METHODS FOR THE CATION EXCHANGE CAPACITY OF SALINE-SODIC SOILS [1]

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ABSTRACT

Cation exchange capacities of four soil profiles representing large ranges in salinity and Na saturation were measured by: 1) the sum of cations (CEC_S) extracted by NH_4OAc at pH 7 minus the cations in saturation extracts, 2) the method of Bower et al (1952) (CEC_B) in which the soil is saturated using NaOAc, the excess salt is removed by washing with ethanol and the Na is removed with NH_4OAc, and 3) the method of Polemio and Rhoades (1977) (CEC_{PR}) in which the soil is saturated with Na using a solution of NaCl-NaOAc in 60% ethanol, the Na is replaced with $Mg(NO_3)_2$ and the Cl concentration in the $Mg(NO_3)_2$ solution is used to correct occluded salt. Values for CEC were essentially the same for all methods in the non-saline and non-sodic Yolo soil and in the surface horizons of the other three soils which were relatively free of salts. However, in the moderately to lighly saline subsoils of the Pescadero, Solano and Pescadero Variant soils, the CEC_S greatly exceeded the CEC_B and CEC_{PR}. Even though the CEC_B and CEC_{PR} generally gave the same values, the CEC_B values were more highly correlated with hygroscopic and saturation water contents. Using these correlations as criteria for a satisfactory method, the CEC_B appears to be the most reliable of the three methods that were compared.

Keywords: Dissolution of minerals, Hygroscopic water content, Sum of cations.

COMPENDIO

Se determinó la Capacidad de Intercambio Catiónico de cuatro perfiles de suelos representativos de un amplio rango de salinidad y saturación de sodio medida por: 1) La suma de cationes (CICs) extraídos con NH_4OAc a pH 7.0 corregidos por cationes en solución, 2) El método de Bower (CIC_B, 1952) en el cual el suelo se satura con NaOAc, el exceso de sal se remueve mediante lavado con etanol y el sodio desplazado con NH_4OAc y 3) El método de Polemio y Rhoades (CIC_{PR}, 1977) en el cual el suelo se satura con Na usando una solución de NaCl-NaOAc en etanol al 60%, el Na se desplaza luego con Mg $(NO_3)_2$ y la concentración de Cl en esta última solución se usa para corregir la sal ocluida. Los valores de la CIC resultaron esencialmente iguales en el suelo Yolo no salino y no sódico y en los horizontes superficiales de los otros tres suelos. (relativamente libres de sales). Sin embargo, en la moderada a fuertemente salinos horizontes subsuperficiales de los suelos Pescadero, Solano y Pescadero Variant, la CICs excede notablemente la CIC_S y la CIC_{PR}. Aún cuando la CIC_B y la CIC_{PR} dan generalmente los mismos valores, los valores de la CIC_B correlacionaron más estrechamente con los contenidos de agua higroscópica y con el agua de saturación. Usando dichas correlaciones como criterio de selección, la CIC_B parece ser el método más confiable de los tres comparados.

Palabras claves: Dilución de minerales, Contenido higroscópico de agua, Suma de cationes

INTRODUCTION

The cation-exchange capacity (CEC), defined as the quantity of readily exchangeable cations neutralizing negative charge in the soil, is an important property of soils. The CEC is dependent on the conditions under which it is measured and it varies with the method used (Chapman, 1965). Ideally the method for determining CEC should be selected to fit the specific soil, but in

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many laboratories a standard procedure for all soil samples is essential for rapid routine analyses (Rhoades, 1982).

Problems of dissolution of minerals and fixation of cations during CEC determinations have been discussed by Chapman and Kelley (1930), Bower (1950, 1955), Bower et al (1952), Babcock (1960), Rhoades and Krueger (1968), Polemio and Rhoades (1977) Sayegh et al (1978), and Rhoades (1982). Methods for alkaline, saline, calcareus, gypsiferous and sodic soils have been proposed by Bower et al (1952), Shatemirov (1960), Peech et al (1962), Vergina and Dokuchayev (1964), Matushevsky (1968), Carpena et al (1972), Papanicolaou (1976), and Polemio and Rhoades (1977).

The objective of the research reported herein was to determine the CEC values of four soil profiles representing extreme ranges in salinity, exchangeable cations and other soils properties . The sum of cations extracted by NH_4OAc was used to determine its limitations and the magnitude of overestimation of the CEC in saline soils. The Bower et al. (1952) method and the Polemio and Rhoades (1977) methods were compared because they have both been recommended for alkaline saline soils.

METHODS AND MATERIALS

Soil Samples

Samples of the horizons of four soil profiles were collected to represent a wide range in salinity and sodicity. The samples were air dried and ground to pass a 2-mm sieve. The profiles were the Pescadero, Pescadero Variant, Yolo and Solano.

The Pescadero soil was classified as a fine montmorillonitic thermic Aquic Natrixeralf. The pH was alkaline and increased with an increase in depth. The organic matter content ranged from 5.8% in the upper layer to 0.79% in the lower layers. The profile was slightly saline at the surface with an electrical conductivity of 3.3 dS m^{-1} which increased to 4.3 dS m^{-1} at the lower horizons. The profile was a silty clay soil to a depth of 73 cm. The dominant minerals in the clay fraction were montmorillonite and kaolinite. Because of high saturation with Na, the soil is dedicated to pasture and has not been irrigated.

The Solano soil was acid to a depth of 26 cm but the rest of the profile was alkaline with an increase in pH with increase in depth to a maximum pH of 8.5 for the lowest horizon. The organic matter decreased with increased depth from 2.44% in the upper layer to 0.26% in the lower layers. The profile was nonsaline to a depth of 42 cm and sodic to a depth of 93 cm. The clay content ranged from 11.2% at the surface layer to a maximum of 38.0% for the B22t (42-64 cm) horizon dominated by montmorillonite, kaolinite and vermiculite. The profile was classified as a loamy mixed thermic Typic Natrargid. This soil is under pasture and has not been irrigated.

The Yolo soil was classified as a fine silty mixed non-acid thermic Typic Xerorthent. It is a silt loam to a depth of 85 cm with a fine sandy layer between 85 and 108 cm. The dominant clay minerals were montmorillonite, kaolinite and vermiculite. It was an alkaline, nonsaline and nonsodic soil with organic matter content ranging from 2.4% to 0.26%. This soil has been irrigated and cultivated for a long time and has evidently been well leached.

The Pescadero Variant soil (fine montmorillonitic thermic Aquic Natrargid) was situated in a depression of the field which is flooded during the rainy season. The pH ranged from neutral to highly alkaline. It was highly saline with electrical conductivities ranging from 7.7 to 28.3 dS m^{-1} and also it had a high Na saturation. This soil is so impermeable that it is unproductive. The average clay content was 34.7%, dominated by montmorillonite and kaolinite.

General Methods

Water lost by drying air-dried soils at 105°C was used as a measure of hygroscopic water (P_W). The water content of a saturated paste (U.S. Salinity Laboratory Staff, 1954) was used as a measure of water content at saturation (SP). Values for pH were determined on the saturated paste and the electrical conductivity of the saturation extract, dS m^{-1}, was used as a measure of soil salinity. The organic matter (OM) was deter-mined by a Walkley-Black procedure (Chapman and Pratt, 1961). Texture analyses were determined using the method of Day (1965).

Cation-Exchange Capacity

Sum of Cations (CEC_S). A 5-g sample was placed in a centrifuge tube and 33-ml aliquot of M NH_4OAc solution adjusted to pH 7, was added. The soil suspen-sion was shaken for 5 minutes, centrifuged at RCF = 1000 until the supernantant liquid was clear and then the supernatant was decanted into a 100-ml volumetric flask. This extraction was repeated a total of three times. The volume of the extract was diluted to 100 ml and the Ca, Mg, Na and K were determined by atomic absorption spectrophotometry (AAS) and flame spectrophotometry (FS). The sum of cations extracted by NH_4 OAc minus the sum of soluble cations in the saturation extract was used as an estimate of the CEC.

Bower Method (CEC_B). A 4-g sample of soil was placed in a centrifuge tube and a 33-ml aliquot of M

NaOAc solution, adjusted to pH 8.2, was added. The soil suspension was shaken for 5 minutes and then centrifuged at RCF = 1000 until the supernatant liquid was clear. The supernatant was then decanted and discarded. The sample was extracted in this manner a total of four times. The sample was then washed four times with 95% ethanol to remove the excess NaOAc solution. The adsorbed Na was replaced by three extractions with 33-ml aliquots of M NH_4OAc solution adjusted to pH 7, and the extracted Na was determined by FS (Bower et al., 1952).

Polemio and Rhoades Method (CEC_{PR}). The method of Polemio and Rhoades (1977) was developed for arid land soils, particularly for those containing carbonates, gypsum and zeolites.

A 4.0-g sample of soil was saturated with Na by four successive equilibrations with 33-ml aliquots of a 60% ethanol solution containing 0.4 M NaOAc-0.1 M NaCl adjusted to pH 8.2. During each equilibration the soil suspension was shaken for 5 minutes, centrifuged until the supernatant was clear after which the supernatant liquid was discarded. The Na-saturated samples plus the occluded saturating solution were extracted three times with 33-ml aliquots of a 0.5 M pH 7 solution of $Mg(NO_3)_2$. Total Na and Cl were determined in the extract. The exchangeable Na was calculated as the total Na minus the occluded soluble Na which was 5 times the occluded Cl.

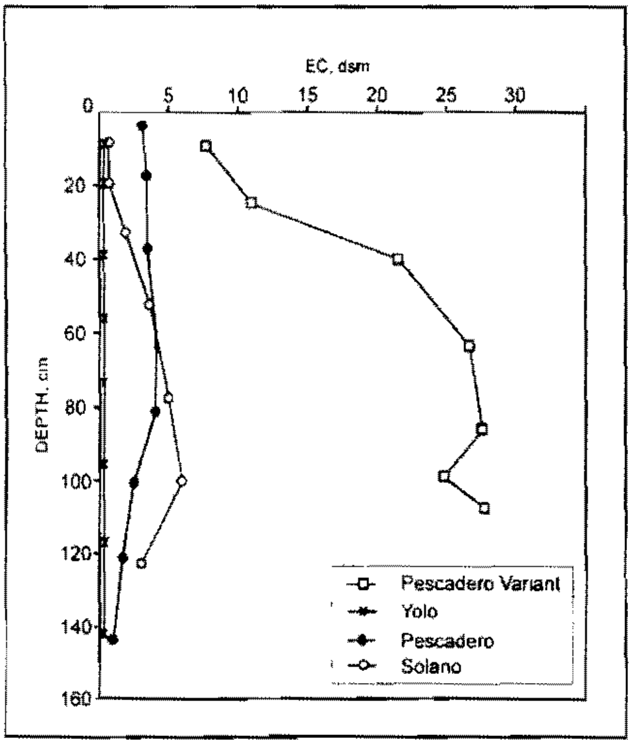

Figure 1. Salinity profiles for four soil profiles of northern Californis

RESULTS AND DISCUSSION

The relationships between salinity, expressed in dS m^{-1}, and depth for four soil profiles are presented in *Figura 1*. The Yolo soil was free of salt through the profile. The Solano soil was nonsaline in the surface but increased to moderate levels of salinity in the subsoil. The Pescadero profile was moderately saline through the first meter and decreased in salinity at deeper depths. The Pescadero Variant soil was saline at all depths and highly saline at depths lower than about 35 cm. For the four profiles the salinity ranged from less than 1 to 28 dS m^{-1}, providing excellent soil materials for testing the reliability of methods for determining CEC.

Data for NH_4OAc-extracted cations, the sum of cations (CEC_S), the CEC_B and CEC_{PR}, all plotted as a function of profile depth, are presented in *Figs. 2 to 5*, respectively, for the Pescadero, Solano, Yolo and Pescadero Variant soils. The Pescadero soil was definitely sodic to a depth of about 60 cm with much lower amounts of extracted Na below that depth. Extracted Mg exceeded extracted Ca throughout most of the profile. The average CEC_B and CEC_{PR} values were essentially the same throughout the profile, but the SC gave a large overestimation of the CEC except in the surface layers. Based on the profiles for extracted cations the overestimation of the CEC by SC resulted from extraction of Ca and Mg from the dissolution of soil minerals in NH_4OAc. The extracted Ca exceeded CEC_B and CEC_{PR} for the deepest depth and the extracted Mg was equal to the average of the CEC_B and CEC_{PR} at one depth. As the difference between CEC_S and CEC_B increased the extracted Na decreased, indicating indirectly that dissolution of Na minerals might have contributed very little to the excess of CEC_S over CEC_B.

For the Solano soil the three methods for determining CEC gave essentially the same values in the three surface horizons. The first two horizons of this soil were slightly acid and the third horizon was only slightly alkaline. All of these surface horizons were relatively free of salt. Below the 42-cm depth the CEC_S exceeded the CEC_S with a dominant effect of Ca and Mg dissolution in the deepest horizons.

The Yolo Soil contained very little extractable Na. The extracted Mg exceeded the extracted Ca by a small amount throughout the profile. The CEC_S agreed well

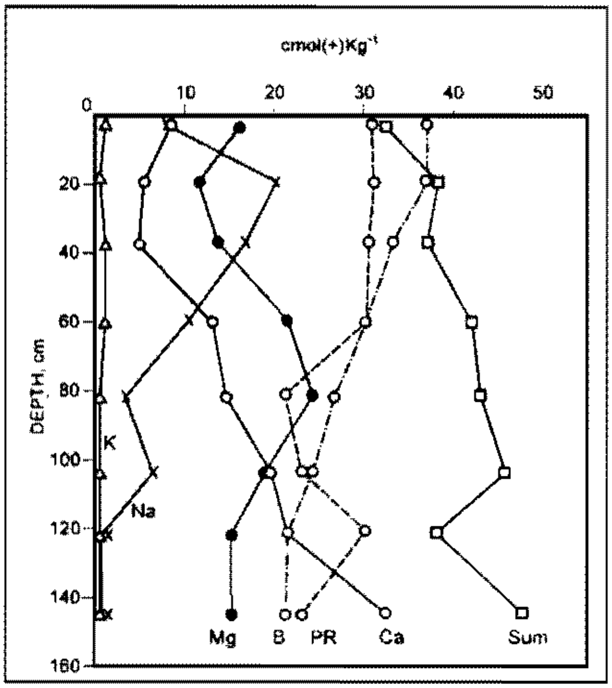

Figure 2. Relationship among the CEC values determined by three methods and the exchangeable cations in the Pescadero Soil

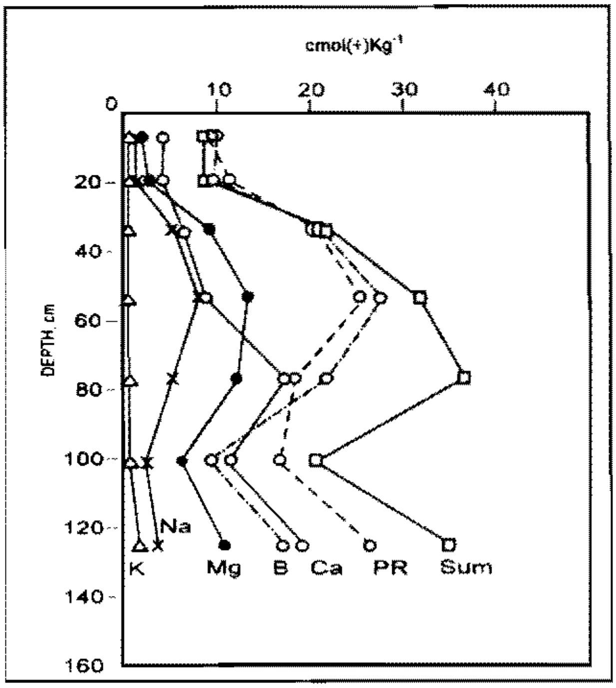

Figure 3. Relationship among the CEC values determined by three methods and the exchangeable cations in the Solano Soil

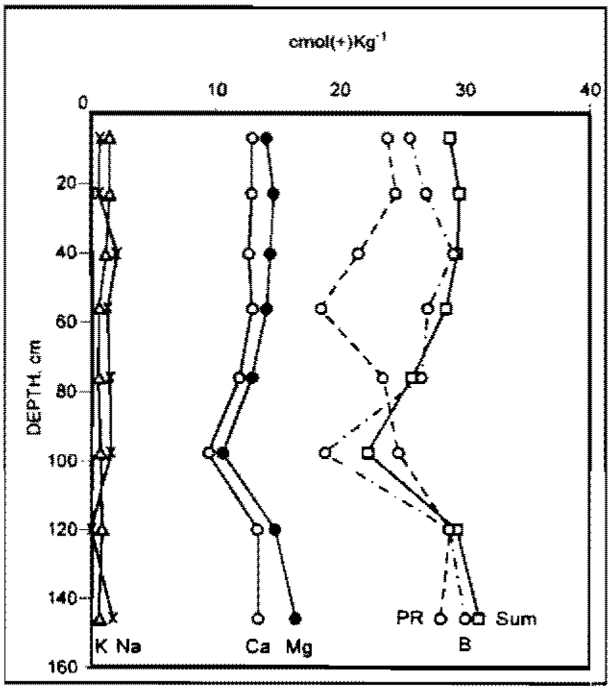

Figure 4. Relationship among the CEC values determined by three methods and the exchangeable cations in the Yolo Soil

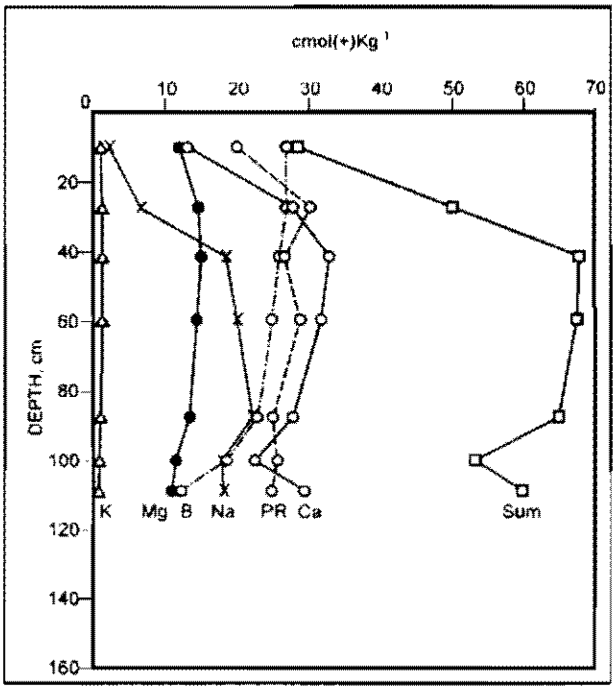

Figure 5. Relationship among the CEC values determined by three methods and the exchangeable cations in the Pescadero Variant Soil

with the CEC_B but the CEC_{PR} was less than the other CEC values for several horizons. The data indicate very little if any dissolution of minerals in NH_4OAc in this soil indicating that the extracted cations are exchangeable cations. This soil is nonsaline nonsodic and because of the consistency and agreements among the CEC values, particularly the CEC_S, it indicates that the methods were appropriately used and that the data for the other three saline-sodic profiles are real and not a result of errors.

For the Pescadero Variant soil the CEC_S was nearly equal to the CEC_B in the surface horizon, but it greatly exceeded the CEC_B for all other depths. The distribution of cations suggests that the dissolution of Ca and Na were likely the cause of high CEC_S values in this profile. Extracted Ca exceeded CEC_B and CEC_{PR} in all except the surface horizon. Extracted Na was correlated with CEC_S whereas extracted Mg was nearly constant throughout the profile. This saline-sodic soil provides an extreme case of dissolution of minerals in NH_4OAc solution and is an excellent example of the overestimation of CEC by the SC extracted in NH_4OAc.

Correlation coefficients for the relationships of CEC values with P_W and SP for individual soil profiles are presented in *Table 1*. The CEC_B was highly correlated with P_W for each soil, whereas the CEC_{PR} was correlated with P_W for only one soil. The CEC_{PR} was not correlated with any. The correlation and regression coefficients for the relationships of CEC_B with organic matter (OM) and clay contents are presented in *Table 2*. There were no significant relationships with OM but the CEC_B was related to clay contents for each soil.

Table 1. Correlation coefficients for the linear relationships of CEC values with soil water contents of air dry soils (P_W) and saturated soils (SP)

SOIL	CEC_B	CEC_{PR}
Pw		
Pescadero	0.986 ***	0.656 ns
Solano	0.990 ***	0.821 *
Yolo	0.991 ***	0.101 ns
Pescadero variant	0.889 *	0.400 ns
All soils	0.802 ***	0.729 ***
Sp		
Pescadero	0.750 *	0.562 ns
Solano	0.933 ***	0.712 ns
Yolo	0.061 ns	0.015 ns
Pescadero variant	0.536 ns	0.630 ns
All soils	0.497 **	0.400 *

ns, *, **, and ***, respectively, indicate nonsignificant at the 95% level and significant at the 95%, 99% and 99.9% levels of probability

Pescadero = fine montmorillonitic thermic Aquic Natrixeralf.
Solano = loamy mixed thermic Typic Natrargid.
Yolo = fine silty mixed nonacid thermic Typic Xerorthent.
Pescadero Variant = fine montmorillonitic thermic Aquic Natrargid.

Table 2. Correlation and regression coefficients for CEC_B values with soil organic matter and clay contents

PROPERTY	SOIL	SLOPE	INTERCEPT	r
Organic matter	Pescadero	0.319	22.90	0.782 ns
	Solano	- 0.384	20.20	0.432 ns
	Yolo	0.166	2.08	0.294 ns
	Pescadero Variant	0.432	19.20	0.582 ns
Clay	Pescadero	0.050	11.10	0.930 **
	Solano	0.068	0.37	0.989 **
	Yolo	0.067	11.90	0.843 *
	Pescadero Variant	0.060	- 0.95	0.882 **

ns Non-significant value
* Significant at the 5% level of significance
** Significant at the 1% level of significance

When multiple correlation was used to evaluate the relation of clay content, organic matter and the water content of the saturated paste, using data for all profiles, the best correlation and regression was:

$$Y = 5.19 + 0.0342X_1 + 0.0233X_2^{1/2}$$

with $R^2 = 0.654$ and $R = 0.0805$

where, $Y = CEC_B$ in cmol (+) kg^{-1}

X_1 = clay content in g Kg^{-1}

X_2 = OM in g Kg^{-1}

The water content of the saturated paste was not significant in multiple correlation and regression largely because it was highly correlated with X_1, the clay content, with $r = 0.84$.

The muiltiple correlation coefficient $R^2 = 0.654$ means that 65% of the variation in the CEC_B was associated with clay and organics metter content. The other 35% was probably related to the CEC_S of the clay fractioins of the four soils. The CEC per Kg of clay average 75, 70 124 and 57 cmol(+) Kg^{-1}, respectively, for the Pescadero, Solano, Yolo and Pescadero Variant soils.

According to Banin and Amiel (1969) two soil properties, the saturation porcentage (SP) and air-dry hygroscopy water content (Pw), are proportional to CEC. Polemio and Rhoades (1977) used these characteristics to test indirectly the accuracy of their CEC method since there exists no absolute reference method. Their coefficients of linear correlation showed better correspondence between CEC and SP, and between CEC and Pw when determined by the newly developed CEC_{PR} method. The same procedure was used to evaluate the results of the present research. The better correspondence was found between the CEC_B and Pw which gave pasitive r values significant at the 1% level. The CEC_{PR} gave a significant r value of 0.82 for only the Solano soil. Also the CEC_{PR} was not correlated with SP for any soil.

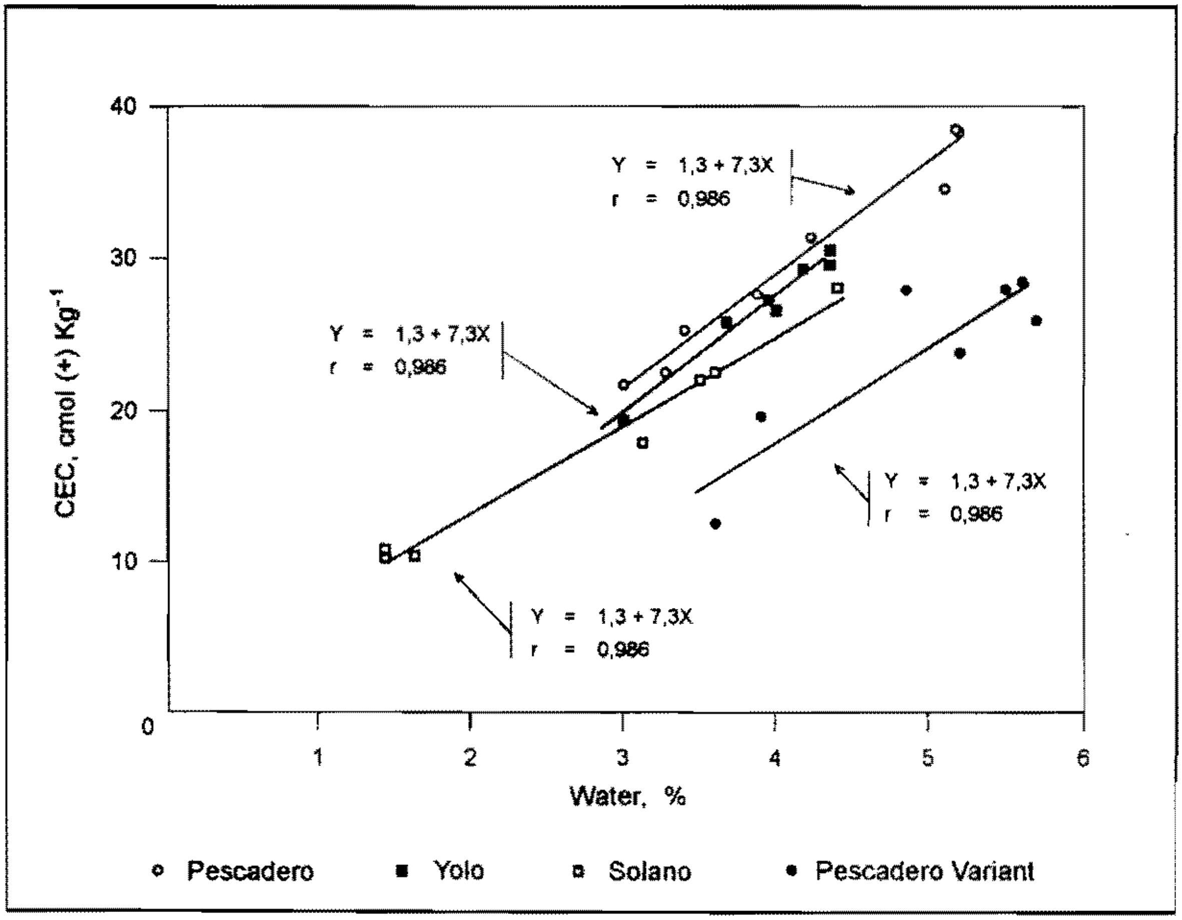

Figure 6. Relationship between CEC_B and the hygroscopic water content for each of four soils

The relationship between CEC_B and hygroscopic water content, Pw, for each soil presented in *Fig. 6*. The regression equations for the Pescadero, Solano and Yolo are essentially the same and the CEC_B values at 4% water have a narrow range of 24 to 28 cmol(+) kg^{-1}. The data for the Pescadero Variant soil, however, show a lower correlation coefficient and a lower CEC per unit of hygroscopic water. This soil also showed the lowest CEC per unit of clay. The data for this soil also explain the lower correlation coefficients for all soils as compared to the coefficients for each soil (*Table 1*).

The lack of correspondence between the CEC_{PR} and the two soil properties for all the soils except for P_w in Solano soil, support the conclusion that this method is not adequate for the CEC determination in the soils studied. Similarly, given the high correlation between CEC and P_w for all the soils, and between CEC and SP for Pescadero and Solano soils when the CEC_B values are used, given credence to the conclusion that the method of Bower et al. (1952) is the most reliable for saline-sodic soils.

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