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EXCHANGE AND ITS APPLICATIONS

Zhang Zhengbin Liu Liansheng
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THE APPLICATION OF LINEAR FREE ENERGY
RELATIONSHIPS IN MARINE CHEMISTRY

Zhang Zhengbin

Department of Marine Chemistry, Shandong College of Oceanology, Qingdao
and *Chen-Tung A. Chen*

College of Oceanography Oregon State University Corvallis, Oregon 97331

ABSTRACT

The widely used concept of linear free energy relationship (LFER) in physical chemistry has been applied to the study of trace metals scavenging by particulates in the oceans. Contrary to the report of Balistrieri, Brewer and Murray, 1981, that pure metal oxides do not interact very strongly with trace metals, we have found that hydrous manganese oxides are as important as organic material in removing trace metals. The LFER has also been related to the study of mean oceanic residence times of elements. It appears that many chemical properties of the ocean environment could be correlated linearly with the use of this relationship.

INTRODUCTION

The linear free energy relationship (LFER) has been used widely in physical chemistry but has not been applied to studies in marine chemistry until recently (Zhang et al., 1984). We feel that many fundamental chemical properties of the ocean environment can be correlated linearly using LFER. Accordingly, we should be able to make predictions for hitherto unstudied systems in the oceans.

We have derived one basic equation of LFER and applied it to the study of trace-metals scavenging by sinking particles in the oceans and related it to mean oceanic residence times of various elements.

BACKGROUND ON TRACE METAL SCAVENGING

Surface interaction, in association with suspended particulate matter, plays an important role in the distribution and fate of trace metals in seawater (e. g., Murray and Brewer, 1977; Chang and Liu, 1977; Turekian, 1977; Pytkowicz, 1983). Many investigators have attempted to determine whether clays, hydrous metal oxides or organic particles are the predominant influence in the distribution of trace metals (Krauskopf, 1956; Schindler, 1978; Brewer and Hao, 1979; Balistrieri and Murray, 1981, 1982, 1983; Balistrieri et al., 1981; Li, 1981, 1983;

Whitfield and Turner, 1982).

Much attention has been focused on hydrous metal oxides (James & Healy, 1972; Stumm et al., 1976, 1980; Davis et al., 1978, 1980; Schindler, 1981; Balistrieri and Murray, 1982) although it is the opinion of some investigators that these oxides do not play an important role in trace-metals distribution (Honjo, 1978; Spencer et al., 1978). The work of Balistrieri, Brewer and Murray (1981) also suggests that the role of oxides is small, as the adsorption of marine particulates in their opinion is controlled by organic coatings.

In this paper we attempt to show that while the importance of organic matter cannot be denied, Balistrieri et al.'s conclusion regarding the relative importance of metal oxides to adsorb trace metals could perhaps be modified. Our investigation of the LFER and the interactions among trace metals, suspended matter and organic material in seawater has shed some light on this problem.

LINEAR FREE ENERGY RELATION

We have recently (Zhang et al., 1983a) applied a frequently-used equation (e. g., Pearson, 1967) for use in seawater. This equation relates the equilibrium constant (K) between an acid A and a base B to the ionic potential (E_A and E_B) and a measure of the hardness-softness (C_A and C_B) of these acids on bases in seawater (Zhang et al., 1983b). The definition of Lewis for acid and base is followed (Lewis and Randall, 1961): i. e., a hard acid is an element that has a high tendency to accept a pair of electrons; a soft acid accepts the pair of electrons less readily. Some available E and C values (Zhang et al., 1983a, b) are listed in Tables 1 and 2. The equation is:

$$\log K = E_A E_B + C_A C_B. \quad (1)$$

Eq. (1) is valid for the interaction between A and B in any system. Now replace A by a metal ion M, B by the surface OH group on the particle under study. Eq. (1) then becomes

$$\log K(1) = E_M E_{OH(1)} + C_M C_{OH(1)}. \quad (2)$$

The same equation is also valid for the interaction of M with the OH group for a reference reaction such as hydrolysis (Balistrieri et al., 1981):

$$\log K(2) = E_M E_{OH(2)} + C_M C_{OH(2)}. \quad (3)$$

Combining Eqs. (2) and (3) we obtain

$$\log K(1) = E_{OH(1)} \log K(2) / E_{OH(2)} + C_M [C_{OH(1)} - C_{OH(2)} E_{OH(1)} / E_{OH(2)}], \quad (4)$$

let

$$m = E_{OH(1)} / E_{OH(2)}$$

$$C = C_M [C_{OH(1)} - C_{OH(2)} E_{OH(1)} / E_{OH(2)}].$$

And Eq. (4) becomes a linear relationship:

$$\log K(1) = m \log K(2) + C. \quad (5)$$

Since $\log K$ is proportional to the change in free energy, the above equation indicates the linear relationship that exists between two free energies, hence LFER. Balistrieri et al. had arrived at the same equation from field observations of the several systems. Other

investigations (e. g., Baes and Mesmer, 1976; Turner et al., 1981) had also reported similar empirical correlations. We have further observed that Eq. (5) is valid for about 150 systems that we have investigated (Zhang et al., 1984). Undetermined equilibrium constants can hence be estimated from Eq. (1) if E and C are known, or from Eq. (5) if K for related systems are available.

Table 1 The hardness-softness scale and ionic potential of some lewis acids.

Acids	C_A	E_A	Acids	C_A	E_A
Au ⁺	-1.77	0.91	Y ³⁺	0.77	3.23
Tl ⁺	-1.01	0.63	Th ⁴⁺	0.78	4.03
In ⁺	-0.97	0.71	La ³⁺	0.82	2.61
Ag ⁺	-0.96	0.79	Ce ³⁺	0.83	2.63
Hg ⁺	-0.96	0.79	Pr ³⁺	0.86	2.68
Cu ⁺	-0.84	1.04	Sr ²⁺	0.91	1.77
Ir ⁺	-0.51	2.20	U ⁴⁺	0.91	4.30
Pb ²⁺	-0.50	1.57	Sm ³⁺	0.92	2.80
Hg ²⁺	-0.47	1.82	Cr ³⁺	0.93	4.55
Sn ²⁺	-0.44	1.82	Mn ³⁺	0.96	4.55
Pt ²⁺	-0.36	2.50	Co ³⁺	0.96	4.62
Pd ²⁺	-0.36	2.50	Fe ³⁺	0.99	4.68
Cd ²⁺	-0.32	2.06	Np ³⁺	1.00	2.97
Os ²⁺	-0.24	2.28	Ti ³⁺	1.00	4.69
Ru ²⁺	-0.24	2.47	Pb ³⁺	1.03	4.77
Cu ²⁺	-0.20	2.50	V ³⁺	1.07	4.62
Ir ³⁺	-0.03	3.75	Tu ³⁺	1.08	1.13
Zn ²⁺	-0.02	2.72	Ga ³⁺	1.10	1.84
Ni ²⁺	-0.01	2.71	Hf ⁴⁺	1.22	4.94
Co ²⁺	-0.01	2.74	Na ⁺	1.22	1.05
Fe ²⁺	0.00	2.70	Pd ⁴⁺	1.25	5.41
Sb ³⁺	0.03	3.26	Ir ⁴⁺	1.34	3.89
Bi ³⁺	0.04	2.78	Zr ⁴⁺	1.37	5.50
Cr ²⁺	0.04	2.56	Pa ⁵⁺	1.43	5.55
Mn ²⁺	0.04	2.56	Ba ²⁺	1.44	1.48
Tl ³⁺	0.20	3.16	Os ⁴⁺	1.44	5.80
Rh ³⁺	0.32	3.85	Sn ⁴⁺	1.47	5.64
Pu ³⁺	0.41	3.00	Pt ⁴⁺	1.47	6.15
Am ³⁺	0.42	3.03	Rh ⁴⁺	1.48	6.16
Nd ³⁺	0.52	2.73	K ⁺	1.48	6.75
Ca ²⁺	0.53	2.02	Ce ⁴⁺	1.55	3.96
Pm ³⁺	0.54	2.78	Li ⁴⁺	1.53	1.67
Eu ³⁺	0.58	2.86	Ru ⁴⁺	1.57	5.96
Gd ³⁺	0.61	2.91	Yb ³⁺	1.60	3.16
U ²⁺	0.61	2.91	Ti ⁴⁺	1.64	5.90

(to be continued)

Table 1 (continued)

Acids	C_A	E_A	Acids	C_A	E_A
In ³⁺	0.61	3.70	El ³⁺	1.68	6.00
Tb ³⁺	0.64	2.97	Cs ⁺	1.86	0.59
Dy ³⁺	0.65	3.00	Hb ⁺	1.91	0.68
Ho ³⁺	0.67	3.03	He ²⁺	1.91	6.45
Er ³⁺	0.68	3.06	Bi ⁵⁺	2.04	6.76
Mg ²⁺	0.69	3.08	Ta ⁵⁺	2.17	7.04
As ³⁺	0.69	4.35	Nb ⁵⁺	2.22	7.14
Sc ³⁺	0.76	3.70	U ⁶⁺	2.24	7.23
Eu ³⁺	0.77	3.23	Ge ⁴⁺	2.42	7.55
			Sb ⁵⁺	2.43	8.07

Table 2 The hardness-softness scale and ionic potential of some lewis bases

Bases		$n=1$	2	3	4			
Cl	I,IV	$E_B=0.25$	$E_B=1.10$	$E_B=0.80$	$E_B=0$			
		$C_B=-0.40$						
	II	$E_B=-0.25$	$C_B=-4.85$	$C_B=-5.55$	$C_B=-5.40$			
		$C_B=-3.60$						
OH	I	$E_B=0.50$	$E_B=4.50$	II	$E_B=4.0$	III	$E_B=5.5$	
		$C_B=0.45$			$C_B=-25$		$C_B=14$	
	II	$E_B=3.75$		$C_B=-2.40$	IV	$E_B=4.0$	IV	$E_B=4.3$
		$C_B=-1.40$				$C_B=15$		$C_B=13$
	IV	$E_B=2.20$						
		$C_B=-0.50$						
	CO ₃	I	$E_B=0.80$					
$C_B=-0.10$								
II		$E_B=4.15$						
		$C_B=-0.40$						
IV		$E_B=2.10$						
		$C_B=-0.40$						
SO ₄	I	$E_B=0.50$						
		$C_B=0.45$						
	II	$E_B=0.80$						
		$C_B=-0.70$						
	IV	$E_B=1.00$						
		$C_B=0.45$						

(to be continued)

Table 2 (continued)

Bases	$n=1$	2	3	4
humic acid	I	$E_B = -2.0$ $C_B = 6.5$		
	II	$E_B = -1.50$ $C_B = -20.0$		
	IV	$E_B = 1.50$ $C_B = -18.0$		

Note: n is the coordination number;

- I involves the interactions of bases with major cations such as Na^+ , K^+ , Ca^{2+} and Mg^{2+} ;
- II involves the interactions of bases with soft acids;
- III involves the interactions of bases with hard acids;
- IV involves other interactions not listed above.

LFER AND TRACE METAL SCAVENGING

Balistreri et al. compared equilibrium constants from field observations of trace-metals scavenging with known laboratory results that define metal interactions with typical metal oxides and organic compounds. We have redrawn their Fig. 7 (our Fig. 1) and have added additional lines based on our data (Chang and Chen, 1984a, b; Zhang et al., 1984). Our results are consistent with those of Balistreri et al. in that the range of equilibrium constants for marine particles falls within the range of constants that describe metal interactions with organic compounds.

We have also redrawn Balistreri et al.'s Fig. 6 (our Fig. 2) and added our data (Chang and Chen, 1984a, b; Zhang et al., 1984) for hydrous manganese oxides. Balistreri et al. came to the conclusion that the interactions between natural marine particles and metals are much stronger (higher $\log K$ values) than the interactions of the metals with the model metal oxides that they used in the laboratory (SiO_2 , $\gamma\text{-Al}_2\text{O}_3$, $\alpha\text{-FeOOH}$ and amorphous $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$; lower $\log K$ values). They further suggest that organic compounds control the metal interactions with marine particles. These conclusions of Balistreri et al. may be only partly valid, as our data show that metals bind more strongly with hydrous manganese oxides in the laboratory than with natural marine particulates (Fig. 2). It appears, therefore, that hydrous manganese oxides could be an important factor in the removal of trace metals.

Balistreri et al.'s statement, therefore, that the use of metal oxides as model substances for marine particulates "will significantly underestimate the complexing ability of the sinking particulate matter" is applicable only for the model oxides they used. Their assertion is not true for hydrous manganese oxides and perhaps other metal oxides not yet studied.

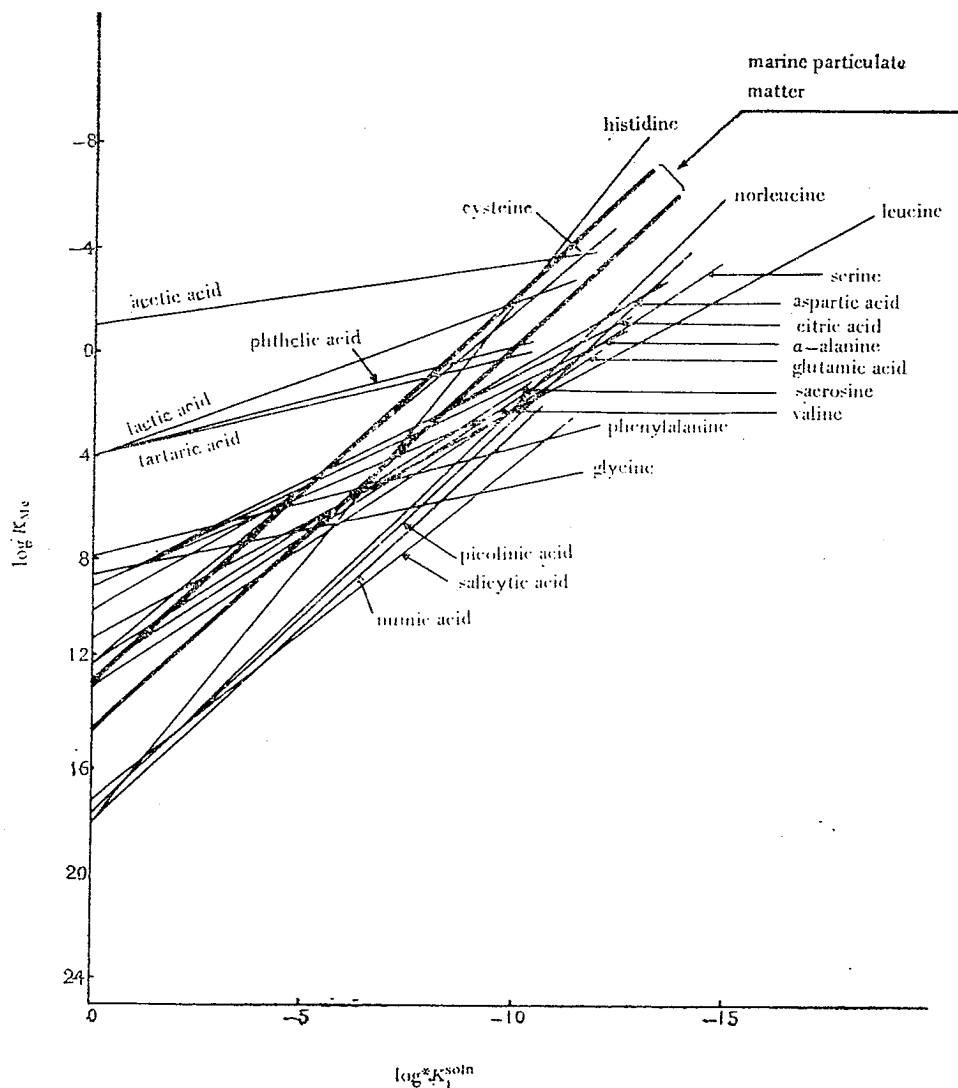


Fig. 1. A comparison of the equilibrium constants that define trace metal interactions with natural marine particles with reference organic compounds of Balistrieri, Brewer and Murray (1981) and with other organic compounds lines added. K_{Me} represents the stability constants for metal interactions with natural marine particles and organic compounds, $*K_1^{soln}$ represents the stability constants of the corresponding metal hydroxides.

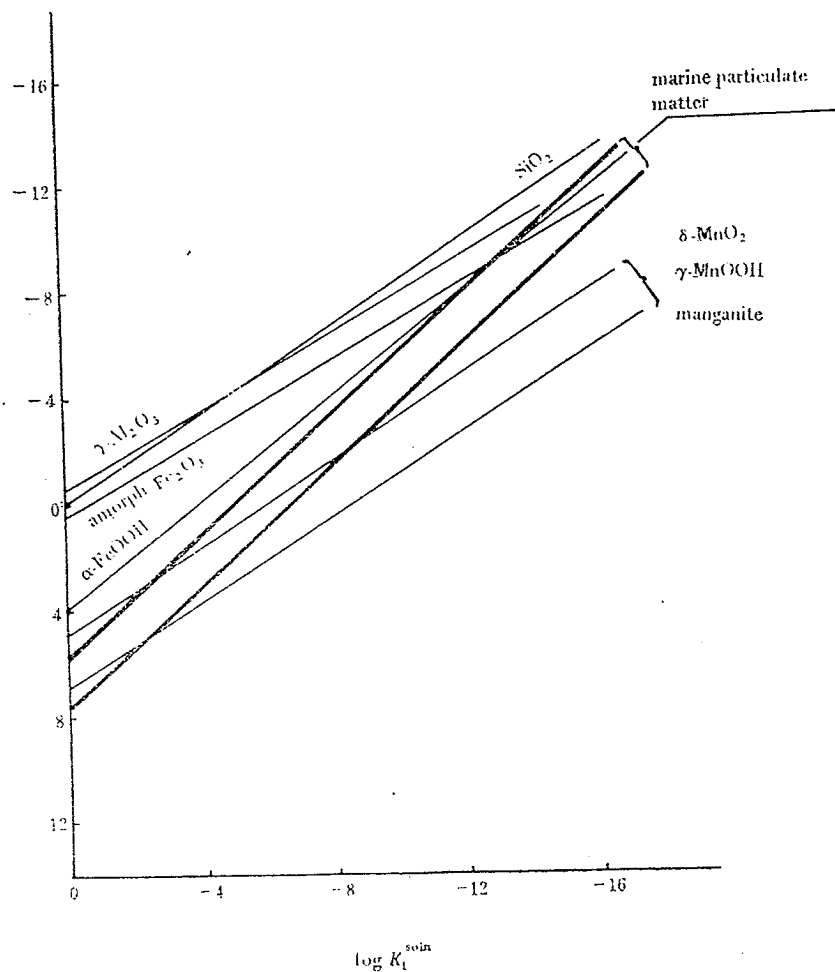


Fig. 2. A comparison of the equilibrium constants that define trace metal interactions with natural marine particles with reference metal oxides of Balistrieri, Brewer and Murray (1981) and with hydrous manganese oxide lines added. K_{Me} represents the stability constants for metal interactions with natural marine particles and organic compounds, $*K_1^{soin}$ represents the stability constants of the corresponding metal hydroxides.

LFER AND MEAN OCEANIC RESIDENCE TIME

We have found that LFER can also be applied to the study of mean oceanic residence times (MORT, τ) of elements in seawater. Previously we have related the mean oceanic residence time to the heat of hydration (L) and the concentration of elements in seawater (C_{sw}), river water (C_{rw}) and sediments (C_{sed}) (Chang et al., 1982). Later correlations are as follows (Zhang and Liu, 1981, submitted later than Chang et al., 1982):

$$\log \tau = -0.001L - 1.0 \log (C_{sed}/C_{sw}) - 3.3 \quad (6)$$

or

$$\log \tau = -0.001L + 1.1 \log (C_{sw}/C_{rw}) - 4.4. \quad (7)$$

The values for τ for a metal is related to LFER (Eq. (5)), e. g., Eq. (29) of Balistrieri et al., 1981:

$$\log \left\{ \left[1 + \sum^n \sum^j \beta_{nj} (L_j)^n \right] (H^+) / a(\text{SOH}) (\tau / \tau_p - 1) \right\} = m \log^* K^{\text{soln}} + C, \quad (8)$$

where β_{nj} is the association constant between the metal and an organic ligand j , n is the number of coordinating ligands, a is the concentration of particulate matter, (SOH) is the concentration of the free surface sites, and τ_p is the residence time of particulate matter.

CONCLUSION

We have applied the Linear Free Energy Relationship to the study of the scavenging and oceanic residence times of trace metals in seawater. Contrary to the reported insignificance of metal oxides as complexing agents, hydrous manganese oxides have been found to be as important as organic material in removing trace metals. LFER has also been related to oceanic residence times of elements. It appears that the application of LFER should be attempted for more systems in the oceanic environment.

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