]$$

The combination of Eq. [1], [2], and [6] produces the expression

$$\text{SAR} = \frac{\alpha_{\text{Na}}}{(\alpha_{\text{Ca}})^{1/2}} \frac{(\text{Ca}_T + \text{Mg}_T)^{1/2}}{\left(\text{Ca}_T + \frac{\alpha_{\text{Mg}}}{\alpha_{\text{Ca}}} \text{Mg}_T\right)^{1/2}} (\text{SAR})_p \quad [7]$$

If $\alpha_{\text{Ca}} \approx \alpha_{\text{Mg}}$, then Eq. [7] reduces to

$$\text{SAR} = \frac{\alpha_{\text{Na}}}{(\alpha_{\text{Ca}})^{1/2}} (\text{SAR})_p \quad [8]$$

The approximation contained in Eq. [8] was found to be a good one for many of the sets of data analyzed in the present study; usually α_{Mg} differed from α_{Ca} by < 10%.

The cationic distribution functions were calculated for all of the sets of data on soil solutions or soil water extracts using the GEOCHEM program. Results of a typical calculation of the distribution functions are given in Table 2. These coefficients then were introduced into Eq. [6] along with the total concentration data to calculate SAR values according to Eq. [7].

Table 2—Typical results of a calculation of the distribution functions (%) for Ca, Mg, K, and Na using the computer program GEOCHEM.

Leaching fraction	Drainage water, calcareous lysimeters								
	Feather River			Grand River			Missouri River		
	0.1	0.2	0.3	0.1	0.2	0.3	0.1	0.2	0.3
Calcium									
Free metal	84.6	87.8	89.7	59.8	69.0	73.8	68.3	75.9	78.4
Bound with CO_3 and HCO_3	15.0	11.7	9.7	15.4	14.2	12.0	10.6	9.4	8.3
Bound with SO_4	0.4	0.5	0.6	24.8	16.8	14.2	21.0	14.7	13.3
Magnesium									
Free metal	84.6	87.9	89.7	62.9	71.4	76.0	71.4	78.2	80.6
Bound with CO_3 and HCO_3	15.1	11.9	9.8	16.4	14.8	12.4	11.2	9.8	8.5
Bound with SO_4	0.3	0.4	0.5	20.7	13.8	11.6	17.4	12.0	10.9
Potassium									
Free metal	100.0	100.0	99.9	94.9	97.5	98.1	96.2	97.9	98.3
Bound with SO_4	--	--	0.1	5.1	1.9	1.9	3.8	2.1	1.7
Sodium									
Free metal	98.1	98.6	98.9	94.5	97.3	97.3	96.2	97.6	98.0
Bound with CO_3 and HCO_3	1.9	1.4	1.1	3.0	1.7	1.7	1.8	1.4	1.2
Bound with SO_4	--	--	--	2.5	0.9	0.9	1.9	1.0	0.9

† Based on chemical analyses published by Rhoades et al. (1973).

Analytical Data on Soil Solutions and Extracts

The chemical data employed in the calculations of SAR were the analyses of total concentrations of the macroions in drainage waters from lysimeters, reported by Rhoades et al. (1973), and in soil saturation extracts comprised in the archives of the U. S. Salinity Laboratory and partially reported in Rhoades and Bernstein (1971). The saturation extract data include analyses for soils in Israel, India, Nigeria, Venezuela, Turkey, and Taiwan, gathered under the auspices of the Foreign Trainee Program; for soil samples 12320-12338, obtained in Nigeria; for soils in Grand Valley, and for the soils listed in USDA Handbook 60 (Richards, 1954, p. 29). In the case of the saturation extract data for Nigerian soils, the total concentration of SO_4 was calculated as the difference between total meq/liter cations and total meq/liter reported for anions. A set of 161 chemical analyses was obtained from the sources of data just enumerated. These analyses were considered to be sufficiently precise and large enough in number to establish unambiguously the relationship between SAR and $(\text{SAR})_p$ according to Eq. [7], using the GEOCHEM program.⁴

SAR AND THE THEORY OF CATION EXCHANGE

It is not our purpose in this paper to enter into a general discussion of the thermodynamic theory of cation exchange as it has been applied to soil systems, since critical reviews of that subject are readily available (Babcock, 1963; Bolt, 1967). Instead, we wish to formulate a thermodynamic description of cation exchange that leads to an unambiguous presentation of the Gapon selectivity coefficient. No implication of preference for one kind of selectivity coefficient over another is intended, as that issue is one best settled on strictly empirical grounds.

In developing the theory, we shall regard a dry, homoionic cation exchanger as a solid phase, with the Standard State being, therefore, that of the pure solid at a chosen temperature and under atmospheric pressure (Garrels and Christ, 1965, p. 5f). Upon being immersed in water or in an aqueous solution, the exchanger will undergo a dissolution

⁴ Tabulated values of SAR and $(\text{SAR})_p$ are available from the authors on written request.

reaction. If the exchanger maintains its integrity as a solid phase, aside from the dissociation of its exchangeable cations, for a period long enough to justify treating it as a stable entity, then the thermodynamics of ionic aqueous solution-solid phase equilibria may be applied to describe the reaction

where M refers to the exchangeable metal cation (with charge $+m$) and X refers to the anionic part of the exchanger (with charge $-x$). The quantities p and q are stoichiometric coefficients. These coefficients will be in part determined by the chemical specification of X (that of M is assumed to be unambiguous) and in part fixed by the requirement of electroneutrality

$$p/q = x/m \quad [10]$$

The precise specification of p and q , insofar as the thermodynamic treatment of Eq. [9] is concerned, is a matter of convention. One convention that is of wide use in the literature of inorganic chemistry is to regard the metal cation in the compound M_pX_q to be the central group, with the anion X as the ligand (see, e.g., Cotton and Wilkinson, 1972). In that case one chooses $p = 1$ and, therefore, $q = m/x$, according to Eq. [10]. In addition, one may set $x = 1$ with no loss in generality and no violation of the macroscopic requirement of electroneutrality. This value for x means, simply, that the basic stoichiometric unit of the exchanger anion is one equivalent. Then Eq. [9] becomes

The convention leading to Eq. [11] may be termed, in the present context, as the Vanselow Convention (Vanselow, 1932). It may be pointed out in passing that the Standard States for the chemical species on the right-hand side of Eq. [11] are those adopted commonly for a solute in aqueous solution and for a solid phase, respectively (see, e.g., Garrels and Christ, 1965). The fact that both M and X are charged species strictly means that the Standard States are not purely thermodynamic ones. However, this extra-thermodynamic aspect of the chemistry of aqueous solution-solid equilibria has long been assimilated into research on ionic solutions and need not be considered further here (see, e.g., Guggenheim, 1967, Chap. 7).

Another convention, which is of wide use in macromolecular chemistry, is to regard X in M_pX_q as the central group, with the metal cation, M , chosen as the ligand (see, e.g., Steinhardt and Reynolds, 1969). Then one sets $q = 1$ and, therefore, $p = x/m$, according to Eq. [10]. Once again x may be set equal to 1. Then Eq. [9] becomes

The convention leading to Eq. [12] may be termed the Gapon Convention (Gapon, 1933). It should be noted that, under this convention, metal cations react in equivalents

with the anion X , whereas under the Vanselow Convention the cations react in molar amounts with X .

The general, stoichiometric cation exchange reaction for a given exchanger now may be formulated using either Eq. [11] or Eq. [12] as a basis. The resulting expressions are

where M and N refer to the exchangeable cations. The corresponding thermodynamic equilibrium constants are

$$K_{\text{VEX}} = \frac{\{M^{+m}\}\{NX_n\}^{m/n}}{\{N^{+n}\}^{m/n}\{MX_m\}} \quad [15]$$

in the Vanselow Convention and

$$K_{\text{GEX}} = \frac{\{M^{+m}\}^{1/m}\{N_{1/n}X\}}{\{N^{+n}\}^{1/n}\{M_{1/m}X\}} \quad [16]$$

in the Gapon Convention, where $\{ \}$ refers to the activity of a chemical species. The Gapon selectivity coefficient, K_G , is obtained from Eq. [16] under the assumptions (whose validity will not be discussed here) that solute activities are numerically equal to molar concentrations and that exchanger activities are equal to equivalent fractions. Thus, with $[\]$ now denoting molar concentration,

$$K_G = \frac{[M^{+m}]^{1/m}}{[N^{+n}]^{1/n}} \frac{E_{N_{1/n}X}}{E_{M_{1/m}X}} (\text{moles/liter})^{1/m - 1/n} \quad [17]$$

where $E_{N_{1/n}X}$ = moles $N_{1/n}X$ /(equivalents of cation exchanger), etc. In the special case of Na-Ca exchange, Eq. [17] takes on the form

$$K_G = \frac{[Na^+]}{[Ca^{2+}]^{1/2}} \frac{E_{Ca_{1/2}X}}{E_{NaX}} (\text{moles/liter})^{1/2}. \quad [18]$$

It is evident that a shift in concentration units from moles/liter to mmoles/liter will bring Eq. [18] into exact numerical equality with Eq. [3], although it should be understood that a compensating shift in the units of the solute activity coefficients that relate K_G to K_{GEX} also is implied. If it is assumed that Ca^{2+} and Mg^{2+} are chemically indistinguishable, insofar as cation exchange is concerned, and that the exchangeable cations in the soil are solely Na^+ , Ca^{2+} , and Mg^{2+} , then Eq. [18] may be rewritten in the form

$$ESP = \frac{(100/K_G)SAR}{1 + (SAR/K_G)} \quad [19]$$

where $ESP = 100 E_{NaX}$, the exchangeable Na percentage. Equation [19] is a relation between the proportion of the exchange sites occupied by Na ions and SAR, as developed from the thermodynamic theory of cation exchange together with assumptions about the activities of the solution and

Fig. 1—The relationship between the sodium adsorption ratio and the practical sodium adsorption ratio for 161 soil solutions and water extracts. The straight line represents a 1:1 functional relationship between SAR and $(SAR)_p$.

solid-phase species involved. It may be employed as a chemical basis for empirical correlations between SAR and ESP for soil systems in states of exchange equilibrium, provided that some experimental evidence exists to support the assumed relations between activities and concentration variables and the concept of a mean value of K_c that is representative of a wide variety of soil cation exchangers.

SAR AND SOLUBLE COMPLEX FORMATION

The distribution function for a free cationic species in a homogeneous solution phase will depend in general on the pH and on the anionic composition of the phase (Stumm and Morgan, 1970, Chapters 5 and 6). For example, if the cation is Ca^{2+} and the soil solution contains the anions CO_3^{2-} , HCO_3^- , and SO_4^{2-} , the distribution function α_{Ca} is given by

$$\alpha_{Ca} = (1 + {}^cK_9\alpha_{OH}OH_T + {}^cK_6\alpha_{CO_3}CO_{3T} + {}^cK_7\alpha_{HCO_3}HCO_{3T} + {}^cK_8\alpha_{SO_4}SO_{4T})^{-1} \quad [20]$$

where cK_m is the equilibrium constant for the m^{th} reaction in Table 1, corrected for ionic strength, and the distribution functions α_{OH} , α_{CO_3} , etc. are defined analogously to what appears in Eq. [6]. Equation [20] actually is one member of a coupled set of algebraic equations, since the distribution functions for the anions depend on those for the cations. This set of equations, of course, is what the program GEOCHEM ultimately solves numerically. The point to be made here is not that, but rather that α_{Ca} is not determined by the cations in the system alone. The distribution function for a

cation is a resultant of chemical equilibrium among all the components and, therefore, would not be expected to be a function simply of $(SAR)_p$ or any other parameter that depends solely on metal concentrations. It follows that, whenever the formation of soluble complexes by Na, Ca, and Mg is significant, there may not be a functional relationship between SAR and $(SAR)_p$. Putting it another way, the relation between SAR and $(SAR)_p$ may be expected to have an important random component, due to the random variation in anionic composition among soil solutions, whenever soluble complex formation is appreciable in those solutions. If this were the case, SAR would only be at best positively correlated with $(SAR)_p$ in a statistical sense.

Figure 1 is a plot of the pair SAR and $(SAR)_p$ for the different soil solutions or soil water extracts analyzed numerically with the help of GEOCHEM. Two general features of the relationship between SAR and $(SAR)_p$ are readily apparent. First, SAR is always greater than or equal to $(SAR)_p$, that is, the true SAR of a soil solution is underestimated by the value of the practical SAR. This result, which was also noted by Rao et al. (1968), may be understood in terms of the data in Table 1, which show that Ca and Mg tend to form more stable complexes with a given anion than does Na. It follows that α_{Ca} and α_{Mg} will tend to be smaller under a given condition of anion concentration than will α_{Na} . The second important aspect of Fig. 1 is the scatter in the data points, which grows significantly as $(SAR)_p$ increases above the value 10. This type of scatter reflects an increasing random component in the SAR- $(SAR)_p$ relationship that is brought on by the random variation in the anionic composition of the soil solutions and water extracts. The significance of this variation for SAR grows with an increase in the amounts of complexing anions (e.g., SO_4^{2-} , HCO_3^- , and CO_3^{2-}), and these amounts increase normally as the total concentration of Na becomes larger. Therefore, except possibly at values of $(SAR)_p < 2$, an exact functional dependence of SAR on $(SAR)_p$ must be ruled out. However, for low values of $(SAR)_p$, a strong, positive statistical correlation between the two parameters is still apparent. The 105 pairs of SAR- $(SAR)_p$ values corresponding to $(SAR)_p \leq 20$ may be fitted to the linear regression equation

$$SAR = 0.08 + 1.115(SAR)_p \quad [27]$$

with a correlation coefficient of 0.9969502 ($r^2 = 0.9939097$) and a standard error of estimate equal to 0.497333. This statistical correlation, of course, has no bearing on the question of the chemical basis of $(SAR)_p$ in relation to Na exchange.

CONCLUSIONS

The Na adsorption ratio has a chemical basis in the theory of cation exchange as formulated under what is termed here the Gapon Convention. In this convention, the anionic part of the cation exchange complex is regarded as the central group and the exchangeable cations are regarded as ligands. This contrasts with what is termed the Vanselow Convention, wherein the exchangeable cation is regarded as the central group and the anionic part of the exchanger is the ligand. Both conventions are thermodynamically permissible.

The practical Na adsorption ratio has only a statistical relationship to the Na adsorption ratio and, therefore, to the theory of cation exchange applied to Na^+ . This is because the relation between the total concentrations of Na, Ca, or Mg and their free cationic concentrations does not depend solely on the metals, but is instead a function of the chemical equilibrium in the system as a whole, including the anions. Since the anionic composition is variable and is not a function of the cationic composition, the relation between the Na adsorption ratio and the practical sodium adsorption ratio has a random component. Accordingly, there is no exact chemical relation between the exchangeable Na percentage and the practical sodium adsorption ratio, although a strictly empirical, statistical correlation between these two entities is always possible and can be of value in practical estimates of the potential Na hazard of an irrigation water.

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APPENDIX

The stability constants incorporated into GEOCHEM for the present investigation were selected after a careful review of the chemical, geochemical, and soil chemical literature. The set of values chosen appears to be the most reliable and internally consistent available. It is important to note in regard to consistency that a given stability constant may depend on other, independently-measured stability constants and, therefore, that a change in the chosen, "best value" for one of the other constants can have broad ramifications. For example, the stability constant for the complex⁵ MgCO_3 calculated by Reardon and Langmuir (1974) depends on the equilibrium constants for the formation of H_2O , MgOH^+ , H_2CO_3^0 , and MgHCO_3^+ . The set of stability constants for all of these five compounds accordingly cannot be selected independently.

The dissociation constants for carbonic acid calculated by Harned and Scholes (1943) have been used widely in carbonate equilibrium calculations. Recently, Nakayama (1970, 1971) confirmed the validity of these constants after including NaCO_3^- and NaHCO_3^0 ion pairs in his calculation. These constants have been adopted here. They form the basis for the calculations of the stability constants for the other carbonate species in Table 1.

After a thorough review of experimental data from various sources, Dunsmore and Nancollas (1964) indicate a log K value of 1.99 ± 0.004 for the formation of HSO_4^- . This value has been included here. Similarly, the common logarithm of the formation constant for liquid water was chosen to be 13.999 after a careful survey of existing data by Olofsson and Hepler (1975).

After an extensive review of experimental data on calcite solubility and the dissociation constants of CaCO_3 , Lafon (1970) concluded that log K for the formation of this ion pair is close to 3.12 ± 0.3 , rather than 4.49 ± 0.08 (Nakayama, 1968). Recent work by Reardon and Langmuir (1974) has confirmed Lafon's

conclusions. Therefore, Reardon and Langmuir's value of 3.15 ± 0.08 has been adopted here.

Using conductance measurements, Jacobson and Langmuir (1974) have determined the formation constant for the CaHCO_3^+ ion pair. Their value of log K , 1.02 ± 0.1 , agrees with the potentiometric determination by Nakayama (1968), which yielded a log K value of 1.25, considering an uncertainty of ± 0.2 assigned to the latter figure by Jacobson and Langmuir (1974). Similarly, the formation constant for MgHCO_3^+ determined by Reardon et al. (1973) from conductance measurements (log $K = 0.96$) has been adopted in preference to Nakayama's (1971) log K value of 1.23.

The common logarithm of the formation constant for the ion pair CaSO_4^0 was calculated to be 2.31 from solubility measurements on gypsum made by Nakayama and Rasnick (1967). This value agrees well with the determination by Bell and George (1953) (log $K = 2.307 \pm 0.044$) and the value (2.316) derived by Helgeson (1967) from a least squares analysis of log K vs. temperature data.

For the ion pair MgCO_3 , Reardon and Langmuir (1974) report a log K value of 2.88 ± 0.05 . They have reviewed the previous data available for this ion pair and point out certain inconsistencies regarding the ionic strength calculations made by Nakayama (1971b) and the omission of other ion pairs by Garrels et al. (1961) in the previous work on MgCO_3 . Therefore, a log K value of 2.88 ± 0.05 has been selected for inclusion in Table 1.

For the MgSO_4^0 ion pair, the logarithms of the formation constants frequently encountered in literature range from 2.20 to 2.36 (Izzat et al., 1969). A recent determination by Hanna et al. (1971), using conductimetric measurements, yields a log K value of 2.236 ± 0.019 . This result has been used in Table 1.

The log K value for the formation of the ion pair CaOH^+ adopted here is 1.39 ± 0.04 (Bell and George, 1953). This value also forms a basis for the log K value for the CaCO_3^0 ion pair (Reardon and Langmuir, 1974).

The formation constant data on the MgOH^+ ion pair has been reviewed by McGee and Hostetler (1975) in addition to their redetermination of this constant by potentiometry. Their log K value of 2.21 ± 0.05 seems the most reliable at present and, therefore, is included in Table 1.

The formation constants for the NaCO_3^- and NaHCO_3^0 ion pairs have been derived by Nakayama (1970, 1971a) from the experimental data of Harned and Davis (1943), and Harned and Scholes (1941). His log K values of 0.55 and 0.16 differ significantly from values 0.91 and -0.18 predicted by the potentiometric determinations by Butler and Huston (1970). As pointed out by Nakayama (1971), further work is necessary to assess the reliability of these two sets of determinations. Until such data are available, the log K values calculated by Nakayama (1970, 1971) have been adopted tentatively.

Using two different techniques, Fisher and Fox (1975) and Fisher (1975) have determined the formation constant of the NaSO_4^- ion pair. These authors also indicate the excellent agreement of their log K values of 1.10 ± 0.08 with the recalculated value of 1.11 ± 0.03 obtained from the data of Jenkins and Monk (1950). Therefore, a log K value of 1.10 ± 0.08 is included here.

The log K value for the formation of the KSO_4^- ion pair is based on a recent potentiometric determination by Truesdell and Hostetler (1968).

The dissociation constants of silicic acid were obtained directly from the critical compilation of Mesmer and Baes (1974).

There is some evidence for the existence of K^+ -carbonate complexes (Lee and Wilmshurst, 1964). A similar view has been expressed by Atkinson et al. (1973). However, the formation constants for these complexes have not yet been determined. It can be safely assumed that these complexes are as weak or weaker than the very weak, corresponding Na^+ -carbonate complexes. Therefore, we do not believe that omitting these complexes from the present compilations will significantly affect our results.

There is also some evidence for the existence of ion triplets such as Na_2CO_3^0 (Garrels and Christ, 1965). This is also a weak com-

⁵We do not distinguish here between the terms *complex* and *ion pair*, as these entities are thermodynamically identical.

plex ($\log K = 0.68$, Truesdell and Jones, 1969) and, therefore, can be omitted safely from the present calculations. It is quite likely that similar ion triplets and higher associations involving other macrocations do exist. But, at present, formation constants for such ion associations simply are not available. It should be noted that, even though the weak complexes such as KCO_3^- , KHCO_3^0 , and Na_2CO_3^0 can be omitted in calculations involving dilute to moderately concentrated solutions, gross errors may result in calculations involving concentrated aqueous solutions if these complexes are omitted.

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TRACE METAL CHEMISTRY OF SOIL SOLUTIONS: ESTIMATED
ASSOCIATION CONSTANTS FOR SOME COMPLEXES OF TRACE
METALS WITH INORGANIC LIGANDS ¹

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SOIL BRIEF

Association constants of complexes of bivalent metals of the first transition series with the ligands CO_3^{2-} , HCO_3^- , SO_4^{2-} , HSO_4^- , PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , Cl^- , and OH^- have been compiled from various published sources. In cases where experimental determinations are lacking, the constants have been estimated by using a theoretical as well as two semi-empirical methods.

TRACE METAL CHEMISTRY OF SOIL SOLUTIONS: ESTIMATED
ASSOCIATION CONSTANTS FOR SOME COMPLEXES OF TRACE
METALS WITH INORGANIC LIGANDS

ABSTRACT

Chemical equilibrium studies of trace metals in soils by an ion-association model require reliable data on thermodynamic association constants for various metal-ligand complexes. Therefore, available experimental data at 25°C were compiled for complexes of the transition metal cations Mn^{2+} , Fe^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} with the ligands CO_3^{2-} , HCO_3^- , SO_4^{2-} , HSO_4^- , PO_4^{3-} , HPO_4^{2-} , $H_2PO_4^-$, Cl^- , and OH^- . However, experimental values of the thermodynamic association constants for many of the complexes were not available. This lack of information was alleviated by employing the theoretical model of Kester and Pytkowicz, and the semiempirical models of Nieboer and McBryde and Van Panthaleon Van Eck to make estimates of the as yet unmeasured association constants. These estimated constants were tabulated in a compact form along with the experimental values. This compilation of 100 association constants, although provisional, should prove helpful in a variety of studies on trace metal equilibria in soils until more reliable experimental data become available.

Additional Index Words: Estimation of association constants, ion-association model, micronutrient chemistry of soils.

1 The study of trace metal chemistry in soils has assumed added
2 importance recently because of the possible deleterious effects on
3 soil organisms, plants, and man that result from the accumulation of
4 these metals to toxic levels in soils to which sewage sludges have
5 been applied. This concern is reflected in a recent report by Page
6 (1974), which examines the multiplicity of fates for trace elements
7 introduced into agricultural soils by the land application of municipal
8 wastes. It has been clear for some time on the basis of research on
9 the soil chemistry of micronutrients (see, e.g., Mortvedt et al., 1972)
10 that an improved understanding of trace metal chemistry can result from
11 studies of the speciation of these metals in the aqueous phase. An
12 evaluation of the effects of accidental spills of geothermal brines
13 on land in terms of the resulting changes in trace-metal speciation
14 in soils will be helpful in assessing the impact of geothermal power
15 development on agriculture (Phelps and Anspaugh, 1976). Such studies
16 require reliable thermochemical data on the formation of ion-pairs and
17 other complexes of trace metals with inorganic and organic ligands.

18 As part of a study of multicomponent trace metal equilibria in
19 soil solutions, we are developing a comprehensive chemical equilibrium
20 computer program (GEOCHEM) based on thermodynamic association constants
21 and mole balance equations (Sposito and Mattigod, 1977). With regard
22 to the trace metal complexes, much of the necessary thermodynamic
23 data can be obtained readily from published compilations (Bjerrum
24 et al., 1958; Yatsimirskii and Vasilev, 1960; Sillén and Martell, 1964,
25 1971; Baes and Mesmer, 1976). Even with the information from these
26 sources, however, it has become clear that thermodynamic association
27

1 constants for a large number of important trace metal complexes with
2 inorganic ligands have not yet been determined experimentally. As
3 a first step in filling this important gap in our knowledge, we have
4 attempted to estimate the association constants for the trace metal-
5 inorganic ligand complexes that we feel are most likely to occur in
6 soil solutions under a wide variety of conditions.

7 In this paper we present association constants at 25 C for complexes
8 formed by the bivalent ions of the trace metals Cu, Fe, Mn, Ni, and
9 Zn with the ligands Cl^- , CO_3^{2-} , HCO_3^- , OH^- , PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- ,
10 SO_4^{2-} , and HSO_4^- . Many of the 100 values of the association constant
11 reported here were compiled from the available experimental data.
12 When such data were not available, the association constants were calcu-
13 lated using the theoretical approach of Kester and Pytkowicz (1975)
14 and the semiempirical approaches of Nieboer and McBryde (1970a, b;
15 1973) and Van Panthaleon Van Eck (1953). The resultant set of thermo-
16 dynamic data, although provisional, should be useful to soil chemists
17 whose research involves the micronutrient and toxic trace metals in
18 multicomponent systems. These estimated values can serve until more
19 reliable experimental values become available.

20 21 DATA AND METHODS

22 Selection of Association Constants

23
24 The criteria used in selecting the values of the association
25 constants were: (1) the reliability of methods (Marcus and Kertes,
26 1969; Yatsimirskii and Vasilev, 1960), and (2) the agreement
27 between values obtained by different methods. In a large number of

1 cases, there were no alternative choices possible, since only a single
2 experimental determination was available. Whenever possible, as in the
3 case of hydrolytic species, critical compilations such as that by Baes
4 and Mesmer (1976) were used in selecting data.

5 In some cases, conditional association constants at ionic
6 strengths other than zero were the only ones available. In such cases,
7 the constants at ionic strengths less than 0.5 were extrapolated to
8 zero ionic strength by the Davies equation (Davies, 1962), a variant of
9 the Debye-Hückel equation. In many cases, conditional constants at
10 ionic strengths greater than 0.5 are available (see, e.g., Inczedy,
11 1976, Chap. 4). It is possible to extrapolate these values to zero
12 ionic strength by the mean salt method and by the use of Harned co-
13 efficients (Berner, 1971). At present, this latter method cannot
14 be used for trace-metal complexes because Harned coefficients for
15 mixtures of trace-metal salt solutions are not available.

16 Estimation of Association Constants

17
18 The methods available for calculating ion-association constants
19 generally fall into two groups:

- 20 1. Theoretical methods based on electrostatics, such as the ones
21 developed by Fuoss (1958) and Kester and Pytkowicz (1975).
- 22 2. Statistical methods, which correlate association constants
23 with properties such as electronegativity, charge, ionic
24 radii, coordination number, etc. (Garrels and Christ, 1965;
25 Nieboer and McBryde, 1970a, b, 1973; Van Panthaleon Van Eck,
26 1953; Mihailov, 1974; Yamada and Tanaka, 1975; Siegel, 1975).

The electrostatic model of ion-pairing of Kester and Pytkowicz (1975) (Method 1), the stability index (Q) approach of Nieboer and McBryde (1973) (Method 2), and the method of Van Panthaleon Van Eck (1953) (Method 3) were used to generate the values of thermodynamic association constants not available in the literature. The reasons for using these methods are the ease of application and the reliability of the predicted association constants as proven from a large number of metal-ligand systems.

Method 1

For the formation of an ion-pair (inner-sphere or outer-sphere complex) represented by the reaction:

the association constant is expressed as:

$$K_{ML} = \frac{\{ ML^{Z_1-Z_2} \}}{\{ M^{Z_1+} \} \{ L^{Z_2-} \}} \quad [2]$$

where { } denotes thermodynamic activity.

The following equation was derived by Kester and Pytkowicz (1975) for the association constant (all units in the CGS system except as noted):

$$K_{ML} = \frac{v v e^b}{(V-M_T v e^b) (V-L_T v e^b)} \quad [3]$$

where, V = total volume of solution

v = volume element of the ion-pair = $4\pi r^3 / 3$

r = radius of ion-pair = $r_M + r_L$

r_M = radius of metal ion (crystal or Debye)

r_L = radius of ligand (crystal or Debye)

M_T = total number of metal ions in volume V

L_T = total number of ligands in volume V

$$b = -U/kT \quad [4]$$

$$U = \frac{|z_1 z_2| e_o^2}{rD (1 + Kr)} \quad [5]$$

$$K = \left[\frac{8\pi e_o^2 NI}{1000 DKT} \right]^{1/2} \quad [6]$$

e_o = electronic charge

N = Avogadro's number

I = Ionic strength (in moles/liter)

D = Dielectric constant of bulk water

k = Boltzmann constant

T = Absolute temperature

For practical work, the number densities M_T and L_T should be converted to molar concentrations. Doing this, we bring Eq. [3] into the form:

$$K_{ML} = \frac{NV ve^b}{(V - NM_T^1 ve^b) (V - NL_T^1 ve^b)} \quad [7]$$

where M_T^1 = Metal concentration in moles/liter

L_T^1 = Ligand concentration in moles/liter

V = 1000 cm³

It is interesting to note that, for cases where $V \gg NM_T^1 v e^b$ and $NL_T^1 v e^b$, Eq. [7] becomes:

$$K_{ML} = \frac{N v e^b}{1000} = \frac{4 \pi N r^3 e^b}{3000} \quad [8]$$

This is the equation derived by Fuoss (1958) for the association constant for ion-pairs.

It was suggested by Kester and Pytkowicz (1975) that the thermodynamic association constants for ion-pairs can be calculated by inserting data into Eq. [8] for total concentrations at 10^{-8} M. They found that for concentrations below this limit, the values of K_{ML} were insensitive to order of magnitude changes in concentrations.

This method for computing association constants appears to be suitable for cases in which statistical methods cannot be used due to lack of extensive data. For instance, there is a lack of data on carbonate and bicarbonate complexes, which therefore precludes the use of statistical methods. In computing association constants using Eq. [7], it is possible to use either the Debye radii (hydrated ionic radii) or the crystal radii (Kester and Pytkowicz, 1975).

In order to choose between the Debye radii and the crystal radii in the present computations, the association constants calculated on the basis of both of these radii were compared with the available

1 experimental association constants for complexes involving the bivalent
2 cations of Mn, Fe, Ni, Cu and Zn. The crystal radii used in these
3 computations were obtained from Nightingale (1959) and Millero (1969)
4 and the Debye radii for various ions were obtained from the tabulations
5 by Klotz (1950).

6 The results of these computations (Table 1) show that, except in
7 cases involving metal complexes with HPO_4^{2-} and Cl^- , use of either set
8 of radii provides poor estimates of the association constants. The
9 crystal radii provided good estimates of association constants for
10 metal- HPO_4^{2-} complexes whereas Debye radii provided reasonable esti-
11 mates for metal- Cl^- complexes. Further, these computations indicated
12 that good estimates can be obtained if the sum of the crystal radii
13 for the metal and ligand are modified. This can be achieved by modify-
14 ing either or both radii. However, it is convenient to modify the
15 crystal radius of the ligand and, therefore, to use the same ion radius
16 for that particular metal in computations involving complexes with
17 other ligands. For example, the crystal radii for Cu^{2+} and CO_3^{2-} are
18 $0.72\text{\AA}$ and $1.73\text{\AA}$, respectively (Nightingale, 1959; Millero, 1969).
19 The use of these radii in the computations yielded an association
20 constant ($\log K_{\text{ML}}$) of 3.63 as compared to the value of 6.73 ± 0.05
21 determined experimentally by Schindler et al. (1968). By using the
22 same crystal radius for Cu^{2+} , but using a radius of $0.68\text{\AA}$ for CO_3^{2-}
23 ion, a computed value of 6.74 is obtained, which agrees well with the
24 experimental value. The estimates for association constants obtained by
25 using a modified ligand radius are also listed in Table 1. It can
26 be seen that modifying the ligand radius to improve the estimates of
27

1 association constants in effect calibrates the method of calculation
2 for complexes involving a particular ligand with various metals.

3 Using Eq. [7], the crystal radii for metal ions, and the modified
4 crystal radii for ligands, thermodynamic association constants were
5 estimated for the ion-pairs for which experimental values are current-
6 ly unavailable. These estimated association constants for ion-pairs
7 involving the bivalent ions of the first transition metal series with
8 the ligands CO_3^{2-} , HCO_3^- , HSO_4^- , PO_4^{3-} , H_2PO_4^- are listed in Table 3.

9 A modified radius of $1.65\text{\AA}$ was used in the computation of asso-
10 ciation constants of complexes involving PO_4^{3-} with Mn^{2+} , Fe^{2+} , Ni^{2+} ,
11 Cu^{2+} and Zn^{2+} . The association constant for CaPO_4^- (Chugtai et al.,
12 1968) was used in computing the modified radius for PO_4^{3-} .

14 Method 2

15 The stability index (Q) method developed by Nieboer and McBryde
16 (1973) is based on linear correlations between the common logarithm of
17 the association constants of ion-pairs and a stability index, Q, which
18 is a function of the electronegativity, ionic charge, and atomic shield-
19 ing constant of the metal ion. It was shown by Nieboer and McBryde
20 (1973) that the linear relationship between $\log K_{\text{ML}}$ and Q was valid for
21 ion-pairs involving metals and a number of organic and inorganic
22 ligands. We decided to explore the possibility of extending this re-
23 lationship to metal-ligand complexes with more than one ligand involved
24 in the association. The association constants determined experiment-
25 ally for a number of metal-chloride (MCl_n , $n = 2, 3, 4$) complexes
26 were plotted against the Q values given by Nieboer and McBryde (1973).
27

1 These resulted in good linear correlations (Fig. 1, 2, and 3). From
 2 these relationships, the association constants for chloride complexes
 3 higher than ion-pairs involving Ni^{2+} , Mn^{2+} and Fe^{2+} were determined.
 4 The stability index method can be used successfully only in cases
 5 where experimental values of association constants for a number of
 6 metals with a particular ligand are available. In some cases, this
 7 approach is not feasible and, therefore, a third method has been used
 8 to estimate the association constants.

10 Method 3

11 This method is based on an empirical relationship between the
 12 stepwise association constant, the first association constant and the
 13 number of coordinating ligands at each step for a particular metal-
 14 ligand system.

15 The equation proposed by Van Panthaleon Van Eck (1953) is:

$$17 \quad \log K_{\text{ML}_n}^1 = \log K_{\text{ML}} - 2\lambda(n-1) \quad [9]$$

19 where

$$20 \quad K_{\text{ML}_n}^1 = \text{Stepwise association constant} = \frac{\{\text{ML}_n\}}{\{\text{ML}_{n-1}\} \{\text{L}\}}$$

$$23 \quad K_{\text{ML}} = \text{First association constant} = \frac{\{\text{ML}\}}{\{\text{M}\} \{\text{L}\}}$$

25 n = Number of coordinating ligands

26 λ = An empirical constant characteristic of each
 27 metal-ligand system.

1 This relationship has been demonstrated to be a good approximation
2 for about seventeen metal-ligand systems (Mihailov, 1974). In addition,
3 this relationship was verified for the experimental data involving the
4 complexes of the metals considered here with ligands OH^- and Cl^- . The
5 results indicated in Table 2 confirm the conclusions of Yatsimirskii
6 (1957) that in many cases, the empirical equation [9] of Van Eck is a
7 good approximation for describing the stepwise complexation. There-
8 fore, Eq. [9] can be expected to provide reasonable values of associa-
9 tion constants for complexes higher than ion-pairs, provided that the
10 characteristic constant λ is known for each metal-ligand system. These
11 constants are not available for the metal-ligand systems considered
12 here, except for the $\text{Cu}^{2+}\text{-CO}_3^{2-}$ system. Therefore, if it is assumed
13 that the λ value for $\text{Cu}^{2+}\text{-CO}_3^{2-}$ system is typical for all systems of
14 bivalent ions of first transition metals and for ligands such as CO_3^{2-} ,
15 HCO_3^- , SO_4^{2-} , PO_4^{3-} , H_2PO_4^- and HPO_4^{2-} , the association constants of
16 higher complexes can be estimated. This appears to be a reasonable
17 assumption for estimating the association constants because all the
18 ligands considered here are hard bases and all the metals included here
19 are borderline acids (except Mn^{2+} , a hard acid) according to the soft
20 and hard acid-base concept of Pearson (1968). For example, the values
21 for λ computed for the complexation of these metals with OH^- (another
22 hard base) are shown in Table 2. These values are similar (ranging
23 from 0.63-0.79) for metals classified as borderline acids. Therefore,
24 the assumption means that the characteristic constant λ for the $\text{Cu}^{2+}\text{-}$
25 CO_3^{2-} system is considered typical for all borderline acid-hard base
26 interactions. Based on this assumption, it is possible to estimate the
27

1 association constants for metal-ligand complexes higher than ion-pairs.
2 These values also are listed in Table 3.

DISCUSSION

3
4
5
6 The estimation of the association constants for various metal-
7 ligand complexes was confined to systems where there is experimental
8 evidence for the existence of such species. For instance, there is
9 sufficient experimental evidence for higher complexes of metals with
10 CO_3^{2-} ion (Schindler et al., 1968; Faucherre and Bonnaire, 1959;
11 Baranova, 1968; Lake and Goodings, 1958; Taketatsu, 1963; Pitwell,
12 1967). Ample experimental evidence exists for metal $-(\text{SO}_4)_2$, metal -
13 $(\text{SO}_4)_3$, and various metal-orthophosphate complexes as evidenced by the
14 compilations of Sillén and Martell (1968, 1971). There is also evi-
15 dence for the existence of complexes such as MnHCO_3^+ and FeHSO_4^{2+} (Hem,
16 1963; Morgan, 1965; Sykes, 1954) but at present there is no experiment-
17 al evidence for metal- HCO_3^- and metal- HSO_4^- associations higher than
18 ion-pairs. However, such associations are likely to exist because
19 higher associations of HPO_4^{2-} and H_2PO_4^- with metals have been
20 reported (Banerjee, 1950; Jameson and Solomon, 1954; Ram et al., 1954;
21 Holyroyd and Solomon, 1957; Faucherre and Msika, 1962).

22 In addition to the mononuclear complexes of metals considered
23 here, polynuclear complexes and mixed complexes (more than one ligand
24 complexing with a metal) have been reported (Holroyd et al., 1957;
25 Holroyd and Solomon, 1957; Ram et al., 1956; Erdmann, 1952; Baes and
26 Mesmer, 1976). Except for a few polynuclear hydrolytic species (Baes
27

1 and Mesmer, 1976), the association constants simply are not available.
2 No theoretical method seems to be apparent even to make estimates of
3 association constants for polynuclear complexes. However, a statistical
4 method has been suggested for estimating the thermodynamic association
5 constants for mixed ligand complexes (Dyrssen et al., 1968).

6 Regarding the necessity of considering these complexes in comput-
7 ing trace metal speciation in soils, it is essential to remember that
8 the significance of some of these complexes at fixed temperature and
9 pressure is dependent upon various factors such as total concentrations
10 of metals and ligands, pH, and the activity of water. It is known that
11 pH of soils can range from 2-10 (Van Breeman and Wielemaker, 1974).
12 We have analysed cases using GEOCHEM in which metal-CO₃²⁻ complexes such
13 as CuCO₃⁰ constituted up to 80% of the dissolved copper. The import-
14 ance of higher complexes of metals with ligands under natural condi-
15 tions has been documented by Dyrssen and Wedborg (1974) and Zirino
16 and Yamamoto (1972). Some of the situations in which the higher
17 complexes of trace metals would tend to be significant are: 1) in
18 saline soils, 2) in the reclamation of sodic soils by the sea water
19 method, and 3) in the trace metal chemistry of soils affected by
20 accidental spills or intrusions of geothermal brines. Therefore,
21 there is considerable justification for the inclusion of these con-
22 stants in a general-purpose, chemical equilibrium computer program
23 such as GEOCHEM.

24 As indicated earlier, the lack of data on association constants of
25 various complexes of trace metals have precluded reliable calculations
26
27

1 of the trace metal speciation in soils. Therefore, it is expected that
2 the present compilation of experimental and estimated thermodynamic
3 association constants (Table 3) for some of the metal complexes will
4 help alleviate this problem, until the determination of experimental
5 values of the constants has been carried out.

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TABLES

Table 1. Comparison of estimated thermodynamic association constants ($\log K_{ML}$) with experimental values for some metal-ligand complexes at 25°C and 1 atm.

Table 2. Verification of Van Pantheleon Van Eck's empirical equation (Method 3) for some metal-ligand systems.

Table 3. Thermodynamic association constants ($\log K_{ML_n}$) for some trace metal-ligand complexes at 25°C and 1 atm.

FIGURES

Figure 1. Thermodynamic association constants ($\log K_{ML_2}$) of metal-(Cl)₂ complexes as a function of stability index Q.

Figure 2. Thermodynamic association constants ($\log K_{ML_3}$) of metal-(Cl)₃ complexes as a function of stability index Q.

Figure 3. Thermodynamic association constants ($\log K_{ML_4}$) of metal-(Cl)₄ complexes as a function of stability index Q.

Table 1. Comparison of estimated association constants ($\log K_{ML}$) with experimental values for some metal-ligand complexes at 25 C and 1 atm.

Species	Calculated from Debye radii	Calculated from Crystal radii*	Calculated from modified ligand radii	Experimental values**
CuCO_3^0	1.88	3.63	6.74	6.73 ± 0.05
MnHCO_3^+	0.74	1.40	1.96	1.95
MnSO_4^0	1.98	3.12	2.31	2.26
FeSO_4^0	1.98	3.17	2.33	2.20
NiSO_4^0	1.98	3.23	2.35	2.33 ± 0.02
CuSO_4^0	1.98	3.21	2.35	2.35 ± 0.04
FeHSO_4^{2+}	1.27	2.21	2.48	2.47***
ZnSO_4^0	1.98	3.19	2.34	2.38 ± 0.02
MnHPO_4^0	1.98	3.22	--	3.58 ± 0.03
FeHPO_4^0	1.98	3.28	--	3.60 ± 0.3
NiHPO_4^0	1.98	3.34	--	2.93
CuHPO_4^0	1.98	3.32	--	3.20
ZnHPO_4^0	1.98	3.29	--	3.30
$\text{FeH}_2\text{PO}_4^+$	0.74	0.97	1.56	2.7 ± 0.2
$\text{ZnH}_2\text{PO}_4^+$	0.74	0.97	1.58	1.60
MnCl^+	0.74	1.03	--	-0.14
NiCl^+	0.74	1.07	--	-0.43
CuCl^+	0.74	1.06	--	0.21 ± 0.04
ZnCl^+	0.74	1.05	--	-0.19
MnOH^+	0.74	1.43	4.16	3.41
FeOH^+	0.74	1.48	4.49	4.50
NiOH^+	0.74	1.53	4.86	4.14
CuOH^+	0.74	1.49	4.71	6.00
ZnOH^+	0.74	1.49	4.56	5.04

* The modified crystal radii for the ligands in angstroms are:

$\text{CO}_3^{2-} = 0.68$, $\text{HCO}_3^- = 0.76$, $\text{SO}_4^{2-} = 3.20$, $\text{HSO}_4^- = 1.75$, $\text{H}_2\text{PO}_4^- = 1.10$, $\text{OH}^- = 0.10$.

The radii for HPO_4^{2-} and Cl^- were not modified. See the text for details.

** For the source of these values, see the footnotes for Table 3.

*** Sykes (1957).

Table 2. Verification of Van Pantholeon Van Eck's empirical equation (Method 3) for some metal-ligand complexes.

Complex	Experimental* $\log K_{ML_n}$	Calculated** $\log K_{ML_n}$	Complex	Experimental* $\log K_{ML_n}$	Calculated** $\log K_{ML_n}$
Mn OH ⁺	3.41	3.38	Cu(OH) ₃ ⁻	14.20	14.19
Mn(OH) ₂ ⁰	5.80	5.79	Cu(OH) ₄ ²⁻	16.40	16.40
Mn(OH) ₃ ⁻	7.20	7.23	Zn OH ⁺	5.04	5.96
Mn(OH) ₄ ²⁻	7.70	7.69	Zn(OH) ₂ ⁰	11.10	10.41
Fe OH ⁺	4.50	4.87	Zn(OH) ₃ ⁻	13.60	13.35
Fe(OH) ₂ ⁰	7.40	8.16	Zn(OH) ₄ ²⁻	14.80	14.79
Fe(OH) ₃ ⁻	11.00	9.87	CuCl ⁺	0.21	0.20
Fe(OH) ₄ ²⁻	10.00	10.00	Cu(Cl) ₂ ⁰	-0.39	-0.39
Ni OH ⁺	4.14	5.14	Cu(Cl) ₃ ⁻	-1.77	-1.77
Ni(OH) ₂ ⁰	9.00	8.85	Cu(Cl) ₄ ²⁻	-3.95	-3.95
Ni(OH) ₃ ⁻	12.00	11.13	Zn Cl ⁺	-0.19	-0.08
Ni(OH) ₄ ²⁻	12.00	11.99	Zn(Cl) ₂ ⁰	0.18	-0.30
Cu OH ⁺	6.00	5.99	Zn(Cl) ₂ ⁻	-1.40	-0.66
Cu(OH) ₂ ⁰	10.70	10.72	Zn(Cl) ₄ ²⁻	-1.52	-1.15

* Values for: M-OH systems from Baes and Mesmer (1976)

Cu-Cl system from Bjerrum (In Sillén and Martell (1968))

Zn-Cl system from Scibona et al. (1964)

** λ values: Mn-OH system: 0.486, Fe-OH system: 0.790, Ni-OH system: 0.714

Cu-OH system: 0.630, Zn-OH system: 0.754, Cu-Cl system: 0.397

Zn-Cl system: 0.069

Table 3. Association constants ($\log K_{ML_n}$) for some trace metal-ligand complexes at 25°C and 1 atm.

Ligand	n	cation	Mn ²⁺	Fe ²⁺	Ni ²⁺	Cu ²⁺	Zn ²⁺
CO ₃ ²⁻	1		6.31	6.57	6.87	6.73	6.63
	2		8.99	9.51	10.11	9.83	9.63
HCO ₃ ⁻	1		1.95 ²	2.05	2.14	2.10	2.07
SO ₄ ²⁻	1		2.26 ³	2.20 ⁴	2.33 ³	2.35 ⁵	2.38 ³
	2		0.88	0.76	1.02	1.06	1.12
HSO ₄ ⁻	1		1.05	1.08	1.10	1.09	1.08
PO ₄ ³⁻	1		6.18	6.32	6.46	6.40	6.35
	2		8.72	9.00	9.28	9.16	9.06
HPO ₄ ²⁻	1		3.58 ⁶	3.60 ⁷	2.93 ⁸	3.20 ⁸	3.30 ⁹
	2		3.52	3.56	2.22	2.76	2.96
H ₂ PO ₄ ⁻	1		1.50	2.70 ⁷	1.61	1.59	1.60 ⁹
	2		-0.64	1.76	-0.42	-0.46	-0.44
Cl ⁻	1		-0.14 ¹⁰	-0.07 ¹³	-0.43 ¹⁰	+0.21 ¹⁰	-0.19 ¹²
	2		-1.88 ¹⁴	-0.59 ¹⁴	0.96 ¹⁴	-0.39 ¹¹	0.18 ¹²
	3		-3.61 ¹⁴	-1.89 ¹⁴	0.18 ¹⁴	-1.78 ¹¹	-1.40 ¹²
	4		-4.67 ¹⁴	-2.80 ¹⁴	-0.55 ¹⁴	-3.95 ¹¹	-1.52 ¹²
OH ⁻¹⁵	1		3.41	4.50	4.14	6.00	5.04
	2		5.80	7.40	9.00	10.70	11.10
	3		7.20	11.00	12.00	14.20	13.60
	4		7.70	10.00	12.00	16.40	14.80

Sources:

- ¹Schindler et al. (1968)
- ²Morgan (1965)
- ³Nair and Nancollas (1959)
- ⁴Izzat et al. (1969)
- ⁵Hemnes and Petrucci (1968)
- ⁶Smith and Alberty (1956)
- ⁷Nriagu (1972a)
- ⁸Sigel et al. (1967)
- ⁹Nriagu (1973)
- ¹⁰Libus and Tialowska (1975)
- ¹¹Bjerrum (In Sillén and Martell (1968))
- ¹²Scibona et al. (1964)
- ¹³Calculated from $\log K_{ML}$ vs. Q curve for M-Cl complexes (Nieboer and McBryde (1973))
- ¹⁴Calculated by the Stability Index Method
- ¹⁵Baes and Mesmer (1976)

Note: All other thermodynamic association constants for ion-pairs were calculated by the method of Kester and Pytkowicz (1975). For higher complexes, the method of Van Panthaleon Van Eck (1953) with a characteristic constant of 1.82 (λ) was used.

Fig.1

Fig.2

Fig.3

THE PRINCIPLE OF HARD AND SOFT ACIDS AND BASES AS APPLIED TO EXCHANGEABLE CATION SELECTIVITY IN SOILS

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ABSTRACT

The principle of hard soft acids and bases, HSAB, which can predict stable complex formation, is reviewed. In the soil system, cation exchange selectivity can be compared to complex formation, which can then be described in terms of HSAB theory. It is then demonstrated by comparing "softness" values to observed cation exchange selectivity in soils, that the majority of soil exchange materials behave as relatively soft bases.

INTRODUCTION

The principle of hard and soft acids and bases, or HSAB principle, can be used in understanding a wide variety of chemical phenomena which include solubility, solution equilibrium, gas phase equilibrium, hydrogen bonding, charge transfer complexes, and metal atom and metal surface behavior (Pearson 1968a). An important result of HSAB theory is that it can be used as a qualitative predicting device for stable complex formation.

In the soil system, complexes can be envisioned to be made of ligands (cations) and central species (exchange materials). Stable complexes are formed when cations become adsorbed to soil exchange surfaces. However, the stability of the cation to remain adsorbed is dependent upon further exchange reactions with other cations in equilibrium with the exchange surface.

Since HSAB theory shows which complexes are relatively more stable, it could be applied to interpret observed cation exchange selectivity series; i.e., given two different cations and the same exchanger, the cation forming the most stable complex (less easily replaced = more strongly adsorbed) can be predicted using the HSAB principle. The HSAB principle has been applied previously to soils, and to cation exchange in a general fashion by Sposito (1977).

By correlating numerical data of hard-soft character with experimentally observed cation exchange selectivity of soil species, the HSAB

behavior of soil mineral and organic materials can be estimated. From this estimate, HSAB theory can then be used to predict ion exchange selectivity for various soil chemical environments.

HSAB THEORY

In 1923 G. N. Lewis proposed a definition of acids and bases as: An acid is a substance which can accept an electron pair from a base; a base is a substance which can donate an electron pair. Due to the broad nature of this definition there have been several attempts to classify Lewis acids and bases into categories with respect to their mutual behavior. One classification of Lewis acids and bases was originated by R. G. Pearson (1963).

Pearson suggested that Lewis acids and bases be classified as "hard" or "soft" if they possess some of the following properties:

- a) Hard acids are usually small in size with a high positive charge, high electronegativity, low polarizability, and do not contain unshared pairs of electrons in their valence shells.
- b) Soft acids are generally large in size with a low positive charge, low electronegativity, high polarizability, and contain unshared pairs of electrons in their valence shells.
- c) Hard bases usually have high electronegativity, low polarizability, and are hard to oxidize.
- d) Soft bases usually have low electronegativity, high polarizability, and are easy to oxidize.

The terms "hard" and "soft" are relative divi-

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sions with no clear cut dividing line. Thus, "borderline" species exist which behave as relatively "hard" or "soft" species depending upon the solution environment. A list of several hard, soft, and borderline acids and bases is compiled in Table 1 (Pearson 1963).

By knowing the relative "hardness" or "softness" of various species in an aqueous solute-solvent system, the stability of complexes formed between species can be predicted by the HSAB principle. This principle is: *Hard acids tend to associate with hard bases and soft acids with soft bases*. For example, Eqs. (1) and (2) are favorable to the right, while (3) and (4) are not.

Equations (1) and (4) have the same form as a cation exchange reaction where A and A' are exchangeable cations of the same charge and B and B' are the exchanger sites for which they are competing. If an exchanger site has soft base character, then the HSAB principle leads to the prediction that, for example, Ag^+ will be preferred over Na^+ [Eq. (1)]. On the other hand, if the exchanger site has hard base character, Na^+ would be preferred over Ag^+ [Eq. (4)]. The same kind of comparison could be made between Ca^{2+} and Cd^{2+} .

Unfortunately, the "hard-soft" characteristics of a chemical system do not solely determine stable complex formation. Stability is also a function of acid and base strength. In order to evaluate Lewis acid and base strength upon complex formation in the soil solution there must be some data on Lewis acid and base strength in a water solvent system. According to Huheey (1972), there are no such data. Thus, stable complex formation due to Lewis acid and base strength cannot be evaluated in soil systems.

HSAB theory describes a wide range of chemical phenomena in a qualitative manner and is helpful as a predictive tool. Nevertheless, it is not infallible. There are often discrepancies and

TABLE 2
Metal Ion Softness*

Oxidation state +1		Oxidation state +2		Oxidation state +3	
Metal ion	Softness	Metal ion	Soft- ness	Metal ion	Softness
H	†	Mg	0.87	Al	0.70
Li	0.36	Ca	1.62	In	2.24
K	0.92	Sr	2.08	Fe	2.37
Na	0.93	Zn	2.34	La	2.45‡
Rb	2.27‡	Ba	2.62	Co	2.56
Cs	2.73	Ni	2.82	Ti	3.23
Cu	3.45	Cu	2.89		
Ag	3.99	Mn	3.03		
		Cd	3.04		
		Fe	3.09		
		Sn	3.17		
		Pb	3.58		
		Hg	4.24		

* Softness increases as values increase.

† Hydrogen ion softness cannot be calculated by Misono's softness equation.

‡ These values were calculated by the author using Misono's softness equation.

TABLE 1
Classification of hard and soft acids and bases

Hard acids	Borderline acids	Soft acids
H^+ , Li^+ , Na^+ , K^+ , Rb^+ , Cs^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , Ti^{4+} , Zr^{4+} , Cr^{3+} , Mn^{2+} , La^{3+} , Fe^{3+} , Co^{3+} , Si^{4+} , Al^{3+}	Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Sn^{2+} , Pb^{2+}	Cu^+ , Ag^+ , Au^+ , Cd^{2+} , Hg^+ , Hg^{2+} , Pi-acceptor M" (metal atoms)
Hard bases	Borderline bases	Soft bases
H_2O , OH^- , O^{2-} , ROH , COO^- , CO_3^{2-} , NO_3^- , PO_4^{3-} , SO_4^{2-} , ClO_4^- , F	Cl^- , NO_2^- , SO_3^{2-} , Br	H, S^{2-} , SH, I, Organic S, P, N

exceptions which indicate that the basic mechanisms responsible for "hard-hard" and "soft-soft" stability are not well known (Pearson 1968b).

Ion exchange selectivity and "softness"

The possibility of using HSAB theory for describing ion exchange selectivity reactions in soil systems arises from experimental observations that ion exchange substances are selective for specific ions in equilibrium with multielectrolyte solutions.

These reactions can be characterized qualitatively by the HSAB principle if a reasonable numerical estimate of "softness" can be obtained. The numerical calculations of "softness" parameters have been treated by two different methods. The approach taken by Misono et al. (1967) assumes "softness" is the consequence of a metal ion forming a dative pi-bond. A "softness" parameter is then calculated as a function of ionization potential, charge of metal ion, and its ionic radius. Misono's "softness" values have a direct relation to Pearson's definitions and are fairly complete (see Table 2). A second approach by Klopman (1968) calculates "softness" by a quantum mechanical perturbation equation. This approach is not as direct as Misono's and only several "softness" values have been calculated. For this reason, Klopman's values

rated² Utah bentonite the relative replacing power is:

$$\begin{array}{ccccccccc} \text{Li}^+ & < & \text{Na}^+ & < & \text{K}^+ & < & \text{Rb}^+ & < & \text{Cs}^+ \\ 0.36 & & 0.93 & & 0.92 & & 2.27 & & 2.73 \\ \text{Softness values (Misono's method)} & & & & & & & & \end{array} \quad (5)$$

For Na-saturated minerals, Dolcater et al. (1968) show the following sequences: (solution concentration of metal chlorides 0.005N)

montmorillonite

$$\begin{array}{ccccccccc} \text{K}^+ & < & \text{Mg}^{2+} & < & \text{Ca}^{2+} & < & \text{Sr}^{2+} & < & \text{Ba}^{2+} \\ 0.92 & & 0.87 & & 1.62 & & 2.08 & & 2.62 \end{array} \quad (6)$$

vermiculite

$$\begin{array}{ccccccccc} \text{K}^+ & < & \text{Ba}^{2+} & < & \text{Sr}^{2+} & < & \text{Ca}^{2+} & < & \text{Mg}^{2+} \\ 0.92 & & 2.62 & & 2.08 & & 1.62 & & 0.87 \end{array} \quad (7)$$

biotite

$$\begin{array}{ccccccccc} \text{Mg}^{2+} & < & \text{K}^+ & < & \text{Ca}^{2+} & < & \text{Sr}^{2+} & < & \text{Ba}^{2+} \\ 0.87 & & 0.92 & & 1.62 & & 2.08 & & 2.62 \end{array} \quad (8)$$

muscovite

$$\begin{array}{ccccccccc} \text{Mg}^{2+} & < & \text{Ca}^{2+} & < & \text{Sr}^{2+} & < & \text{K}^+ & < & \text{Ba}^{2+} \\ 0.87 & & 1.62 & & 2.08 & & 0.92 & & 2.62 \end{array} \quad (9)$$

Further experimental evidence of ion exchange selectivity has been compiled by Wiklander (1964) for various exchange materials. The first set of data is for various NH_4^+ -saturated minerals in equilibrium with metal chloride solutions (0.005N).

kaolinite

$$\begin{array}{ccccccccccccccc} \text{Li}^+ & < & \text{Na}^+ & < & \text{H}^+ & < & \text{K}^+ & < & \text{Rb}^+ & < & \text{Mg}^{2+} & = & \text{Ca}^{2+} & = & \text{Sr}^{2+} & = & \text{Ba}^{2+} & < & \text{Cs}^+ \\ 0.36 & & 0.93 & & - & & 0.92 & & 2.27 & & 0.87 & & 1.62 & & 2.08 & & 2.62 & & 2.73 \end{array} \quad (10)$$

biotite

$$\begin{array}{ccccccccccccccc} \text{Li}^+ & < & \text{Na}^+ & < & \text{Mg}^{2+} & < & \text{Ca}^{2+} & < & \text{Sr}^{2+} & < & \text{K}^+ & < & \text{Cs}^+ & < & \text{Ba}^{2+} & < & \text{Rb}^+ & < & \text{H}^+ \\ 0.36 & & 0.93 & & 0.87 & & 1.62 & & 2.08 & & 0.92 & & 2.73 & & 2.62 & & 2.27 & & - \end{array} \quad (11)$$

will not be used in this paper.

The difference in methods of "softness" calculations indicates many factors contribute to

A second replacement sequence of H^+ -saturated humus in equilibrium with neutral salts follows the order: (concentration: 0.01–0.1 N)

$$\begin{array}{ccccccccccc} \text{Li}^+ & < & \text{Na}^+ & < & \text{K}^+ & < & \text{Mg}^{2+} & < & \text{Ca}^{2+} & < & \text{Sr}^{2+} & < & \text{Ba}^{2+} & < & \text{La}^{3+} \\ 0.36 & & 0.93 & & 0.92 & & 0.87 & & 1.62 & & 2.08 & & 2.62 & & 2.45 \end{array} \quad (12)$$

HSAB interactions and that "softness" values must not be considered as absolute ones.

With the knowledge of some "softness" values, an attempt to quantify ion exchange selectivity using the HSAB principle can be made. Krishnamoorthy and Overstreet (1949) have shown experimentally that for a NH_4^+ -satu-

Mitchell (1964) has stated that trace metal constituents, in equilibrium with soil exchange materials, are correspondingly difficult to displace. The order of difficulty of displacement is approximately:

² There are no calculated data for NH_4^+ softness.

It has been pointed out by Wiklander (1964) that there is no single universal order for the replacing power of cations. Experimental observations have shown that cation selectivity is a function of several properties which include the nature of exchange material, concentration of metal species in solution, type of ion adsorption originally on exchange surface, temperature, and pH. The exact chemical speciation of the macrosolutes and trace elements (i.e., free ionic, complexed, precipitated) will affect the degree of their hard-soft characteristics. The chemical speciation will thus cause a change in the extent of cation interaction with soil exchangers.

CONCLUSIONS

Given the natural variations inherent with exchange reactions, as illustrated above, the presented data still indicate several distinct trends.

- The oxidation state of an ion appears to be the dominant factor controlling cation selectivity, where the relative oxidation state follows the order: $M^{+} < M^{2+} < M^{3+}$.
- By comparing Misono's "softness" values for each replacement sequence, there seems to be a strong tendency for "softness" to increase toward the most stable species within a fixed oxidation state.
- Equations (5) through (12) generally indicate that "softer" hard acid cations (Ba, Sr, Cs, Rb) are preferred by soil exchange materials.
- Equation (13) shows that when transition metals (usually borderline acids) are included in soil exchange reactions they are preferred over hard acid cations.

If it is assumed that Misono's values are a good measure of cation "softness" in the soil system, then these trends suggest that soil exchange surfaces form the most stable complexes with softer, hard acid and borderline cations. This tendency indicates that soil exchange surfaces behave as soft bases *relative* to water which is a hard base.

The conclusion that soil exchange materials are relatively more soft than water is also consistent with the Hofmeister series which states

that an ion with a smaller hydrated radius tends to displace an ion of larger hydrated radius (Stumm and Morgan 1970). For example, Na^{+} , which has a large hydrated radius, prefers to be associated with water instead of soil exchange materials, while Ba^{2+} has a much smaller hydrated radius (less affinity for water) but has a greater affinity for soil exchange materials.

With soil exchange materials classified as relatively soft bases, the HSAB principle would predict that softer cations will replace harder cations on soil exchangers. This is not entirely correct. The data indicate that harder cations will usually be replaced only by softer cations of the same oxidation state. For example, in soils aluminum (.70) is usually never replaced by sodium (.93). However, variation of cation position within a fixed oxidation state is not always consistent with the hypothesis that a softer cation will replace a harder cation. This variation is demonstrated by the transition metals in Eq. (13). Other discrepancies appear when softness values are very close together. For example, sodium (.93) is consistently replaced by potassium (.92). For these reasons, conclusions made about cation exchange selectivity based upon HSAB can only be considered an approximation.

However, a significant result of HSAB exists in its potential ability for predicting ion exchange of any species (organic or inorganic) with soil components if the "hard-soft" character of the ionic species is known. Thus, given a multicomponent soil system with a unique chemical environment, natural or contaminated, qualitative predictions can be made as to what constituents in solution will form stable associations with soil substances based upon the HSAB principle.

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